THE CYANINE DYES AND RELATED COMPOUNDS

This is the eighteenth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*



THE CYANINE DYES AND RELATED COMPOUNDS

Frances M. Hamer
Formerly Research Chemist, Kodak Ltd., London, and Honorary Lecturer, Imperial College of Science and Technology, London

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The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

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ARNOLD WEISSBERGER

Preface

The author's introduction to research in the summer of 1917 at Cambridge, under Sir William Pope and Dr. W. H. Mills, began with the preparation of a series of isocyanines, followed by the establishment of the constitution of Pinacyanol. Seven years' research on cyanines in the Cambridge University Chemical Laboratory were followed by a few months in the Davy Faraday Research Laboratory of the Royal Institution. Then came 5½ years with Ilford Ltd., 18½ years with Kodak Ltd., and, through the kindness of Sir Patrick Linstead, six years at the Imperial College. During these 37 years devoted to cyanines, either in research or in their preparation for industrial use, notes on the published methods had accumulated. This book was begun with the feeling that it would be a great waste *not* to put the information on record, as it might be useful to others working on the subject. The author little thought that the writing would take another 5½ years! An attempt has been made to cover the literature up to the end of 1959.

Emphasis has been laid on the preparative methods rather than on the theoretical aspect of the subject. The first chapter is mainly introductory, explaining the connection of the cyanines with photography, summarising their early chemistry and following with an account of the pioneer work on the constitution of typical cyanines. Apocyanines, in which the nuclei are directly linked, are included in this first chapter. Methincyanines, in Chapter II, are grouped according to methods of synthesis, each group being subdivided according to the type of dye, and this is the system followed throughout. Chapter III deals with methincyanines which are substituted on the chain. Chapters IV and V cover, respectively, symmetrical and unsymmetrical trimethincyanines having an unsubstituted chain, whilst chain-substituted trimethincyanines are described in Chapter VI. In Chapter VII, on pentamethincyanines, both symmetrical and unsymmetrical types, including those with substituents on the chain, are considered. The same applies to Chapter VIII on heptamethincyanines; cyanines with still longer chains are included in that chapter. In the cyanines of

Chapter IX, the odd-numbered carbon chain, which links the nuclei, is cyclic, or part of it is. Chapter X deals with the variations in the nuclei which enter into cyanine molecules, including the use of unusual nuclei. Bases, of which cyanines are the quaternary salts, are in Chapter XI. Chapter XII comprises azacyanines where one or more :CH· groups of the chain are replaced by :N. Numerous types of dyes related to cyanines are gathered together in Chapter XIII and include *p*-dimethylaminostyryl salts and the corresponding anils, hemicyanines, oxonols, open-chain dyes, and cyanine analogues derived from oxonium or sulphonium salts. The merocyanines are non-ionic acidic dyes, which were prepared from cyanine intermediate compounds and which are so important that they required Chapter XIV to themselves. Here they are grouped according to the length of chain, simple merocyanines, with the nuclei directly linked, being followed by sections on di-, tetra-, and hexa-methinmerocyanines. Next comes an account of quaternary salts of merocyanines, which are important in the preparation of trinuclear cyanines, then various types of merocyanines with a substituent on the chain are considered, and others in which part of the chain is cyclic. Variations in the nuclei which enter the merocyanine molecule include the use of unusual nuclei; modification of the chain led to aza analogues. A brief account of work on the colour of merocyanines is followed by one on open-chain related compounds. In Chapter XV, on trinuclear and polynuclear cyanines, most of the sections are preceded by a table summarising the various types included in the sub-sections. Chapter XVI is on the relationship between the colour and constitution of cyanines, and Chapter XVII deals with photographic sensitisation and other properties of these dyes.

In the index, the names of the heterocyclic nuclei are followed by their numbers in the second edition of *The Ring Index* (RRI). Where the ring is substituted, to give, for example, a di- or tetra-hydro derivative, the number reference is in a different form (see RRI).

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FRANCES M. HAMER

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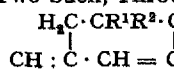
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CHAPTER I

Mainly Introductory

1. The Connection of the Cyanines with Photography

Many representatives of the proverbial man-in-the-street class would interpret the phrase "the dyes used in photography" as covering the dyes that they see in colour photographs, and those alone. Yet there are other, unseen dyes,—the photographic sensitisers,—that have made colour photography and high speed photography possible, and they belong, almost exclusively, to the cyanine or related groups.

The sensitivity of the human eye extends over the spectrum from the violet at 4000 Å to the red at 7000 Å, with the greatest sensitivity in the yellow. Undyed photographic material, on the other hand, is sensitive only to the invisible ultraviolet and to blue light, and therefore gives a very false, and a very incomplete, picture of what we see. The wedge spectrogram in Figure 1A shows the sensitivity of a modern gelatino silver chloride emulsion, such as is used for photographic papers, whilst that in 1B shows the sensitivity of a bromide emulsion.

In 1873 H. W. Vogel observed that certain dyed photographic plates were sensitive not only to blue light also to green, and that the green sensitivity disappeared on removal of the dye.[1] He bathed photographic plates in dilute solutions of various dyes, and discovered that certain of them, including cyanine, possessed the power of making photographic emulsions sensitive to colours other than blue.[2] At first other workers contradicted and even ridiculed his results, but his work was confirmed by E. Becquerel, who discovered the sensitising action of chlorophyll,[3] and by J. Waterhouse, working "under the glowing sun of India",[4] who discovered in 1875 the sensitising action of eosin to green and yellow light.[5] In 1882 patents for sensitising gelatin emulsions with eosin were obtained and "isochromatic" plates were manufactured.[6] In 1883 J. M. Eder found that erythrosin is a better sensitiser than eosin for green light,[5] and the first "orthochromatic"

plates were made.[6] Chlorophyll, eosin, and erythrosin, the last of which was used commercially for many years, are exceptional in that they do *not* belong to the cyanine or related types.

In those early days, although colour sensitive plates had been put on the market, the property of photographic sensitising seemed of little practical importance. Cyanine did indeed sensitise to green light and even into the red (see Figure 1C), but it gave chemical fog. It has been reported that even one part of cyanine in five million of emulsion stained the plate.[7] The observation in 1903, however, that the isocyanines sensitised to green light (see Figure 1D) without fogging[8] was followed by German patents which were largely the work of E. König,[6] and various sensitising dyes of this group became available (see II-1-C). Pinacyanol, the first sensitiser to red light (see Figure 1E) was prepared by B. Homolka,[6] by carrying out an isocyanine condensation in the presence of formaldehyde.[9]

At the outbreak of the First World War, the supply of sensitising dyes to the Allies was cut off, for all these dyes were made in Germany. Yet sensitising dyes are essential for taking photographs from aeroplanes, because the atmosphere scatters blue light more than it scatters light of longer wavelength. At the request of the British War Office, the problem of supplying photographic sensitisers was taken up at Cambridge University by W. J. Pope and W. H. Mills, and that led Mills to his study of the constitution of all the cyanine dyes known at that time. It has seemed best to consider this fundamental scientific work in one section (section 3), following a section (section 2) on the chemistry of the subject up to 1919. To the vast superstructure, which has been built up on the scientific foundation, many workers, in various countries, have contributed, and their names are recorded in the bibliographies at the end of each chapter. The subject of the cyanine dyes is closely connected with the photographic industry, and much of the information is in the patent literature. By means of photographic sensitisers, it is possible to attain a true rendering of colour in monochrome. Also, by making film sensitive to colour other than blue, its speed has been increased, i.e., exposure times have been reduced. It has been noted that, in the motion picture industry, sensitisers made possible the replacement of arc lamps by silent filament lamps, which was necessary for sound recording.[10]

It was observed by H. W. Vogel that the sensitising maximum of each dye approximates to the absorption maximum of its solution

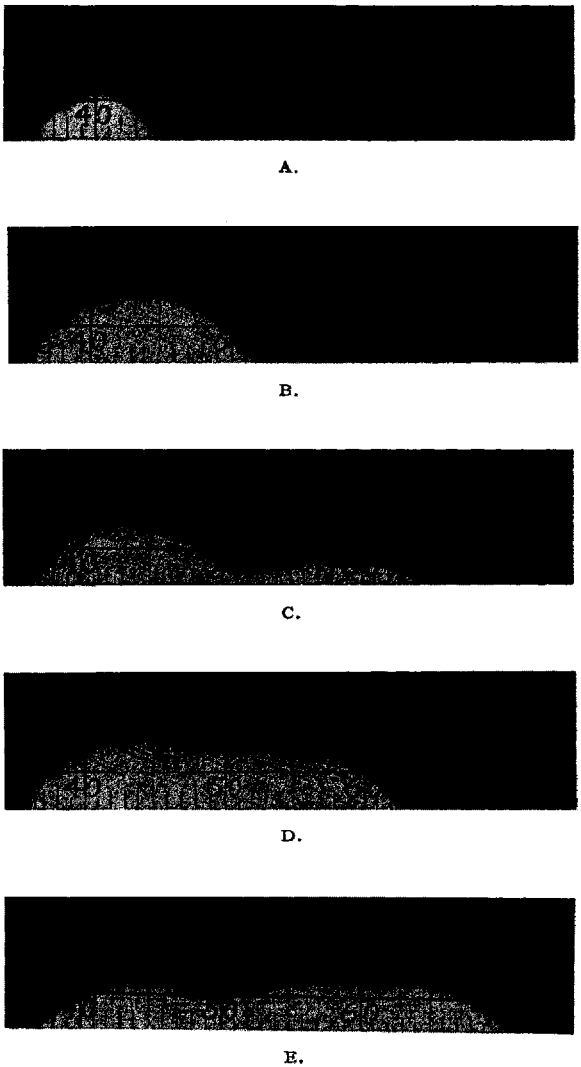


Fig. 1. Wedge spectrograms. (A) Chloride emulsion; (B) bromide emulsion; (C) B dyed with cyanine; (D) B dyed with isocyanine; (E) B dyed with pinacyanol. [From F. M. Hamer, *Quart. Revs. London*, **4**, 327 (1950), Plate 1. By courtesy of the Chemical Society.]

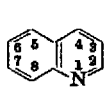
but lies at a slightly longer wavelength.[11] For various scientific purposes it is convenient to have photographic material which is sensitive to a particular region of the spectrum. Photography in colour depends on the availability of photographic material which has been sensitised to different colours.

Some cyanines absorb infrared light and sensitise to the infrared. Dicyanine (see section 3-G) was an early infrared sensitiser, which was used for spectrum photography,[12] but kryptocyanine (see section 3-F; IV-2-C) was easier to use; by means of it, the most distant photographs on record were taken by A. W. Stevens, the furthest being at 330 miles, although cyanines sensitising at a much longer wavelength than kryptocyanine are known.[13] In photographs taken by infrared light, with a filter to cut out the light of shorter wavelength, blue skies appear dark whilst trees appear light. Some interesting pairs of photographs on an orthochromatic and on an infrared sensitive plate have been published.[14] The sensitising, and other, properties of the cyanines are considered in the last chapter. Although value as dyes is ascribed to very few of the compounds, the term "cyanine dye" is justified, in that the cyanines do dye silver halide. At the beginning of this century, various photographic sensitisers were on the market, but nowadays the nature of the particular sensitisers used is a trade secret and practically none are for sale.

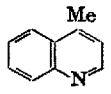
2. The Chemistry of the First Sixty-Three Years (up to 1919)

It was in 1856 that C. H. Greville Williams, who was then working at Glasgow University and was twenty-seven years old, noted the tendency of quinolinium salts to give intense colours,[15] for instance on heating with silver oxide. A year later von Babo independently obtained "one of the most beautiful substances of organic chemistry" from the salts which quinoline formed with alkyl sulphates, and these he called methyl- and ethyl-irisines.[16] Greville Williams, in comparing quinolines obtained by distillation of coal, bituminous shale, bone oil, and cinchonine, found general agreement in physical properties, with minor differences, and the most striking of these was[17,18] that the distillate from cinchonine, when its salt with amyl iodide was heated with ammonia, gave "a magnificent blue colour". He realised the impurity of the base and, by a graduated action of potash on the salt,

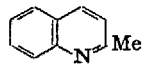
was able to get first a purer blue colour, then a red one, and sometimes an emerald-green colour.[18] In 1863 it was recognised[19] that the quinoline contained another base, which had been named lepidine.[20] A gold medal and a prize of 10,000 francs had been suggested as a reward for making stable the beautiful colours dyed by cyanine,[19] as the blue dye was now known commercially.



(I)



(II)



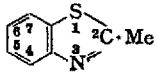
(III)

Quinoline, I, was synthesised in 1880;[21] soon afterwards lepidine was recognised[22] as its 4-methyl homologue, II, and its 2-methyl homologue, quinaldine, III, was synthesised[23]. In 1883 it was found that synthetic quinoline did not give rise to cyanine and it was demonstrated that it is the mixture of quinoline alkiodide and lepidine alkiodide that is operative.[24,25] When the perfectly correct general equation of that date, showing the formation of cyanine from alkiodides, is written for ethiodides, it becomes:

$$C_9H_7N \cdot C_2H_5I + C_{10}H_9N \cdot C_2H_5I \longrightarrow C_{23}H_{23}N_2I + H_2 + HI \qquad (1)$$

Two sets of observers independently[25,26] obtained a redder dye by the action of alkali on a mixture of quinoline ethiodide and quinaldine ethiodide. For this dye, one pair of workers proposed the name diethylisocyanine iodide and they considered that it also had the formula $C_{23}H_{23}N_2I$.[25]

In 1886 it was noted that when 2,4-dimethylquinoline methiodide was treated with sodium hydroxide solution and left standing in the air, there was formed a violet-blue dye, which was considered to be related to cyanine,[27] and was later called Dicyanine. In 1887 the production of a purple dye from the alkiodides of benzothiazole and 2-methyl-



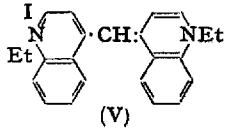
(IV)

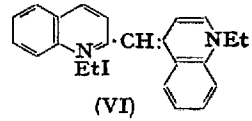
benzothiazole, IV, by the action of ammonia was observed and the dye was regarded (naturally, but incorrectly) as cyanine in which two quinoline nuclei were replaced by two benzothiazole nuclei.[28]

The valuable photographic sensitising properties of the isocyanines were patented in 1902.[8] As the other discoverer of isocyanine believed two extra hydrogen atoms to be present, his formula was $C_{23}H_{25}N_2I$,[26] and this was supported by others in 1904.[29] They examined the conditions of formation of the isocyanine, which was now commercially known as Ethyl Red. The best yields were obtained by heating two mols. of quinoline ethiodide, one mol. of quinaldine ethiodide, and two mols. of caustic potash in alcoholic solution. Another isocyanine was prepared by the action of potash on quinaldine ethiodide, in the absence of quinoline ethiodide, but that dye, Quinaldine Red, was not a useful photographic sensitiser. From the fact of the formation of Quinaldine Red, it was concluded that in isocyanines the quinoline nuclei must be linked in the 2- and 4-positions and the formation of isocyanine was pictured as taking part in four stages: (1) conversion by alkali of quinolinium salt into ammonium base; (2) passage of this into 1-ethyl-4-quinolone, with elimination of two hydrogen atoms; (3) by these, hydrogenation of the quinaldinium salt in the 3,4-positions; (4) condensation of dihydroquinaldinium salt and quinolone, with removal of water. Ethyl Red easily took up two iodine atoms; it was concluded that such products could not be periodides but that the addition must take place across the double bond of the methin group joining the nuclei. By the action of silver salts on the isocyanine, its iodine atom was replaced by other acid radicals. Cyanine itself was examined too.[30] So was the blue dye, Dicyanine, obtained from 2,4-dimethylquinoline ethiodide, by the oxidising action of air and alkali: it was concluded that that belonged to a different class from cyanine.[31]

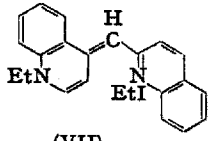
In a remarkable paper in 1906, there was attacked, on purely theoretical grounds, both the proposed mechanism of dye formation and the formula itself, since this afforded no explanation of the blue colour of the cyanines and the red of the isocyanines.[32] Although the 4-quinolone was accepted as a possible intermediate, it was pointed out that there was no evidence that the methyl group of quinaldine ethiodide or of lepidine ethiodide would retain its reactivity in the dihydro-derivatives, but rather the contrary. The observation that the best yield results with two mols. of quinoline ethiodide to one of quinaldine ethiodide was regarded as evidence against the conclusion that molecular proportions react. The formula poorer in hydrogen, $C_{23}H_{23}N_2I$, was favoured, and with surely a flash of genius, the structures V and VI for cyanine and isocyanine, respectively, were proposed. By

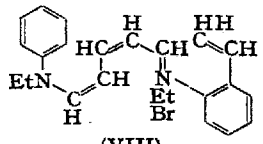
these formulae the addition of two iodine atoms could be explained, but the products were regarded as periodides. It was claimed that these formulae explained the colours of the dyes, since in the blue cyanine, V, the


(V)

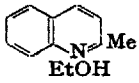

(VI)

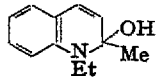
two nitrogen atoms are joined by a seven-carbon chain, having three double bonds, and in the red isocyanine, VI, by a five-carbon chain, having two double bonds. These formulae also explained the analogy between the cyanines and the yellow to orange dyes which had been obtained[33,34] by treating pyridinium salts with amines; thus isocyanine, VII, was compared with a hypothetical dye, VIII, of that kind, for which a scheme of synthesis was suggested.[32]

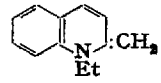

(VII)

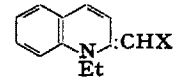

(VIII)

The formula $C_{23}H_{23}N_2I$ for isocyanine was supported in 1908:[35] since isocyanine formation was prevented when the methyl group of the quinaldinium salt was replaced by isopropyl or by benzylidene, it was concluded that the methyl group is essential. It was suggested that alkali converts the quinaldinium salt into the ammonium base, IX, which passes into the carbinol base, X, and that into the methylene


(IX)


(X)

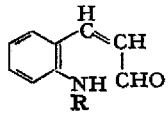

(XI)


(XII)

base, XI (which was called the isobase), and that it is this last which is operative in dye formation. By oxidation of the isocyanine to 1-ethyl-2-quinolone, the presence in the dye of the grouping, XII, was deduced. The occurrence of isocyanine formation on bringing together, in the presence of benzene, the carbinol base from quinaldine methiodide and 4-chloroquinoline methochloride indicated that the 4-position of

the quinoline nucleus was involved. Evidence was adduced that 1-ethyl-2-quinolone and 1-ethyltetrahydroquinoline cannot be intermediates in isocyanine formation, and it was suggested that loss of quinoline ethiodide by conversion into such compounds may explain why an excess must be used in order to get the best yields of isocyanine.

In 1911 it was pointed out[36] that earlier observers[25b,29] had been wrong in saying that quinolinium salts, in the absence of salts of lepidine or quinaldine, do not give dyes when heated with alkali. Dyes are in fact formed and these differ from the cyanines in that they are not instantly decolorised by mineral acids. They were called apocyanines. Thus a solution of quinoline ethiodide in methanol was boiled with potash and a yellow dye, xanthoapocyanine, was first filtered off. On cooling, the main product crystallised. It was a red dye, which was called erythroapocyanine, and was regarded as being the monoacid salt of 1,1′-diethyl-2,2′-diquinolenyl,[36] though it was recognised that, if that were correct, it should be possible to isolate the free base.[37] It was said that in the formation of apocyanines, or of true cyanines, there should always be insufficient alkali to decompose all the quinolinium salt. The pseudo-base was formulated as an *o*-alkylaminocinnamic aldehyde, XIII, which condensed with unchanged quinolinium salt to give apocyanines, or with the methyl group of lepidinium or quinaldinium salts to give true cyanines.[36]



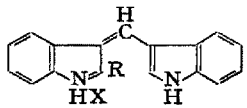
(XIII)

With the then existing evidence for the presence of one 4-linked quinoline nucleus in isocyanine[29,32,35] it is surprising to find a suggestion in 1911[37] that isocyanine is the 2,2′-analogue of V or VI.

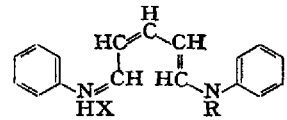
It was realised that quinolones could not be intermediates in cyanine dye formation, since they are inert, but it was suggested that the carbinol base, X, might condense with quinaldine ethiodide to give a leuco compound, which was subsequently oxidised to isocyanine. In the following year, the evidence as to the structure of the cyanines was summarised and further evidence adduced.[38] The dyes were described as monoacid salts of a diacid base; from the colourless acid solution, a neutral diacid salt could be obtained, but it readily reverted

to dye and acid, whereas the monoacid salts are very stable. As the intact methyl group of quinaldine had proved necessary for isocyanine formation, the dye was formulated as $RN:C_9H_6:CH\cdot C_9H_6:NRI$. Besides the 2-quinoline linking, two lines of evidence showing a 4-quinoline linking were provided: (1) Quinaldine ethiodide could condense with 2-phenylquinoline methiodide to give an isocyanine, but not with 4-phenylquinoline ethiodide, where the 4-position was blocked; (2) with a readily removable substituent in the 4-position, condensation could occur: thus quinaldine ethiodide gave the same isocyanine with 4-chloro-2-phenylquinoline ethiodide as it did with 2-phenylquinoline ethiodide, and with 4-chloroquinoline ethiodide it gave the unsubstituted isocyanine. The formula poorer in hydrogen was established, since dye formation proceeded with elimination of hydrochloric acid, and it was concluded that isocyanine is represented either by VI or by a formula having the acid radical on the other nitrogen atom. An attempt was made to decide this point by splitting off alkyl iodide from the 2-phenylisocyanine and then oxidising the base.[38]

In 1912 dyes such as XIV (R = H or Me) were obtained by condensing β-formylindole (or its α-methyl derivative) either with indole, or with itself, in the presence of mineral acids, and it was pointed out that they had the same chromophore as the pyridine dyes, XV. It was



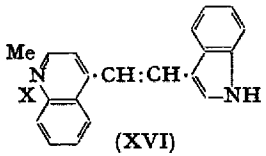
(XIV)



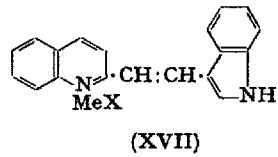
(XV)

also noted that both aldehydes condense, in alcohol in the presence of piperidine, with quaternary salts having reactive methyl groups; those prepared from β-formyl-α-methylindole with lepidine methiodide and quinaldine methiodide (or methoperchlorate) were investigated and formulated as XVI and XVII.[39] By condensing *p*-dimethylaminobenzaldehyde with a lepidinium or quinaldinium salt, in alcohol in the presence of piperidine, dyes of further types, XVIII and XIX, were made. It was considered that the formulae for the indole dyes, XVI and XVII, were so like those for cyanine, V, and isocyanine, VI, that there should be a greater similarity in properties than in fact exists. For, whereas, the indole dyes were unaffected by strong acids or

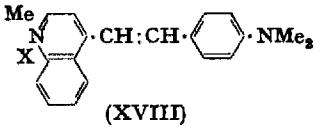
by nitrous acid, the cyanines were discoloured by acid and with nitrous acid gave, momentarily, yellowish solids, which were regarded as nitrosoamines. Hence it was concluded that it was right to regard the



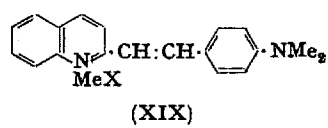
(XVI)



(XVII)

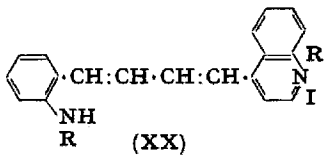


(XVIII)

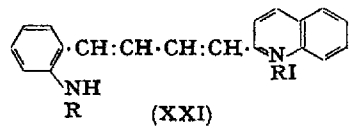


(XIX)

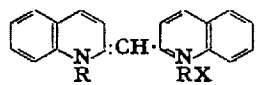
cyanines as derivatives of *o*-alkylaminocinnamic aldehyde, XIII, and the earlier formulae, V and VI, for cyanine and isocyanine, respectively, were considered less probable than the open-chain formulae, XX and XXI.[40] It is ironical that just as other chemists[38] were supporting the earlier formulae (their paper was sent to the *Berichte* on April 20th, 1912), their proposer was abandoning them[40] (in the *J. Prakt. Chem.* for July 2nd, 1912).



(XX)



(XXI)



(XXII)

In 1918, it was remarked that, although quinaldine ethiodide has a strong tendency to couple with quinoline ethiodide in the 4- position, yet if that position is blocked, as in 4-phenylquinoline ethiodide, then a red dye is formed, the parent substance of which must be the 2,2'-isomeride of V and VI, and this, XXII, was called pseudoisocyanine.[41]

Pinacyanol, a valuable sensitiser to red light, had been prepared by the action of caustic alkali and formaldehyde on quinoline ethiodide and quinaldine ethiodide in hot alcoholic solution.[9] In discussing this

reaction, it was noted that the same dye was formed from quinaldine ethiodide alone as from the ethiodides of quinaldine and quinoline; it was considered, wrongly, that formaldehyde played the part of an oxidising agent and that its residue did not enter into the pinacyanol molecule; the presence of a 2,2'-linking in pinacyanol was recognised, and a formula was suggested: dyes of that type were named pseudodicyanines.[41] The blue dyes prepared by the action of alkali and an oxidising agent on 2,4-dimethylquinoline alkiodides[27,31] also had valuable sensitising properties and had been patented.[42] It was realised that in these so-called dicyanines there is present a 2,4'- linking.[41]

It has seemed convenient to make this historical introduction to the chemistry of the cyanines cover the first sixty-three years, i.e., up to the end of 1919, and it is interesting to glance at the list of cyanines given in a paper[41] of the previous year, so as to review what was known of them at that date. The general term quinocyanines for cyanines containing quinoline nuclei[41] has found a limited application in subsequent literature. Five classes of these are given: apocyanines, isocyanines, lepidine cyanines, pinacyanols, and dicyanines. It was known that the apocyanines have two quinoline nuclei directly linked; the empirical formulae of the isocyanines and cyanines were known, the positions of linking of their nuclei known, and alternative structures had been proposed; the positions of linking in pinacyanol and in the dicyanines had been correctly surmised.

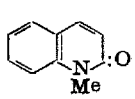
In 1920 came the first of a series of papers by W. H. Mills and his co-workers. These papers, in a short space of time, mapped the fundamental chemistry of the existing cyanines and opened out an unsuspected vista. In the next section the establishment of the constitution of these dyes will be dealt with, after which it will be convenient to proceed to a definition of the cyanines and then to consider each group systematically.

3. Establishment of the Constitution of the Typical Cyanines Known in 1920

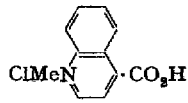
A. The Constitution of Isocyanine

The constitution of isocyanine was established in 1920.[43] 1,1'-Dimethylisocyanine acetate was oxidised with alkaline permanganate and it was observed that 3½ atoms of oxygen were required per molecule. From the solution 1-methyl-2-quinolone, XXIII, was isolated,

and, after acidification with hydrochloric acid, cinchoninic acid methochloride, XXIV. The yields of crude products were, respectively, 80 %



(XXIII)



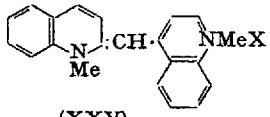
(XXIV)

and 70 %. Together these two compounds accounted for all the carbon atoms, and the molecules together contained 3 atoms of oxygen:

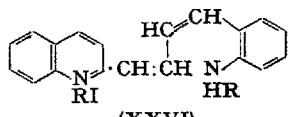
$$C_{21}H_{19}O_3N_2X + 3O \longrightarrow C_{10}H_9ON + C_{11}H_{10}O_2NX \qquad (2)$$

Thus the formula of isocyanine was established as XXV. In formula VI the acid radical was on the other nitrogen atom but it was considered that the two formulae represented virtually tautomeric compounds.

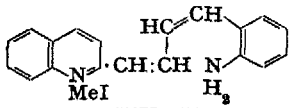
The open-chain formula for isocyanine was XXVI (R = alkyl). In 1920 the closely related XXVII was synthesised as follows. *o*-Nitrocinnamic aldehyde was condensed with quinaldine, by heating with



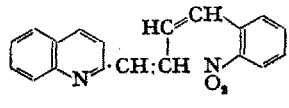
(XXV)



(XXVI)



(XXVII)



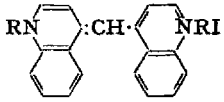
(XXVIII)

zinc chloride, to give XXVIII, which was then reduced to the amino-compound; the amino-group was protected by acylation and the acylamino-compound was converted into its methiodide. The formyl derivative was found to give the best results and its methiodide on hydrolysis with dilute hydrochloric acid gave *o*-aminocinnamylidenequinaldine methiodide, XXVII. This compound showed little analogy with isocyanine. It formed reddish brown aqueous solutions, which became pale yellow on addition of acid. It showed general absorption and no photographic sensitising properties. However it was noted that a compound of this structure should be capable of existence in

four geometrically isomeric forms, only one of which is closely related in configuration to isocyanine.[44] The spectroscopic evidence supported the ring formulae for cyanine and isocyanine as against the open-chain formulae.[45]

B. The Constitution of Cyanine

The cyanines correspond so closely with the isocyanines in formation, composition, and general properties, that their constitution, XXIX, followed from the establishment of the constitution of the isocyanines.[43]



(XXIX)

At that time the starting point, XXV, of the oxidative breakdown seemed perfectly satisfactorily named as 1,1′-dimethylisocyanine acetate, whilst the cyanine, XXIX, would be called 1,1′-dialkylcyanine iodide. Later on, with the multiplication of trivial names in the group, it seemed better to call XXV 1,1′-dimethyl-2,4′- cyanine acetate, and to specify XXIX more exactly as 1,1-dialkyl-4,4′- cyanine iodide.

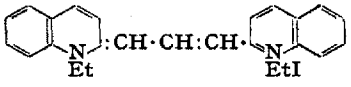
C. The Constitution of Pinacyanol

The formula, XXX, for pinacyanol[46] was established in 1920.[47] Although two formulae had been suggested previously, one did not agree with the analytical results and neither explained the colour of the dye. Careful analysis showed that two molecules of quinaldine ethiodide were concerned in the formation of pinacyanol, and that the formaldehyde residue did enter into the molecule. The probable reaction for dye formation was therefore:

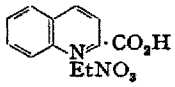
$$2\,C_{10}H_9N,\,C_2H_5X + CH_2O \longrightarrow C_{25}H_{25}N_2X + H_2O + HX + 2H \qquad (3)$$

It was proved that a quinoline alkiodide, if present, takes no direct part in the condensation. Pinacyanol bromide was oxidised by heating with dilute nitric acid and from the reaction mixture quinaldinic acid ethonitrate, XXXI, was isolated in about 90% yield. Since it was so smoothly formed, this indicated the presence in pinacyanol of the

group XXXII. Oxidation of pinacyanol acetate with alkaline permanganate in aqueous acetone at 0° gave a 79% yield of 1-ethyl-2-quinolone, which proved that the second quinoline nucleus is present in the form XXXIII. It was suggested that the first condensation of quinaldine ethiodide and formaldehyde gives XXXIV, which first



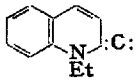
(XXX)



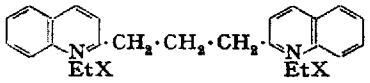
(XXXI)



(XXXII)



(XXXIII)



(XXXIV)

loses hydrogen iodide, and then loses two hydrogen atoms from the chain. The loss of two hydrogen atoms also occurs in isocyanine formation.

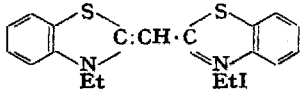
In the cyanine series, cyanine, with a 4,4′-linking, and isocyanine, with a 2,4′- linking, had been known for a long time, but at that time the 2,2′- cyanines had not been characterised. Pinacyanol corresponded with the last. The existence of pinacyanol analogues, having a 2,4′- and a 4,4′- linking, was predicted.[47]

In the three types of cyanine, the nuclei were linked by one methin group, whereas in pinacyanol and its possible isomers, the linking was by a three-carbon chain. As a basis for the systematic nomenclature, the name carbocyanine was proposed[46] and this term proved very convenient over a period of years. Thus pinacyanol, XXX, was named 1,1′-diethylcarbocyanine iodide. Subsequently, after the fulfilment of the prediction, it was more exactly described as 1,1′-diethyl-2,2′-carbocyanine iodide, in which name the positions of linking of the nuclei were specified.

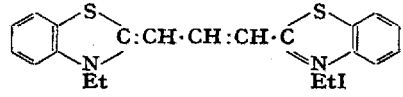
D. The Constitution of Cyanines of the Benzothiazole Series

The purple dye which was prepared in 1887 by the action of ammonia on the amyliodides of benzothiazole and 2-methylbenzothiazole was regarded as the cyanine of the benzothiazole series[19] and this view was accepted[40,41] even so late as 1918. It was found in 1920

that with ethiodides, the yield by the original method was very small, and that the condensation proceeded better in the presence of pyridine. By heating the salts together in this medium at 100° for several hours, crystals of the purple dye were obtained, together with a larger quantity of a yellow one. The former crystallised in steel-blue prisms and gave purplish-red solutions, which were decolorised by excess of a mineral acid, so that it strongly resembled the isocyanines and was clearly the diethyl analogue of the original diamyl compound. It was a powerful photographic sensitiser for green, yellow, and orange light. The less soluble yellow compound was also a quaternary iodide and was a sensitiser for silver chloride emulsions. The investigation of the two substances led to the surprising conclusion that it was not the red dye but the yellow one which was the cyanine, XXXV, of the benzothiazole series, whilst the red dye was the analogue, XXXVI, of pinacyanol.[48]



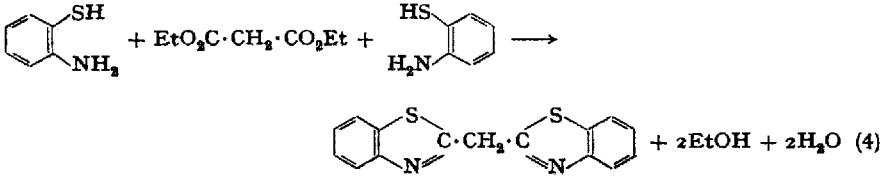
(XXXV)



(XXXVI)

The former was called a thiocyanine and the latter a carbothiocyanine.[48] Subsequently the latter name was modified to thiocarbocyanine,[49] so as to be more consistent with other names which had been proposed. In 1934 the names became thiacyanine and thiacarbocyanine. In 1922 the numbering of the benzothiazole ring differed from that accepted, by international agreement, in 1939. Thus XXXV would now be called 3,3′-diethylthiacyanine iodide, and XXXVI would be called 3,3′-diethylthiacarbocyanine iodide.

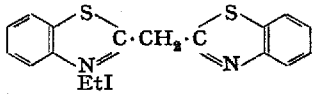
The constitution of the thiacyanine, XXXV, was established[48] by its synthesis from *o*-aminothiophenol, by heating two molecular proportions with one of ethyl malonate, according to equation 4:



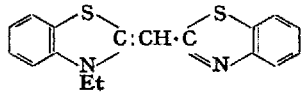
(XXXVII)

(4)

The resultant dibenzothiazolylmethane, XXXVII, formed a monoethiodide, XXXVIII. Treatment with alkali eliminated acid, giving the yellow base, XXXIX, m.p. 162°. Its ethiodide proved identical with XXXV. The corresponding series of reactions was also carried out in the methyl series and the resultant iodide was found to be identical with the yellow dye prepared from benzothiazole methiodide and 2-methylbenzothiazole methiodide.



(XXXVIII)



(XXXIX)

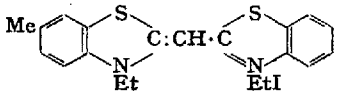
Dye formation was also carried out[48] by the action of pyridine on a mixture of benzothiazole ethiodide and 2,6-dimethylbenzothiazole ethiodide. Analysis showed that the thiacyanine was formed from one molecule of each ethiodide. In the purple dye both nuclei were derived from the 2,6-dimethyl compound. The two residues of this salt accounted for twenty-two out of twenty-three carbon atoms in the molecule of dye. It appeared that the part played by benzothiazole ethiodide was to provide the monocarbon residue. Because of the similarity between the two purple dyes and pinacyanol, it was concluded that the two benzothiazole nuclei were linked through the 2-methyl group, and that the purple dyes had the structure XXXVI and its 6,6'-dimethyl derivative. An alcoholic solution of XXXVI had its principal absorption maximum at 5590 Å and another at 5250 Å. The crystals of XXXVI were holohedral monoclinic.

E. Preparation of Unsymmetrical Methincyanines

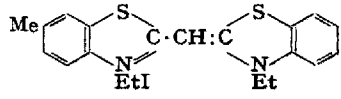
Cyanine itself, XXIX, may be described as a symmetrical methincyanine, for it is a cyanine in which the nuclei are linked by one methin group, those nuclei are similar, and the position of linking is the same in each. Thiacyanine, XXXV, also is a symmetrical methincyanine. On the other hand, isocyanine, XXV, is an unsymmetrical methincyanine, for although the two nuclei are similar, one is linked through the 2-position and the other through the 4-position to the central methin group.

The following two thiacyanine syntheses were effected by heating

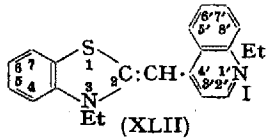
in pyridine.[50] In the first, 6-methylbenzothiazole ethiodide was condensed with 2-methylbenzothiazole ethiodide, which was expected to give XL; this was accompanied by the thiacarbocyanine, XXXVI. In the second, 2,6-dimethylbenzothiazole ethiodide was condensed with benzothiazole ethiodide, which was expected to give XLI; this was accompanied by the 6,6′-dimethyl derivative of XXXVI. That the unsymmetrical thiacyanines, XL and XLI, were in fact identical was proved by comparison of melting points, mixed melting points and solubility, and by demonstrating that neither would dissolve in a saturated solution of the other. At that date, this was regarded as evidence of virtual tautomerism, with the possibility that, in the future, a decision in favour of either XL or XLI might be made.[50] Today both XL and XLI are regarded as resonance extremes of one and the same dye.



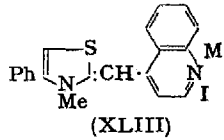
(XL)



(XLI)



(XLII)



(XLIII)

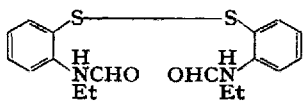
A new type of unsymmetrical methincyanine, XLII, was prepared by replacing quinaldine ethiodide in the isocyanine condensation by 2-methylbenzothiazole alkiodide.[51] It could also be replaced by the salt of a simpler base, such as 2-methyl-4-phenylthiazole methiodide, to give XLIII.[52] To prepare XLII, sodium hydroxide in alcoholic solution was boiled with a mixture of quinoline ethiodide and 2-methylbenzothiazole ethiodide, whereupon a red colour developed and dye crystallised on cooling. Six compounds of this type were prepared and were found to be photographic sensitisers for green light. At that time, it was supposed that the acid radical was attached to what was, presumably, the more basic part of the molecule.

These dyes were named thioisocyanines—now thiaisocyanines—because of their analogy with the isocyanines, XXV,[51] but the name thia-4′-cyanine is more explicit. The positions of substituents in the benzothiazole ring were indicated by plain numerals, with a dash

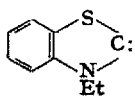
added to numerals which showed the positions of substituents in the quinoline nucleus. Since that date, the numbering of the benzothiazole nucleus has been changed; the modernised version of the name for XLII is 3,1′-diethylthia-4′-cyanine iodide. Individual names such as this have been useful in the past and the general term thia-4′-cyanine is still a useful one.

It was found that it is not possible in the isocyanine condensation to replace quinoline ethiodide by benzothiazole ethiodide[51] and this was attributed to the effect of alkali on the base from the benzothiazolium salt.[53] However it was found that when di-[*o*-*N*-ethylformanilido] disulphide, XLIV, and 2-methylbenzothiazole ethiodide were heated together, in pyridine solution, they gave a mixture of thiacyanine, XXXV, and thiacarbocyanine, XXXVI. Therefore two types of reaction occurred. In the first place the disulphide provided the residue, XLV, which condensed with 2-methylbenzothiazole ethiodide to give the thiacyanine, XXXV. Secondly, it provided a methin group, which condensed with 2 mols. of the quaternary salt to give the thiacarbocyanine, XXXVI.[53]

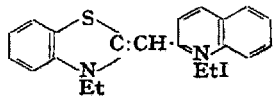
A similar reaction was carried out[53] with quinaldine ethonitrate, by heating it with the disulphide, XLIV, in pyridine. As in the other instance two dyes were produced, of which one was the blue pinacyanol, XXX. The other was an orange-brown dye, which was converted into iodide and, from its composition and method of formation, could only be XLVI. It was given the name of thiopseudocyanine,



(XLIV)



(XLV)



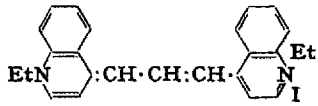
(XLVI)

which later became thiapseudocyanine. This was also written thia-ψ-cyanine, but thia-2′-cyanine is better. With the present numbering of the benzothiazole ring, the name for XLVI would be 3,1′-diethylthia-2′-cyanine iodide.

The corresponding reaction was also effected[53] with lepidine ethonitrate and gave an orange-red and a blue dye, both of which were isolated as iodides. The former was identical with the thia-4′-cyanine, XLII, which had been prepared by condensation of quinoline ethiodide and 2-methylbenzothiazole ethiodide.

F. The Constitution of Kryptocyanine

The blue dye which accompanied the thia-4′-cyanine was isomeric with pinacyanol and must have the structure XLVII. It formed beautiful pleochroic crystals and its alcoholic solution was a greener blue than that of pinacyanol. It was a powerful sensitiser for light of wavelengths

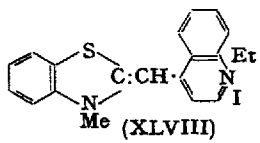


(XLVII)

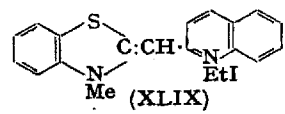
6500 to 7900 Å, with the sensitising maximum at 7430 Å.[53] It was identified[53] with "kryptocyanine". Various dyes of this type had been prepared[54,55] in an impure condition, by the action of alkali and formaldehyde, or chloroform, on a hot alcoholic solution of lepidine alkiodide, and had proved valuable sensitisers for infrared light.

G. The Constitution of Dicyanine

The general method of heating a quaternary salt in pyridine with a disulphide, such as XLIV, was applied[56] to a mixture of the ethonitrates of quinaldine and lepidine with di-[*o*-*N*-methylformanilido] disulphide, a reaction which in theory should give five dyes. The first, XLVIII, crystallised as nitrate, which was converted into iodide. The filtrate was then treated with potassium iodide, the product was



(XLVIII)

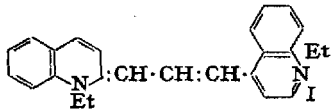


(XLIX)

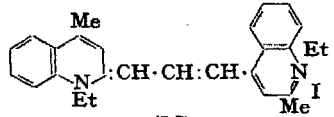
worked up to remove starting materials and by-products from the dyes, and these were separated by fractional crystallisation from methanol and benzene. In the first place, the disulphide, by providing a benzothiazole nucleus, gave with the lepidinium salt the thia-4′-cyanine, XLVIII, and, with the quinaldinium salt, the thia-2′-cyanine, XLIX; these were identified with samples prepared by reaction of the disulphide in pyridine with a lepidinium salt and a quinaldinium salt, respectively. Further, the disulphide, by providing the central

carbon atom of the three-carbon chain, should give rise to the 2,2'- and 4,4'-carbocyanines (pinacyanol and kryptocyanine) and also to an unknown 2,4'- carbocyanine, L. By great good fortune it happened that the 2,2'- and 4,4'- isomers were only formed in very small quantity, indeed the latter could only be detected spectroscopically, and the main product was L.

The new dye, 1,1'-diethyl-2,4'-carbocyanine iodide, L, formed green lustrous crystals, m.p. 240–241° (decomp.); their deep-blue alcoholic solution was decolorised by acids. The dye was a powerful photographic sensitiser for red light. The absorption curves (Figure 2)[56]



(L)



(LI)

of alcoholic solutions of the 2,2'-, 2,4'-, and 4,4'-carbocyanines all showed a well-defined primary maximum, and also a secondary one: the spectrum of the 2,4'-carbocyanine was intermediate between that

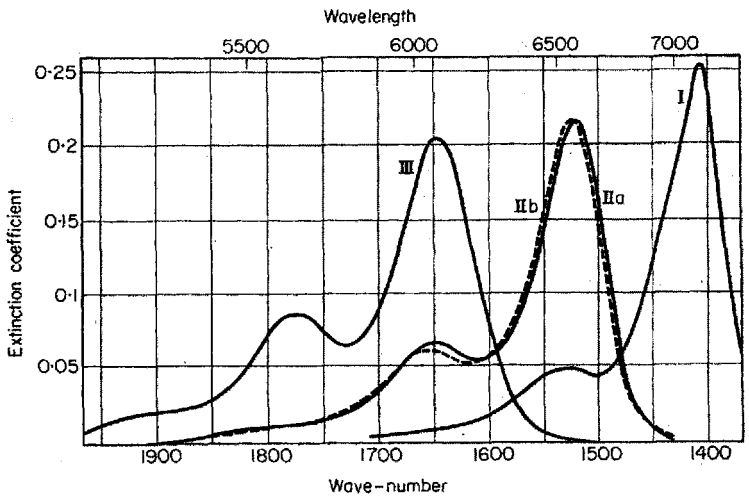


Fig. 2. [From Mills and Odams (56). By courtesy of the authors and the Chemical Society.]

of the 2,2'- and 4,4'-carbocyanines. It was pointed out that, in each, the two nitrogen atoms are linked by a chain of conjugated double

bonds and that the carbon chain is composed of five atoms in the 2,2′-carbocyanine, of seven atoms in the 2,4′-carbocyanine, and of nine atoms in the 4,4′-carbocyanine.

This synthesis of 2,4′-carbocyanine was undertaken[56] in the expectation that it would throw light on the constitution of the dicyanines. These dyes were produced by the action of alkali and an oxidising agent on quaternary salts of 2,4-dimethylquinolines[27,31,42], and sensitised in the red and into the infrared, as far as 9000 Å or beyond.[57] Dicyanine A was the commercial name of a German sensitising dye. Details of the preparation of dicyanines had been described,[58] their constitution had been discussed and a 2,4′-linking postulated; a formula had been suggested,[41] but this did not agree with analysis nor explain the colour of the dyes. A carbocyanine iodide was now prepared from 2,4-dimethylquinoline ethiodide[56] by a method based on that for the 6,6′-diethoxy-derivative.[58] Analysis showed that it must be formed by condensation of two mols. of the ethiodide with a monocarbon residue: condensation could only take place through the reactive methyl groups, so that the dye must be a dimethyl derivative of a carbocyanine. In Figure 2, the dotted curve shows the absorption of this dye: it lies so close to the curve of the 2,4′-carbocyanine as to prove that dicyanine must be of that type.[56]

This dicyanine, LI, from 2,4-dimethylquinoline ethiodide may be called 1,1′-diethyl-4,2′-dimethyl-2,4′-carbocyanine iodide.

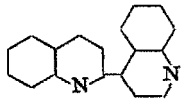
H. The Constitution of the Apocyanines

The constitution of all known types of cyanines, with the exception of the apocyanines, had now been established; this remaining problem was solved in 1928[59] when it was noted that the formulation of erythroapocyanine as a diquinolenyl hydriodide (see I-2) did not explain either the stability of the dye to alkali nor its intense colour. It was found that the red dye from quinoline ethiodide was smoothly oxidised by potassium permanganate, or by iodine, and that the oxidation proceeds thus:

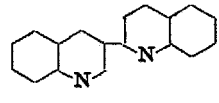
$$[C_{18}H_{18}N_2(C_2H_5)_2]I + I_2 \longrightarrow [C_{18}H_{12}N_2(C_2H_5)_2]I_2 + HI \qquad (5)$$

The product was concluded to be the diethiodide of a diquinolyl. By heating the corresponding diethochloride in a vacuum, the diquinolyl itself was isolated. From what was then known of the colour of the

cyanines, it appeared that, in order to account for the colour of erythroapocyanine, the diethiodide must be derived from a diquinolyl in which the two nitrogen atoms are separated by an odd number of carbon atoms: the two possible skeletons were LII and LIII. From



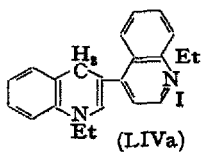
(LII)



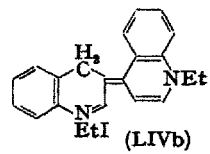
(LIII)

diethiodides of diquinolyls of this kind, the dyes would be obtained by addition of one hydrogen atom and removal of one iodine atom per mol. To leave a conjugated chain of double bonds between the nitrogen atoms, the added hydrogen must be in the 4-position. That resulted in formulae LIVa or LIVb for erythroapocyanine and in formulae LVa or LVb for xanthoapocyanine.[59]

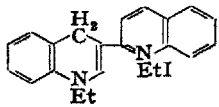
The constitution of erythroapocyanine was established by the following synthesis. Ethyl 4-quinolylpyruvate was heated with *o*-aminobenzaldehyde and gave ethyl 3,4′-diquinolyl-2-carboxylate, LVI (equation 6). The ester was hydrolysed to the acid, which lost carbon dioxide on heating, giving 3,4′-diquinolyl. Its ethiodide was identical



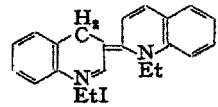
(LIVa)



(LIVb)

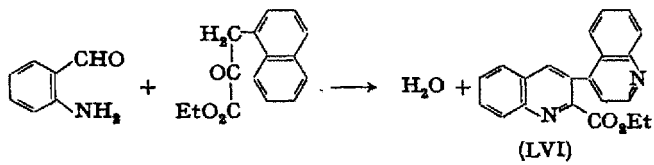


(LVa)



(LVb)

with that obtained by oxidising erythroapocyanine with iodine. By starting with ethyl 2-quinolylpyruvate, there were similarly synthesised 3,2′-diquinolyl-2′-carboxylic acid and 3,2′-diquinolyl.[59]

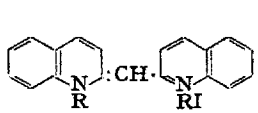


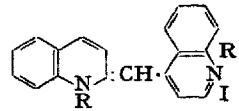
(LVI)

(6)

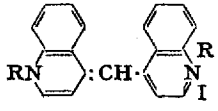
I. Summary, and Some Developments

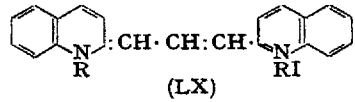
It is useful now to review the position attained as a result of the scientific work on the constitution of the cyanine dyes and then to note briefly some developments. First we have two types of apocyanines, in which the quinoline nuclei are directly linked in the 2,3′- and 4,3′-positions, respectively. Then there are three types of cyanines, in which two quinoline nuclei are linked through a methin group in the 2,2′-, 2,4′-, and 4,4′-positions, respectively, LVII, LVIII, and LIX.

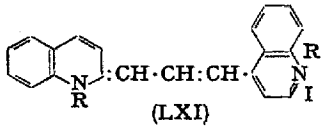

(LVII)

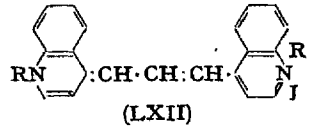

(LVIII)

Corresponding with these there are three types of carbocyanines, in which two quinoline nuclei are linked through a trimethin chain in the 2,2′-, 2,4′-, and 4,4′- positions, respectively, LX, LXI, and LXII. Corresponding with the three methincyanines of the quinoline series, there is one methincyanine of the benzothiazole series, XXXV, and corresponding with the three trimethincyanines of the quinoline series, there is one trimethincyanine of the benzothiazole series, XXXVI. Further there are types of dyes, in which a quinoline nucleus is linked through its 2- or 4-position to a benzothiazole nucleus: such are XLVI and XLII. A monocyclic nucleus had been introduced in the thiazolo-4′-cyanine.[52] Once this scientific foundation had been laid,


(LIX)


(LX)

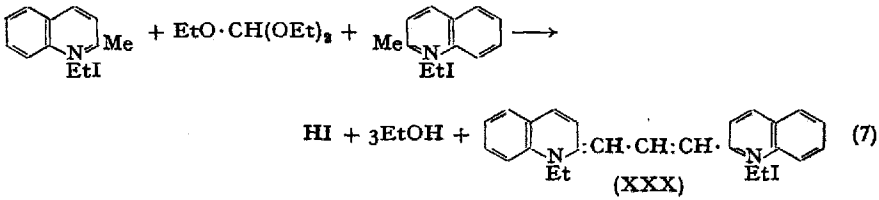

(LXI)


(LXII)

further scientific work was built upon it, and a short account of some developments makes it possible to visualise the magnitude of the still growing structure.

In 1922, the formula for pinacyanol received support, partly

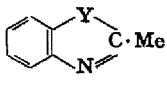
because of a spectroscopic comparison of it with the 2,2′-cyanine, LVII, and partly because of the synthesis of pinacyanol by heating together quinaldine ethiodide and ethyl orthoformate in the presence of acetic anhydride (equation 7).[60] The ethyl orthoformate synthesis



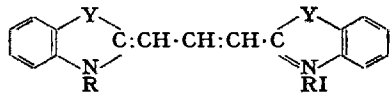
(7)

of symmetrical carbocyanines was applied to other heterocyclic quaternary salts having a reactive methyl group, namely to alkiodides of 2,3,3-trimethylindolenine, LXIII (Y=CMe_2), which gave LXIV (Y=CMe_2);[61] of 2-methylbenzothiazole, LXIII (Y=S), which gave the thiacarbocyanine, LXIV (Y=S);[62] and of 2-methylbenzoxazole, LXIII (Y=O), which gave LXIV (Y=O).[62]

The first azacyanine, in which the methin group of the chain was replaced by nitrogen, was synthesised in 1924.[63] By use of ethyl orthoacetate, instead of ethyl orthoformate, in the preparation of a trimethincyanine, the first dye of this kind to carry an alkyl group on the chain was prepared.[64] Not only 2,2′-cyanines, LVII, but various other 2′-cyanines were synthesised in 1928 and were found to comprise photographic sensitisers.[65]



(LXIII)



(LXIV)

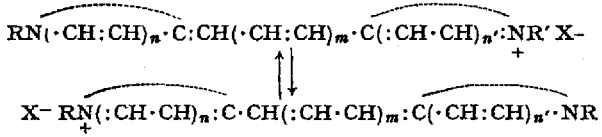
In 1929 diphenylformamidine, PhN:CH·NHPh, was used instead of ethyl orthoformate in the preparation of carbocyanines; the enormous importance of this reactant lay in the fact that intermediate products could be isolated, so that unsymmetrical carbocyanines could be prepared.[66] A homologue of diphenylformamidine, namely β-anilinoacraldehyde anil hydrochloride, PhN:CH·CH:CH·NHPh,HCl was used soon afterwards to give pentamethincyanines.[67] In the same way glutaconic aldehyde dianilide hydrochloride was condensed with quaternary heterocyclic salts, having a reactive methyl group, to give

cyanines in which the two nuclei were linked by a heptamethin chain, and these dyes sensitised to red and infrared light.[67–69] Unsymmetrical dyes of both classes were prepared, and subsequently the chain was further lengthened.

Many other nuclei, including other monocyclic nuclei, were introduced into the molecule. Certain intermediate compounds which had been used for preparing cyanines were found to be applicable to the preparation of new dyes, which were definitely not cyanines. Other new dyes approached the cyanines more nearly. Certain cyanines were accompanied by trinuclear dyes and, in the later years, various types of tri- and poly-nuclear dyes have been synthesised. At this point it seems necessary to discuss what is meant by a cyanine dye.

4. Definition and Nomenclature

A dinuclear cyanine, formulated as below, is a mono-acid salt, in which the nitrogen atoms of two heterocyclic nuclei are linked by a chain of conjugated double bonds, so that this chain necessarily consists of an odd number of carbon atoms.



According to this definition, each compound is regarded as a resonance hybrid of two canonical structures and no single formula is a complete representation. One nitrogen atom is tertiary and the other quaternary and early attempts were made to determine which was which, until in 1920 the conception of the virtual tautomerism of the isocyanines was introduced[43] (see section 3-A). This was applied by other workers to thiacyanines,[50] various 2′-cyanines,[65,70,71] indocyanines,[72] and carbocyanines,[73,74] until it was outdated by the resonance theory in 1939.[75]

X in the formulae represents an acid radical. R was at first, and is generally, an alkyl group, but it may also be aryl (see X-4-C). May it alternatively be hydrogen? In 1920 it was regarded as obvious that the nitrogen atoms must carry alkyl groups in order to permit the formation of dyes capable of existence in alkaline solution.[76] The author agrees in not regarding dyes with an *NN′*-diH structure as

true cyanines, hence they are dealt with separately (see X-4-D),[25] as also are bases of which cyanines are the quaternary salts (see Chapter XI).

As regards the length of the chain, *m* can be 0, 1, 2, 3, or more, but instability increases on ascending the series. *n* and *n'* are usually 0, but where lepidine nuclei are involved, their values become 1. Cyanines in which the nuclei are directly linked are exceptional and are considered in the last section of the present chapter (section 5). The hydrogen atom of one or more methin groups in the chain may be replaced, and such chain-substituted dyes have been considered in the chapters that follow (Chapters III, VI, VII, and VIII). There is also a chapter (Chapter IX) on cyanines where the normal chain linking the nuclei, or part of it, is cyclic, and another (Chapter XII) on cyanines where one or more of the :CH· groups is replaced by N.

Compounds where only one nitrogen atom forms part of a ring, notably the *p*-dimethylaminostyryl dyes, have often been classed as cyanines, but are here dealt with separately (see XIII-1). That chapter contains an account of various other kinds of compounds related to cyanines, such as some in which neither nitrogen atom is cyclic (see XIII-5), and others in which oxygen or sulphur takes the place of NR (see XIII-6). The merocyanines, which are non-ionic dyes with an even-numbered carbon chain joining the nuclei, required a chapter (Chapter XIV) to themselves. Following, that is, a consideration of more complex tri- and poly-nuclear dyes (see Chapter XV), which need more complex formulae than those above to represent them, and yet are essentially cyanines.

The term "cyanine" was originally applied to one compound but was subsequently extended to the group of dyes. In the early days the nomenclature was simple. When the only known cyanines had two quinoline nuclei linked by a methin group, it was convenient to describe those having a trimethin chain as carbocyanines. When cyanines with a pentamethin chain were discovered, it was logical to call them dicarbocyanines, and, later, those with a heptamethin chain were named tricarbocyanines. The terms tetracarbocyanines and pentacarbocyanines were also added, but are of doubtful value. The introduction of nuclei other than quinoline, such as benzoxazole, benzothiazole, and 3,3-dimethylindolenine, led to the introduction of terms such as oxa-, thia-, indo-cyanines, and -carbocyanines, etc. These still retain a definite usefulness, as a shorthand description of types of compounds. It became clear, however, that the discovery of new kinds of cyanines

was outgrowing the nomenclature. A special difficulty arose when cyanines having monocyclic nuclei, such as pyridine or thiazole, were synthesised, because these were simpler than the first cyanines, and a fresh trivial name had to be introduced to cover each new type. Dr. F. Richter suggested the desirability of giving the systematic name of each cyanine described, as in the 1936 edition of Beilstein's *Handbuch der organischen Chemie*, of which he was editor. Hence in 1937 these systematic names were given, in addition to the trivial names.[77,78] The writer feels it undesirable to make further additions to the trivial names, since the systematic names fully describe the compounds. The advantage of this nomenclature lies in the fact that it is only necessary to presuppose a knowledge of the fundamental structure of a cyanine, as formulated above. The name then specifies the nature of the nuclei, their positions of linking, and the length of the chain joining them. A few examples of the systematic names are given in the pages that follow (see section 5-C; II-1-B and C; IV-2-B, C, D, and E; IV-6-D; IX-7; X-5-A). Following rule 33 of the I.U.C. Committee that "the termination -ine is reserved exclusively for nitrogenous bases",[79,80] the author has always used the terms methin, dimethin, etc., but notes that others prefer methine, dimethine, etc.

5. Cyanines in which the Nuclei are Directly Linked (Apocyanines)

A. General

According to a patent of 1903,[81] the action of caustic alkali on hot alcoholic solutions of quinoline alkiodide gave red and yellow dyes, which differed from cyanine and isocyanine in that their aqueous solutions were not instantly decolorised by mineral acids. The compounds prepared from quinoline ethiodide, methiodide, and methochloride, and from some substituted quinolinium alkiodides were specified. Both types were said to be useful in photography, but no details were given.

In spite of this patent, in 1911 the discovery was announced of red and yellow dyes, formed by the action of alkali on quinolinium salts only, in the absence of quinaldinium or lepidinium salts. Two mols. of quinoline alkiodide condensed, with elimination of one of hydriodic acid. The dyes were called erythroapocyanines and xantho-

apocyanines, respectively, and the former was formulated as 1,1'-dialkyl-2,2'-diquinolenyl hydriodide.[36] Correct formulae were suggested in 1922, but without published evidence.[60] The constitution was established in 1928 (see section I-3-H).

In 1924 apocyanines were made by the method of the patent, with the object of investigating their antiseptic action. It was found that although with quinoline methiodide or ethiodide as starting point, the red compound preponderated, other quinolinium salts gave the yellow compound and practically none of the red one. Thus xanthoapocyanines were prepared from 6- and 8-methylquinoline methonitrates, 6-methylquinoline ethonitrate, and 6-methoxyquinoline methonitrate. From acetylaminoquinolinium salts, followed by hydrolysis, there were prepared the 6,6'-diamino-1,1'-dimethyl-, 6,6'-diamino-1,1'-diethyl-, and 5,5'-diamino-1,1'-dimethyl-xanthoapocyanine iodide hydrochlorides.[82]

B. Preparation and Properties

To prepare LIV and LV, quinoline ethiodide (2 mols.) was dissolved in the least possible amount of boiling methanol and was treated with a methanolic 10% solution of potassium hydroxide (1 mol.) in two equal portions, the second of which was added after 10 minutes' boiling. After further boiling, and then dilution with methanol, the dyes crystallised and were separated by recrystallising from ethanol, in which the erythroapocyanine was the more soluble.[59,81] The yield of erythroapocyanine could be as much as 40%,[81] whilst that of xanthoapocyanine might reach 5%.[59] By effecting the condensation with sodium ethoxide in ethanol, the yield of the latter was increased at the expense of the former[81] and reached 15–20%.[81,83] For recrystallisation, 1 g. of LIV required 23 c.c. of ethanol but 1 g. of LV required 200 cc of methanol.[83]

Erythroapocyanine, LIV, formed reddish-brown crystals with a green reflex (decomp. 210–220°).[59,81] The absorption maximum of a methanolic solution was at 5150 Å, and the sensitising action was very weak.[83]

Xanthoapocyanine, LV, was an orange crystalline powder, m.p. 320° (decomp.).[59,81] A methanolic solution had its absorption maximum at 4610 Å, with a weaker band at 3620 Å. Sensitisation was very weak.[83]

Since the establishment of the constitution of the apocyanines

over thirty years ago, no further work on this class of dyes has been carried out, and the conclusion seems inevitable that that is because they have found no application in photography. It is possible to formulate related dyes in which an *N*-alkyldihydroquinoline nucleus is linked through its 3-position either (*a*) directly to a heterocyclic nucleus other than quinoline or (*b*) through a dimethin chain to a heterocyclic nucleus, but such developments have not ensued.

C. Nomenclature

According to the systematic nomenclature, the erythroapocyanine, LIV, is called [3-(1-ethylquinoline)] [4-(1-ethylquinoline)]cyanine iodide; the xanthoapocyanine, LV, is called [2-(1-ethylquinoline)]-[3-(1-ethylquinoline)] cyanine iodide.

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CHAPTER II

Methincyanines

1. 4′-Cyanine Condensation (Involving Elimination of HX + H_2)

A. General

The first methincyanines were prepared[1–6] by heating an alcoholic (or aqueous) solution containing a quaternary salt of quinoline and one of lepidine or quinaldine with caustic alkali, whereby reaction proceeded according to equation 1.

$$C_9H_7N \cdot RI + C_{10}H_9N \cdot RI \longrightarrow C_{19}H_{18}N_2I + H_2 + HI \qquad (1)$$

The acid which is eliminated forms a salt with the caustic alkali. As the reactive methyl group of the lepidinium or quinaldinium salt condenses in general at the 4-position of the quinolinium salt, this method is conveniently called the 4′-cyanine condensation. It is characterised by the fact that two hydrogen atoms and 1 molecule of acid are eliminated. It was recognised at an early date that use of excess of quinolinium salt gives improved yields, and it is probably concerned with removal of the hydrogen atoms. Molecular proportions that have been used are shown in Table I. The yields given are those of purified dye, since yields of crude products are of little interest. The method consists in treating a boiling alcoholic solution of the heterocyclic salts with one of sodium hydroxide or potassium hydroxide[11] or, perhaps more conveniently, with one of sodium dissolved in ethanol.[12]

The condensation has a certain generality in that any heterocyclic quaternary ammonium salt having a reactive methyl group can condense through it with the 4-position of a quaternary quinolinium salt: that led to the various types of 4′-cyanines, which are considered in appropriate sections below.

If the 4-position of the quinoline nucleus is blocked, a condensation of the 4′-cyanine type may be forced to occur in the 2-position. Thus

the action of potassium hydroxide on a mixture of 4-phenylquinoline ethiodide with quinaldine ethiodide or 2,4-dimethylquinoline ethiodide gave red 2,2′-cyanines[15] instead of purple 2,4′-cyanines. Similarly, when lepidinium salts were acted on by hot alcoholic alkali, condensation occurred in the 2-position, giving 2,4′-cyanines.[16,17]

TABLE I. Molecular Proportions of Reactants in 4′-Cyanine and in Thia-4′-cyanine Condensations

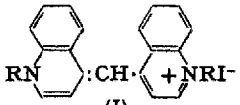
Iodide with reactive methyl		Quinolinium iodide	KOH (or NaOH or NaOEt)	% Yield	Ref.
Quinaldinium (or Lepidinium)	1	2	1	28, 43 (KOH)	7, 8
Quinaldinium (or Lepidinium)	1	2	1·5	—	5a
Quinaldinium (or Lepidinium)	1	2	2	31, 29	9, 10
Quinaldinium (or Lepidinium)	1	2	1·2	37 (NaOEt), 13	11, 12, 13
Quinaldinium (or Lepidinium)	1	3	3	76 (NaOEt)	13
Quinaldinium (or Lepidinium)	1	3	3	82 (KOH)	13
2-Methylbenzo-thiazolium	1	1	1 (KOH)	16	14
2-Methylbenzo-thiazolium	1	2	1 (KOH)	19	14
2-Methylbenzo-thiazolium	1	2	2 (KOH)	59	14
2-Methylbenzo-thiazolium	1	3	3 (KOH)	63	14

One product of heating together benzothiazole ethiodide and 2-methylbenzothiazole ethiodide in pyridine was identified as thiacyanine (I-3-D).[18] This is a reaction of the same type as a 4′-cyanine condensation, because one molecule of dye is formed from equimolecular quantities ot the quaternary salts, with elimination of one molecule of acid and two hydrogen atoms.

B. 4,4′-Cyanines

Comparatively few 4,4′-cyanines, I, have been prepared and this is no doubt connected with their lack of practical value in photography,

for their sensitising action is marred by chemical fogging. The first 4,4′-cyanines were prepared from amyl iodides,[1–3,4b] methiodides,[4b] and ethiodides[1,10] of quinoline and lepidine, also from their methochlorides and ethobromides, and from a mixture of the methiodides of 6-methylquinoline and lepidine.[5b] Their instability proved independent of the acid radical and occurred whether the cyanine was in



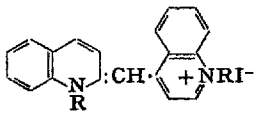
(I)

the form of iodide, chloride, nitrate, or sulphate.[19] 4,4′-Cyanines prepared from 6-dimethylaminoquinoline ethiodide with lepidine ethiodide and with 6-dimethylaminolepidine ethiodide were said to have interest as photographic sensitisers.[20]

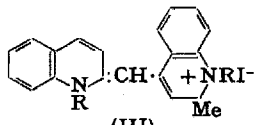
Under the name Cyanine, the dye was first marketed in 1861. It was also known as Quinoline Blue and as Ethyl Cyanine T. I (R=Et) may be called 1,1′-diethyl-4,4′-cyanine iodide or bis-[4-(1-ethylquinoline)]methincyanine iodide.

C. 2,4′-Cyanines

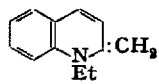
The purple isocyanines, II, prepared by the action of alkali on a hot solution of the quaternary salts of quinoline and quinaldine, were discovered independently[5,6] in two countries. The formation of an isocyanine by the action of alkali on quinaldine ethiodide, or propiodide, in the absence of a quinolinium salt, was also independently observed:[5b,21] these would be represented by III. The substituted ethiodide, III, was a much poorer sensitiser than II.[9] By the action



(II)



(III)

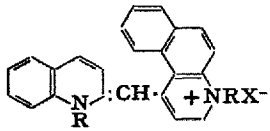


(IV)

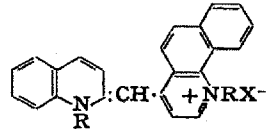
of suitable silver salts on II, the iodide was converted into nitrate, sulphate, and acetate, all of which were more soluble in water than was the iodide.[9] The methylene base, IV, prepared from quinaldine ethiodide, was condensed in alcoholic solution with quinoline ethiodide

(giving II), 6-methylquinoline methiodide, and 6-acetylaminoquinoline methiodide, or condensed with itself, in the presence of alcohol or water (giving III), but no dye formation took place when the dried base was heated in benzene or ether.[7] An 8-methylquinolinium salt did not give an isocyanine either with IV[7] or with alkali and a quinaldinium salt.[15]

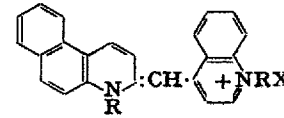
At the beginning of this century, the practically valuable sensitising properties of the isocyanines were patented; the ethiodide, II (R=Et), proved better than other homologues, II (R=Me, Pr, Bu, C_5H_{11}, C_6H_{13}).[22] Other 2,4′-cyanines, which were valuable as photographic sensitisers, were prepared from alkyl halides of 5- and 6-methylquinolines and -quinaldines[23,24] and of methoxy- and ethoxy-quinolines and -quinaldines.[25] Also an alkyl halide of 5,6- or 7,8-benzoquinoline could be condensed with one of quinaldine, or of a 5- or 6-methylquinaldine, to give, e.g., V and VI; an alkyl halide of quinoline, or of 5- or 6- (but not 8-) methylquinoline, could be condensed with one of 5,6- (but not 7,8-) benzoquinaldine to give, e.g., VII.[23]



(V)



(VI)



(VII)

Instead of using alkyl halides for making quaternary salts for isocyanine preparations, the use of alkyl sulphates was patented.[26,27] Dyes from such salts have the advantage of increased solubility. The use of sulphonic acid esters, such as methyl and ethyl toluene-*p*-sulphonates was advantageous because of their cheapness.[28] These salts also gave more soluble dyes and the esters were not toxic like methyl sulphate.

In the scientific literature there are described substituted 2,4′-cyanines, made by condensing quinaldine ethiodide with 6-chloroquinoline ethiodide[29] and with 2-phenylquinoline methiodide: introduction of the 2-phenyl group shifted the absorption maximum to a longer wavelength.[7] The absorption maximum of an isocyanine was compared with those of its 6,6′-dimethyl and of three methyl derivatives.[30] The preparation and sensitising properties of a series of twenty isocyanines were described. The groups attached to nitrogen were various: methyl, ethyl, n-propyl, and n-butyl. Into the 2-linked quinoline nucleus of

II (R=Me) were introduced the groups 5- or 6-acetylamino- or -amino-, 6-cinnamoylamino- or -ethoxy-, and 5,6-benzo-; into the 4-linked quinoline nucleus were introduced 6-acetylamino-, -amino-, and -methoxy-, and 2-methyl, -cyano-, or -phenyl. This 2-substitution depressed the sensitising action.[11] In a series of seven isocyanines, II (various values for R), there was a dimethylamino- or diethylamino-group in the 6-position of one nucleus, with a methyl group in the 6-position of the other, and, in addition, one dye having a dimethylamino-group in both 6-positions; two of them, prepared by condensation of 6-dimethylaminoquinaldine alkiodide with itself, had a 2-methyl group in the 4-linked quinoline nucleus. Yet all indiscriminately were said to be of interest as sensitisers.[20] In another series of sixteen isocyanines there were introduced into the 2-linked nucleus of II (R=Me) the substituents 5-, 6-, or 7-cinnamoylamino-, -acetylamino-, or -amino-, and into the 4-linked quinoline nucleus the same substituents in the 6- and 7-positions. Failure to obtain isocyanines from quinaldine methiodide with 5-acetylamino- or 5-cinnamoylamino-quinoline methiodide was attributed to steric hindrance. The amino-derivatives of II (R=Me) were prepared by hydrolysis of the acetylamino-dyes. The cinnamoylamino- and acetylamino- groups usually depressed sensitisation whilst the amino-group enhanced it.[12] Sensitising and absorption data of the series were recorded.[31] For an investigation of antiseptic action, a series of twelve isocyanines was prepared; they comprised the parent dyes, II (R=Me or Et), and derivatives of II (R=Me) in which a 6-amino-, -methoxy-, or -methyl group was introduced into either nucleus, a 6-ethoxy- or 7-amino-group into the 2-linked quinoline nucleus, also one having a 6-methyl group in both nuclei, and another having 6-methyl in both nuclei and 2-methyl in the 4-linked quinoline nucleus.[32]

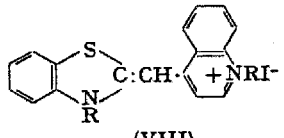
A study of the sensitising action of seventeen isocyanines, known in Japan as dyes of the Lumol series, comprised those having methyl or ethyl groups attached to nitrogen, with substituents such as 6-methoxy- or -ethoxy- in either nucleus or in both, four of them having also a 2-methyl group in the 4-linked quinoline nucleus; two had a 6,7-ethylenedioxy-group.[33] In another series, the parent isocyanine, II (R=Me), was compared with derivatives having the following substituents in the 4-position of the 2-linked quinoline nucleus: hydroxy-, methoxy-, methyl,[9,34] chloro-, ethoxy-, ethyl-, iodo-, phenyl-, and phenylamino-, and with one having 4-chloro-6-methyl.[8] Isocyanines, II

(R = Et), having 6,6′-dimethoxy- or 6,6′-diethoxy-groups are described as powerful orthochromatic sensitisers, of which the latter is the stronger.[35] Sensitising and absorption data are given for three 2,4′-cyanines, VII (R=Et, X=I), in which the 4-linked quinoline nucleus has the substituents 6-methyl, 6-ethoxy-2-methyl, and 2,6-dimethyl, respectively.[36]

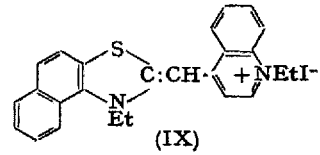
The parent dye, II (R=Et), is called 1,1′-diethyl-2,4′-cyanine iodide or [2-(1-ethylquinoline)] [4-(1-ethylquinoline)]methincyanine iodide. It was marketed as Ethyl Red and III (R=Me) was called Quinaldine Red. In Germany the trade names of other isocyanines were Pinaverdol, Pinachrome, Pinachrome Blue, Pinachrome Violet, Orthochrome T, Homocol, Isocol, and Pericol; the British equivalent of the first was Sensitol Green.

D. Thia-4′-, Oxa-4′-, and Selena-4′-cyanines

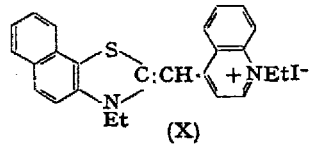
When 2-methylbenzothiazole ethiodide, instead of an alkiodide of lepidine or quinaldine, was condensed with quinoline ethiodide, by heating an alcoholic solution of the salts with caustic alkali, the product was the thia-4′-cyanine, VIII (R=Et); five other compounds of this type were prepared, having other alkyl groups attached to nitrogen, and with a 6-methyl- or -ethoxy-group introduced into either nucleus. They were bright red and gave orange alcoholic solutions, which were decolorised by mineral acids; all were powerful sensitisers to green light.[37] Those having a substituted amino-group in the benzothiazole nucleus were found to be especially useful.[38,39] In preparing VIII (R=Et), the proportions of reactants were varied, as shown in Table I, and a 63 % yield was achieved.[14] By reaction of 2-methyl-4,5(or -6,7)-benzobenzothiazole ethotoluene-*p*-sulphonate and quinoline ethiodide,



(VIII)

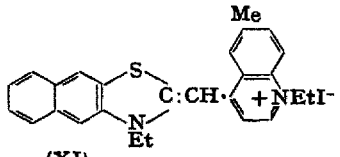


(IX)

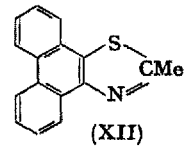


(X)

there were prepared the thia-4′-cyanines, IX and X, respectively, which sensitised further into the red than did VIII,[14,40] IX being a stronger sensitiser than X.[14] There was not such a great shift of absorption and sensitising for a 5,6-benzo-group, *e.g.*, in XI.[41] The base, 2-methylphenanthro[9,10-d]thiazole, XII, was synthesised and, by



(XI)



(XII)

condensing its ethotoluene-*p*-sulphonate with quinoline ethiodide, by heating with potassium hydroxide in alcohol, it gave XIII, which is the 4,5,6,7-dibenzo-derivative of VIII.[14] XIV, which is a tetrahydro-derivative of a homologue of VIII, was obtained by condensing a 2-methyltetrahydrobenzothiazolium salt with a quinolinium salt.[42] Some of the properties of these dyes are compared in Table II.

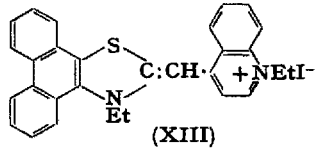
TABLE II. Properties of Derivatives of Thia-4′-cyanine, VIII (R = Et)

Substituent	Formula	Appearance	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
—	VIII	Red needles	283	5030 (and 4890)	5250	5800	37
4,5-benzo-	IX	Reddish-brown needles; green reflex	248–250	5225	5400	6000	14, 40
6,7-benzo-	X	Scarlet needles	285–288	5215	5400		14
5,6-benzo-	XI[a]	Red needles	—	[b]	5300	5700	41
4,5,6,7-dibenzo-	XII	Reddish-brown	244–247	5300	—	6400	14
6-NMe_2	—	—	—	—	5550	—	38
6-NMe_2	—	—	—	5300[c]	6000[c]	—	39
6-NEt_2	—	—	—	5450	5700	6700	38
4,5,6,7-tetra-H	XIV	—	—	5150	—	—	42

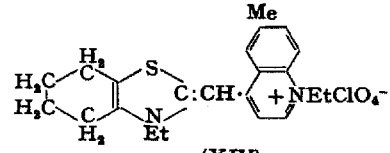
[a] 6-Me in quinoline nucleus. [b] Impossible figure given. [c] MeI.

The oxa-4′-cyanine, XV, prepared by condensation of 2-methylbenzoxazole ethiodide with quinoline ethiodide, absorbs at 4700 Å,[43] i.e., at a shorter wavelength by 330 Å than does the thia-4′-cyanine,

VIII. A bathochromic shift of 200–250 Å occurs on introducing a 4,5-, 5,6-, or 6,7-benzo-group into the benzoxazole nucleus.[43,44] Useful sensitising to blue-green, green, and yellow light has been claimed for these benzo-substituted oxa-4′-cyanines.[44,45]

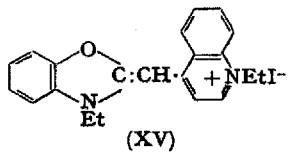


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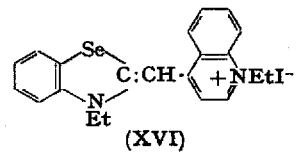


(XIV)

Although the selena-4′-cyanine, XVI, with its absorption maximum at 5070 Å[43] absorbs only 40 Å nearer to the red than the thia-4′-cyanine, VIII, it has been claimed that the sensitising range is 100 Å nearer to the red and that selena-4′-cyanines are valuable for orthochromatic sensitising. Absorption and sensitising data were given for



(XV)

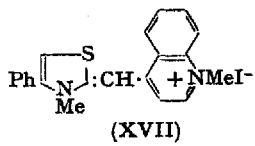


(XVI)

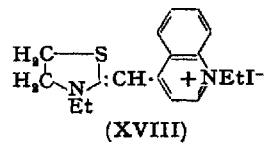
XVI and seven derivatives; in these, substituents such as 5-chloro-, -ethoxy-, -methyl, or 6-iodo- were introduced into the benzoselenazole nucleus, and 8-methoxy-, 6- or 7-methyl, or 5,6-benzo- into the quinoline nucleus.[46] Derivatives of XVI having a 6,7-benzobenzoselenazole nucleus are also good orthochromatic sensitisers[47] (see section 2-D).

E. Thiazolo-4′- and Thiazolino-4′-cyanines

It was discovered as long ago as 1922 that the methiodides of 2-methyl-4-phenylthiazole and quinoline condense, when their alcoholic



(XVII)



(XVIII)

solution is boiled with sodium hydroxide, giving XVII. This thiazolo-4′-cyanine was the first cyanine containing a monocyclic nucleus. The

colour of its alcoholic solution was orange-red.[48] The unsubstituted *NN'*-diethyl parent dye corresponding with XVII had its absorption maximum at 5050 Å,[49] i.e., practically the same as that of VIII. XVII sensitised to 6000 Å with the maximum at 5300 Å.[48] In view of this 1922 publication, it is curious to find the sensitising action of thiazolo-4'-cyanines patented in 1931 and 1941.[49,50]

2-Methylthiazoline ethiodide also condenses with quinoline ethiodide, by heating the alcoholic solution with potassium hydroxide, giving a 38% yield of XVIII. The absorption maximum of this, at 4590 Å,[51] lay at a wavelength shorter by 460 Å than that of the thiazolo-4'-cyanine. The maximum of its sensitising action towards a silver chloride emulsion was at 4800 Å.[51] In the patent on the sensitising action, seven such dyes are described, having various alkyl groups on the nitrogen atoms, and sometimes a methyl group in the quinoline nucleus.[52]

F. Thiacyanines

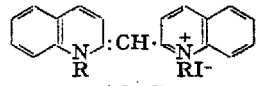
When 2-methylbenzothiazole ethiodide and benzothiazole ethiodide were heated together in pyridine, it was discovered that the purple trimethincyanine was accompanied by the yellow methincyanine having two benzothiazole nuclei (I-3-D).[18] The latter was in fact the main product but the yield of crude dye was only 16–21 %.[18] A methyl derivative was also prepared, either by heating a mixture of 2,5-dimethylbenzothiazole ethiodide and benzothiazole ethiodide, or one of 2-methylbenzothiazole ethiodide and 5-methylbenzothiazole ethiodide, in pyridine.[53] The method has no practical value now, as better methods of preparation have been developed (section 2-L, 3-C, and 4-K), but it is interesting that a condensation of this type, in which two hydrogen atoms as well as one molecule of acid are eliminated, can take place in the benzothiazole series.

2. ψ-Cyanine Condensation (Involving Reactive I, Cl, CN, or SO_3R, and Elimination of 2HX)

A. General

It was recorded in 1912 that a red dye was formed by the action of potassium hydroxide on an alcoholic solution of quinaldine ethiodide and 2-iodoquinoline ethiodide.[7] To the simplest homologue was assig-

ned formula XIX (R=Me) and the name ψ-isocyanine.[54] The term ψ-cyanine[55] is preferable.



(XIX)

The ψ-cyanine condensation, between quinaldine alkiodide and 2-iodoquinoline alkiodide, proceeds with elimination of two molecules of acid, according to equation 2.

$$C_{10}H_9N \cdot RI + C_9H_6NI \cdot RI \longrightarrow C_{19}H_{18}N_2I + 2HI \qquad (2)$$

It is thus more straightforward than the 4'-cyanine condensation, where two hydrogen atoms are eliminated in addition to one molecule of acid. The alkali necessary to remove the acid is usually used in slight excess.

In 1928 a series of 2,2'-cyanines was prepared by the action of potassium hydroxide on a boiling alcoholic solution of a quinaldine alkiodide and a 2-iodoquinoline alkiodide, and it was found that they comprise valuable sensitisers to blue-green light. The yield was less when an aqueous instead of an alcoholic medium was used. The condensation proved a general one in that the part played by quinaldine alkiodide could be taken by other heterocyclic quaternary salts having a reactive methyl group. Thus lepidinium salts gave 2,4'-cyanines, 2-methylbenzothiazolium salts gave thia-2'-cyanines, and 2-methylindoleninium salts also condensed.[56] In the same way 4-iodoquinoline ethiodide was condensed with quinaldine ethiodide to give 2,4'-cyanine.[13] In 1935 a great improvement consisted of the replacement of caustic alkali by a strong organic base, such as triethylamine: the better yields obtained[57,58] are shown in Table III. Anhydrous potassium carbonate also gives improved yields,[59] but triethylamine is especially convenient. Its use made possible the preparation of new types of 2'-cyanines, which are dealt with in the sections below.

The use of a quaternary salt having a reactive chlorine atom, in place of one having a reactive iodine atom, is historically interesting. Thus in 1908 the colour change that occurred on reaction of the methylene base from quinaldine methiodide with 4-chloroquinoline methochloride indicated that isocyanine formation had taken place.[29]

TABLE III. % Yields of Purified 2′-Cyanines with KOH and with NEt_3

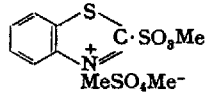
Dye	Yield with KOH	Yield with NEt_3	Section reference in II-2
2,2′-	72	87	B
2,4′-	74	93	C
oxa-2′-	3	43	F
selena-2′-	55	72	F
thia-2′-	72	88	F
2-pyrido-2′-	10	41	H

It was followed by the observation in 1912 that isocyanine is formed by the action of alkali on a solution of quinaldine ethiodide and 4-chloroquinoline ethiodide; moreover when alkali acted on a mixture of quinaldine ethiodide with 4-chloro-2-phenylquinoline ethiodide, the substituted isocyanine was the same as that obtained by a 4′-cyanine condensation from quinaldine ethiodide and 2-phenylquinoline ethiodide: these observations helped to establish the constitution of isocyanine.[7] In 1925 an isocyanine was obtained by the action of ammonia on 4-chloroquinaldine methiodide,[60] namely [2-(4-chloro-1-methylquinoline)] [4-(1,2-dimethylquinoline)]methincyanine iodide. A dye, which in 1894 had been obtained by heating methylacetanilide with phosphorus oxychloride and making the product alkaline[61], was identified with this isocyanine.[60] In general, a salt having a reactive chlorine atom cannot with advantage replace one having such an iodine atom, but the 4-iodopyridine alkiodide required for preparing a 4-pyrido-4′-cyanine could not be made, and in that instance the use of 4-chloropyridine methiodide led to a successful synthesis (see section 2-H).[62]

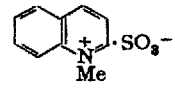
Again, there is no advantage in using a quaternary salt having a cyano-group in place of one having an iodine atom, but quaternary salts having a reactive methyl group have in fact been condensed with 4-cyanoquinoline alkiodide to give thia-4′-cyanines and a selena-4′-cyanine, and with 2-cyanoquinoline methiodide to give a thia-2′-cyanine.[13]

On the other hand, the use of a quaternary salt having a sulphonic ester group, e.g. XX, in place of one having an iodine atom, has the advantage that dyes other than iodides can be directly prepared, whilst the obnoxious smell evolved in the alkylthio method (see section 4) is absent. Moreover it may be applied to the preparation of such dyes

as thiacyanines (see section 2-L) which are not accessible through a ψ-cyanine condensation involving a reactive iodine atom. Instead of a sulphonate, a betaine, e.g. XXI, may be used.[63]



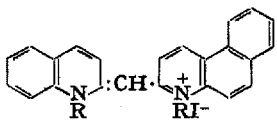
(XX)



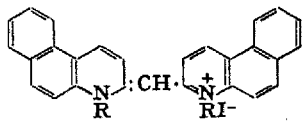
(XXI)

B. 2,2′-Cyanines

A series of eight 2,2′-cyanines, XIX, was prepared by heating a mixture of a quinaldine alkiodide and a 2-iodoquinoline alkiodide with potassium hydroxide in alcohol, for 30 minutes. A red colour developed, the solids dissolved, and dye crystallised on cooling, and was usually recrystallised from methanol. Different alkyl groups were attached to nitrogen and there was sometimes a 6-methyl group as substituent in one nucleus. Two of the compounds had a 5,6-benzo-group, introduced by use of 2-methyl-5,6-benzoquinoline alkiodide.[56] One such dye, XXII (R=Me), was also prepared by condensing quinaldine alkiodide with 2-iodo-5,6-benzoquinoline alkiodide, and two



(XXII)



(XXIII)

others of the same type similarly; whilst by condensing 2-methyl-5,6-benzoquinoline alkiodide with 2-iodo-5,6-benzoquinoline alkiodide there were prepared three dyes of formula XXIII.[64,65] The betaine, XXI (see section 2-A), was boiled with quinaldine ethiodide and triethylamine in alcohol to give a dye of type XIX.[63] Some of the properties of 2,2′-cyanines are summarised in Table IV.

C. 2,4′-Cyanines

The preparation of two 2,4′-cyanines, II (R=Me or Et), by a ψ-cyanine condensation by heating an alcoholic solution of lepidine alkiodide and 2-iodoquinoline alkiodide with caustic potash, was a confirmation of the constitution of isocyanine. The yields were 34%

and 45%, respectively.[56] Condensation of lepidine ethiodide with 2-iodo-5,6-benzoquinoline ethiodide gave VII.[57,66] By the reaction of 4-iodoquinoline ethiodide with quinaldine ethiodide, on heating in alcohol with triethylamine, the yield of II (R=Et) was 67%.[13]

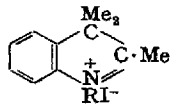
D. Thia-4'- and Selena-4'-cyanines

By condensation of 4-cyanoquinoline alkiodide with a 2-methylbenzothiazole alkiodide in the presence of potassium hydroxide or potassium carbonate in alcohol, one mol. of hydriodic acid and one mol. of hydrocyanic acid were removed, and thia-4'-cyanines were produced; the yields, in three instances, varied from 30–37%.[13] A 6-nitrothia-4'-cyanine was made by heating 4-iodoquinoline ethiodide and 2-methyl-6-nitrobenzothiazole ethochloride with triethylamine in ethanol, and converting into iodide.[67]

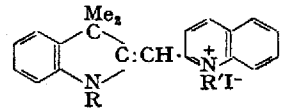
A selena-4'-cyanine was prepared in 35% yield by heating together 4-cyanoquinoline methiodide, 2-methylbenzoselenazole ethiodide, and potassium carbonate in alcohol (see also section 1-D and 4-C).[13]

E. Indo-2-'cyanines

2-Methylindoleninium quaternary salts, such as XXIV (R=Me), were used in 1924 in the preparation of trimethincyanines.[68] In 1928 the two salts XXIV (R=Me or Et) were condensed with 2-iodoquinoline alkiodide, by use of potassium hydroxide in alcohol, to give



(XXIV)



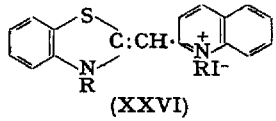
(XXV)

XXV (R=R'=Me or Et), in yields of 26% and 22%, respectively. Their sensitising action was weak and they depressed the blue sensitivity of photographic material (see Table IV).[56] By use of triethylamine in ethanol the former dye was obtained in 72% yield before recrystallisation.[58]

F. Thia-2'-, Oxa-2'-, and Selena-2'-cyanines

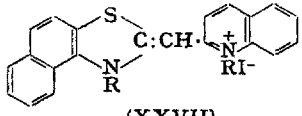
The first thia-2'-cyanine, XXVI (R=Et), was obtained in 1923 by reaction of quinaldine ethonitrate with di-[*o*-*N*-ethylformanilido]

disulphide in pyridine (see section 6-C and also I-3-E).[69] This and three others, with different alkyl groups attached to the nitrogen atoms, were synthesised by boiling 2-methylbenzothiazole alkiodide and 2-iodoquinoline alkiodide with potassium hydroxide in alcohol for

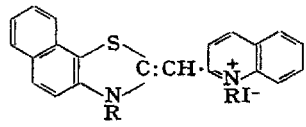


(XXVI)

30 minutes, and recrystallising from rectified spirit. All were photographic sensitisers.[56] A thia-2′-cyanine was prepared, but only in 10% yield, by heating 2-cyanoquinoline methiodide, 2-methylbenzothiazole methiodide, and potassium carbonate in alcohol, whereby the alkali removed one mol. of hydriodic acid and one mol. of hydrocyanic acid.[13] 2-Methyl-4,5- and 2-methyl-6,7-benzobenzothiazole methiodide and ethiodide condensed with 2-iodoquinoline alkiodide, to give XXVII and XXVIII, of which the latter type was obtained in better yield than the former. For XXVIII (R=Et), the yield was 30% with



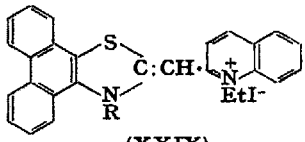
(XXVII)



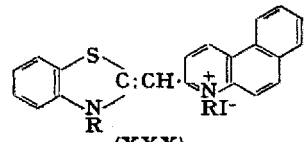
(XXVIII)

potassium hydroxide as condensing agent;[70] with triethylamine to cause condensation of the ethotoluene-*p*-sulphonate of 2-methyl-6,7-benzobenzothiazole with 2-iodoquinoline ethiodide, the yield was 70%.[14] Four dyes of each formula, with different values for R, were made: all were sensitisers for blue-green light. Introduction of the benzo-group shifted the absorption maximum about 150 Å and the sensitising maximum 100–200 Å towards the red (see Table IV).[70] Just as XII was used for preparing thia-4′-cyanines (see section 1-D), so similarly its salts were condensed with 2-iodoquinoline ethiodide to give XXIX (R=Me or Et), but even with triethylamine in alcohol the yields were only 18% and 8%, respectively. The dyes were weaker sensitisers than XXVIII (R=Et), whilst this was weaker than XXVII (R=Et).[14] Likewise, just as 2-iodo-5,6-benzoquinoline alkiodide was used for preparing 2,2′-cyanines (see section 2-B), so also it was conden-

sed with 2-methylbenzothiazolium alkiodides to give three dyes of type XXX.[64,71] As with thia-4'-cyanines (see section 1-D), so also with thia-2'-cyanines, introduction of an amino-group into the benzothiazole nucleus was said to confer valuable sensitising properties: the 6-acetylamino-[38] and 6-dimethylamino-groups[39] were introduced. Similar introduction of an alkylthio- or alkylseleno-group gave a displacement of sensitivity towards the red.[72] 6-Chloro- and 6-bromo- were introduced into the molecule of XXVI (R=Et). In preparing the former dye, a



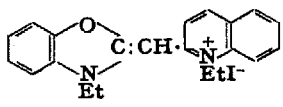
(XXIX)



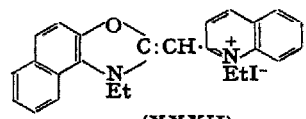
(XXX)

38 % yield resulted when sodium ethoxide was the condensing agent, but with anhydrous potassium carbonate (section 2-A) the yield was 66 %.[73] By the method in which the sulphonic ester, XX (see section 2-A), was boiled with quinaldine ethiodide and triethylamine in alcohol, the yield of recrystallised thia-2'-cyanine was 69 %. The quaternary salt of a 6,7-benzobenzothiazole-2-sulphonate was similarly applied to the preparation of a dye of type XXVIII.[63]

The oxa-2'-cyanine, XXXI, prepared in 43 % yield by boiling 2-methylbenzoxazole ethiodide, 2-iodoquinoline ethiodide, and triethylamine in alcohol, proved a sensitiser for gelatino silver chloride photographic emulsions (Table IV).[57] When the salts were heated together in diethylaniline, the yield of XXXI was increased to 89 %.[57,74] Its 4,5-benzoderivative, XXXII, was prepared by heating together



(XXXI)

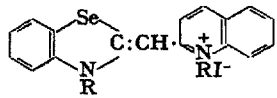


(XXXII)

2-methyl-4,5-benzobenzoxazole ethotoluene-*p*-sulphonate and 2-iodoquinoline ethiodide in quinoline, and was precipitated by ether.[74] The 4,5,6,7-tetrahydro-derivative of XXXI was similarly prepared with 2-methyl-4,5,6,7-tetrahydrobenzoxazole ethotoluene-*p*-sulphonate.[75]

The selena-2'-cyanines, XXXIII, including those having anions other than halide or alkylsulphate, were good sensitisers for green and

yellow light, without the sensitising gap characteristic of erythrosin.[76] XXXIII (R=Et) was obtained in 72% yield by boiling 2-methylbenzoselenazole ethiodide, 2-iodoquinoline ethiodide, and triethylamine



(XXXIII)

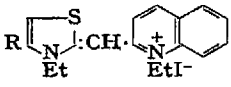
in alcohol, followed by recrystallisation from methanol.[57] Introduction of an acylamino-substituent into the benzoselenazole nucleus improved the sensitising.[38,77]

TABLE IV. Some Properties of 2′-Cyanines

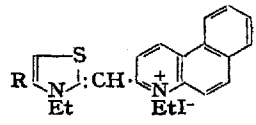
Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å) in alcohol	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
XIX (R = Et)	bluish red	277	5250 (and 4900)	5700	6000	56
XXII (R = Et)	dark green	273	5380 (and 5000)	5750	6100	56
XXIII (R = Et)	green and gold	310	5500 (and 5100)	5700	6300	63
XXV (R = R′ = Et)	brown; green lustre	222	4800	5250	5800	56
XXVI (R = Et)	scarlet needles	285	4850 (and 4600)	5300	5600	56
XXVII (R = Et)	red	265	5000	5500	6100	40, 70
XXVIII (R = Et)	red	296	5000	5400	—	70
XXIX (R = Et)	dull red	248–250	5100	—	—	14
XXX (R = Me)	scarlet	282	4850	5350	6000	63
XXXI	orange-yellow needles	290–292	4350	4700	5150	57, 74
XXXII	yellow-orange needles	—	—	—	5250	74
XXXIII (R = Et)	red needles; blue reflex	280–283	4875	5340	5750	57, 76

G. Thiazolo-2′-, Thiazolino-2′-, Oxazolo-2′-, and Selenazolo-2′-cyanines

By heating with triethylamine in alcohol, 2-methylthiazole ethiodide reacted with 2-iodoquinoline ethiodide to give the thiazolo-2′-cyanine, XXXIV (R=H), which was obtained in 61 % yield after recrystallisation from methanol. As shown in Table V, its absorption maximum underwent a bathochromic shift of 180 Å on introducing the 5,6-benzo-group into the quinoline nucleus to give XXXV (R=H). With XXXIV (R=H) the entry of a methyl or phenyl substituent



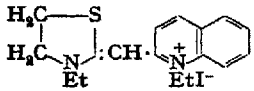
(XXXIV)



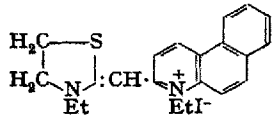
(XXXV)

into the thiazole nucleus, giving XXXIV (R=Me or Ph), caused a bathochromic shift of 75 Å in the absorption maximum, whereas on passing from XXXV (R=H) to XXXV (R=Me or Ph) the shift was only 45 Å.[78,79] The sensitising action of thiazolo-2′-cyanines was noted.[50,78–80] Presence of a 4-carbethoxy group in the thiazole nucleus improved both yield and sensitising.[81] A 4-aminothiazolo-2′-cyanine was prepared by condensation of 4-amino-2-methylthiazole methiodide and 2-iodoquinoline ethiodide.[82]

By condensing 2-methylthiazoline ethiodide with 2-iodoquinoline ethiodide, the thiazolino-2′-cyanine, XXXVI, was obtained, the yield after recrystallisation being 61 %. Its alcoholic solution showed two almost equal absorption maxima, which lay at a far shorter wavelength than that of the thiazolo-2′-cyanine (see Table V).[51] This and three homologues with different alkyl groups attached to nitrogen were sensitisers for silver chloride emulsions.[52] Its 5′,6′-benzo-derivative,



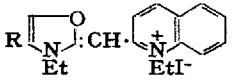
(XXXVI)



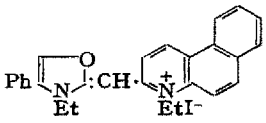
(XXXVII)

XXXVII, was prepared in 25 % yield; this also had two absorption maxima, but the band nearer the red was the stronger,[51] which is usual with double-banded cyanines.

Use of triethylamine as condensing agent made possible the preparation of oxazolo-2′-cyanines, XXXVIII (R=Me or Ph), in yields of 49% and 19%, respectively: the 5′,6′-benzo-derivative, XXXIX, was obtained in 2% yield.[78] They sensitised chloride emulsions (see Table V).[78,79]

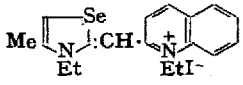


(XXXVIII)

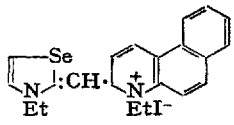


(XXXIX)

The use of triethylamine also made possible the preparation of selenazolo-2′-cyanines, XL and XLI,[78] which were photographic sensitisers.[78,79] On passing from XXVI (R=Et), containing a benzothiazole nucleus, to XXXIII (R=Et), containing a benzoselenazole nucleus, the absorption maximum shifted only 25 Å towards longer wavelengths



(XL)

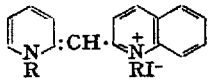


(XLI)

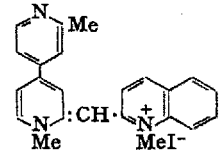
(see Table IV). With the simpler nuclei, however, replacement of sulphur by selenium, on passing from XXXIV (R=Me) to XL, caused a bathochromic shift of 125 Å (see section 4-F).[78]

H. 2-Pyrido-2′-, 2-Pyrido-4′-, 4-Pyrido-2′-, and 4-Pyrido-4′-cyanines

The first 2-pyrido-2′-cyanines, XLII, were prepared in 1931 by heating a mixture of 2-iodopyridine alkiodide, quinaldine alkiodide, and potassium hydroxide in alcohol,[64,83] but the alternative pair of quaternary salts gave a negative result. The absorption maxima of alcoholic solutions of the dyes lay at a wavelength shorter by 270–500 Å



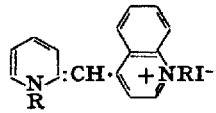
(XLII)



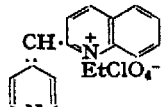
(XLIII)

than those of the corresponding 2,2′-cyanines, XIX. They were weak sensitisers, the maximum of XLII (R=Me) lying at 5200 Å and sensitisation extending to 5600 Å.[64] In 1935 the introduction of triethylamine as condensing agent (see section 2-A) not only gave a much better yield of XLII (R = Et) (see Table V) but also gave a 35 % yield by the alternative method, in which 2-picoline ethiodide and 2-iodoquinoline ethiodide were the reactants.[57] In applying the betaine method (see section 2-A) in this group, quinaldine ethiodide, the *N*-methylbetaine of pyridine-2-sulphonic acid, triethylamine, and ethanol were boiled together but only a yield of crude dye (110 %) is recorded.[63] The name 2-pyrido-2′-cyanine, suggested in 1935[57] is preferable to an earlier suggestion[84] of the name mesocyanine. By heating 2,2′-dimethyl-4,4′-bipyridine methiodide, 2-iodoquinoline methiodide, and triethylamine in ethanol, there resulted XLIII, which had its absorption maximum at 5030 Å.[85]

The isomeric 2-pyrido-4′-cyanine, XLIV, was prepared in 22 % yield by heating together 2-iodopyridine ethiodide, lepidine ethiodide,



(XLIV)



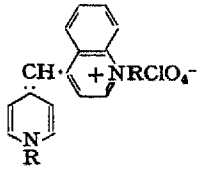
(XLV)

triethylamine, and n-propanol. It sensitised but details were not published.[57]

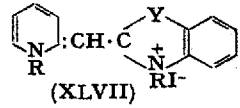
A 4-pyrido-2′-cyanine was made by heating together 4-picoline ethotoluene-*p*-sulphonate, 2-iodoquinoline ethiodide, and triethylamine in ethanol, and was isolated as perchlorate, XLV, the yield after recrystallisation being 12 %. Again details of the sensitising action are absent.[57]

4-Chloropyridine, unlike 2- or 4-chloroquinoline, could not be converted into the methiodide or ethiodide of the corresponding iodocompound. However the last member of this quartet of dyes, the 4-pyrido-4′-cyanine, XLVI (R=Me), was prepared by heating together 4-chloropyridine methiodide, lepidine methiodide, triethylamine, and n-propanol, and converting to perchlorate (26 % yield) (see section 4-G).[62]

Some properties of these dyes are given in Table V.



(XLVI)



(XLVII)

I. 2-Pyridothia- and Oxa-2′-pyrido-cyanines

By heating together 2-iodopyridine ethiodide, 2-methylbenzothiazole ethotoluene-*p*-sulphonate and triethylamine in ethanol, there was obtained the 2-pyridothiacyanine, XLVII (Y=S, R=Et).[58]

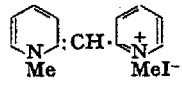
TABLE V. Some Properties of 2′-Cyanines having a Monocyclic Nucleus

Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
XXXIV (R = H)	red needles; blue reflex	267–269	4650	5175	5500	78
XXXV (R = H)	orange-brown; green reflex	268–270	4830	5250	—	78
XXXVI	yellow-orange prisms	226–227	4275, 4400	4600	5150	51, 52
XXXVII	scarlet needles	263–266	4375, 4575	4750	—	51
XXXVIII (R = Ph)	yellow-brown prisms	262–264	4350	4775	—	78
XXXIX	reddish brown	279–282	4475	4900	—	78
XL	reddish brown needles	259–260	4850	5350	5900	78, 79
XLI	reddish brown needles; green reflex	275–277	5000	5400	—	78
XLII (R = Et)	reddish brown; green reflex	237–239	4925 (and 4700)	—	—	57
XLIV (R = Et)	reddish brown tablets	194–196	5200	—	—	57
XLV	dark red; blue and green reflex	211–214	5075 (and 4825)	—	—	57
XLVI (R = Me)	reddish; metallic reflex	220–221	5285	5450 (and 5050)	6200	62
XLVII (Y = O, R = Et)	pale yellow prisms	—	—	—	4800	74

Similarly, from 2-iodopyridine ethiodide and 2-methylbenzoxazole ethiodide, there resulted the oxa-2′-pyridocyanine, XLVII (Y=O, R=Et), a sensitiser for silver chloride emulsions (Table V) (see section 4-H).[74]

J. 2,2′-, 2,4′-, and 4,4′-Pyridocyanines

By heating together 2-picoline methiodide, 2-iodopyridine methiodide, and triethylamine in n-propanol, the 2,2′-pyridocyanine, XLVIII, was prepared in 14% yield. Its methanolic solution had two

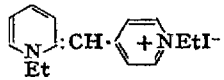


(XLVIII)

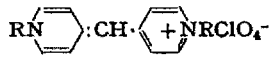
almost equally intense absorption bands; the corresponding diethyl homologue was also prepared[57]. The name, pyridocyanine, suggested in 1935,[57] is preferable to an earlier name, protocyanine.[84]

By reaction of 4-picoline ethotoluene-*p*-sulphonate, 2-iodopyridine ethiodide, and triethylamine in n-propanol, there resulted the 2,4′-pyridocyanine, XLIX, in 10% yield. It had a single absorption band (see Table VI).[57]

An attempt to prepare a 4,4′-pyridocyanine by condensation of 4-chloropyridine methiodide with 4-picoline methotoluene-*p*-sul-



(XLIX)

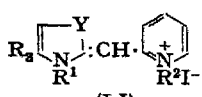


(L)

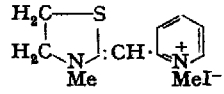
phonate, by heating with triethylamine in n-propanol, was not altogether successful, but L (R=Me or Et), both very good sensitisers, were arrived at by the arylthio-method (section 4-I).[62] The properties are, however, included in Table VI.

K. Thiazolo-2′-, Thiazolino-2′-, Oxazolo-2′-, and Selenazolo-2′-pyridocyanines

The sensitising action of thiazolo-2′-, oxazolo-2′-, and selenazolo-2′-pyridocyanines, LI (Y=S, O, or Se), was patented, as also of thiazolino-2′-pyridocyanines, LII.[86] Each of these types was prepared



(LI)



(LII)

by heating 2-iodopyridine alkiodide with an appropriate quaternary salt, having a reactive methyl group, and triethylamine in ethanol (Table VI) (see section 4-J).[58,86]

TABLE VI. Some Properties of 2'-Cyanines having Two Monocyclic Nuclei

Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
XLVIII	orange-brown; green reflex	315–317	4550, 4775	4600, 5000	5300	57, 86
XLIX	dull reddish flakes	163–166	4800	—	—	57
L (R = Me)	reddish brown needles; greenish reflex	263–265	5025	5300	5900	62
LI (Y = S, $R^1 = R^2 =$ Et, R^3=Me)	yellow or orange needles	—	—	4800	5400	86
LI (Y = O, $R^1 = R^2 =$ Et, R^3=Me)	yellow needles	—	—	—	—	86
LI (Y = Se, $R^1 = R^2 =$ R^3 = Me)	brown	—	—	4800	5500	86
LII	deep yellow needles	256–257	—	4300	4600	86

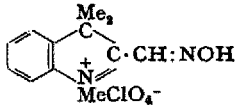
L. Thiacyanines

2-Iodobenzothiazolium salts are not reactive,[87] though the contrary has been stated.[88] Because of this non-reactivity, methincyanines having two benzothiazole nuclei are not accessible by an ordinary ψ-cyanine condensation. However, by heating the sulphonate, XX, with 2-methylbenzothiazole methomethylsulphate and triethylamine in alcohol, followed by treatment with potassium iodide, a symmetrical thiacyanine iodide was prepared. The method was also applied to the preparation of an unsymmetrical dibenzothiacyanine (see section 1-F; 3-C; 4-K; 6-A, B, C, and D).[63]

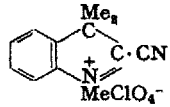
3. Nitrite Method

A. General

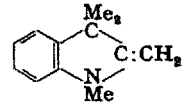
A patent of 1927 described the preparation of yellow to orange-red dyes by reaction of a 1,3,3-trialkylindoleninium salt, or the corresponding methylene base, with an ester or salt of nitrous acid, by heating in the presence of acetic anhydride. These dyes were erroneously formulated as β-azatrimethincyanines.[89] Analysis showed that a molecule of the so-called Indolenine Yellow contains an HCN molecule less than was required by that formula and the dye was identified as the symmetrical methincyanine of the indolenine series. Moreover an oxime intermediate product was isolated, whence unsymmetrical indocyanines were prepared.[90] The behaviour of 2-methylbenzothiazolium salts on heating with amyl nitrite and acetic anhydride was studied and in this series also the products were identified as methincyanines, namely the known thiacyanines.[91] The method was applied to the preparation of the then unknown selenacyanines[92] and the oxacyanines, which were especially interesting as being the first colourless cyanines.[93] In its day, this was a valuable preparative method, which led to new types of dyes, but it has now been superseded. Apart from the indocyanines, only symmetrical dyes have been obtained by the nitrite method.



(LIII)

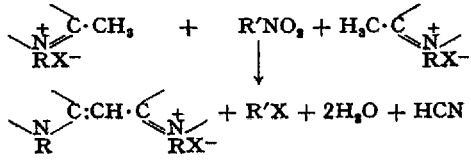


(LIV)



(LV)

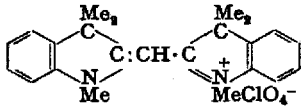
The mechanism of reaction is curious, but since an oxime salt, LIII, was isolated in the indocyanine series, it was suggested that this split off water to give LIV, which then condensed with the methylene base, LV, with elimination of HCN.[90] The net result is that two mols. of quaternary salt condense with one of nitrite, to give one mol. of methincyanine, as indicated by equation 3.



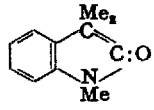
(3)

B. Indocyanines and Intermediate Compounds

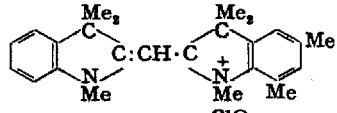
The method of the patent was to dissolve 1,3,3-trimethyl-2-methyleneindoline, LV, in acetic anhydride and to add sodium nitrite or amyl nitrite. After heating, the yellow reaction mixture was treated with water, and sometimes with bisulphite, and the dye was salted out.[89] Alternatively it, or an intermediate compound, could be obtained by reaction of the methylene base, LV, with nitrosyl chloride in acetic anhydride[94] or with nitrosylsulphuric acid in acetic acid or anhydride.[95] When a cooled solution of the methylene base, LV, in acetic acid was gradually treated with an aqueous solution of sodium nitrite, followed by one of sodium perchlorate, the oxime perchlorate, LIII, crystallised in almost quantitative yield. On warming it with the methylene base in acetic anhydride, it gave the indocyanine, LVI, in 60 % crude yield. In the absence of methylene base, the oxime, LIII, breaks down



(LVI)



(LVII)



(LVIII)

smoothly into the indolinone, LVII, and a 25 % yield of this accompanied the indocyanine. By condensing the oxime with 1,3,3,5,7-pentamethyl-2-methyleneindoline, the unsymmetrical indocyanine, LVIII, was obtained. It was identical with the sample prepared by the alternative method of condensing LV with 1,3,3,5,7-pentamethyl-2-oximinomethylindoleninium perchlorate.[90]

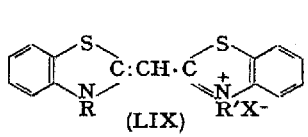
The chloride corresponding with LVI was called Indolenine Yellow.[96]

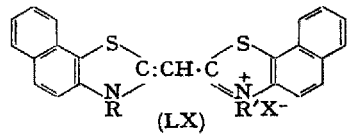
C. Thiacyanines

A thiacyanine had been synthesised in 1922 (see I-3-D);[18] besides this, two preparative methods were known in 1930, but they suffered from the disadvantage that thiacyanine was not the sole dye produced, so that the yields were low: 16–21 % by heating a benzothiazolium salt with a 2-methylbenzothiazolium salt in pyridine (see I-3-D; and section 1-F),[18] and 11 % by the disulphide method (see I-3-E; and section 6-C).[69] The nitrite method was an improvement, as thiacyanines only were produced, the yields after recrystallisation being 18–33 %.[91] It arose through applying the method of the patent[89] to benzothiazolium salts

1350

having a reactive methyl group. Thus on warming 2-methylbenzothiazole ethochloride with amyl nitrite and acetic anhydride, a dye chloride was produced; it was converted into the corresponding bromide and iodide. From analyses, together with a comparison of the iodide with a genuine sample, these dyes were identified as thiacyanines, LIX (R=R′=Et, X=Cl, Br, or I). The three corresponding dimethyl dyes were also prepared, and, by use of 2-methyl-6,7-benzobenzothiazole alkochloride, the six compounds, LX (R=R′=Me or


(LIX)

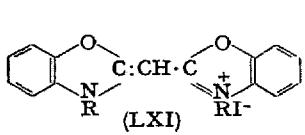

(LX)

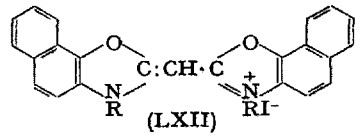
Et, X=Cl, Br, or I). All of them were photographic sensitisers to silver chloride emulsions. The absorption maxima of alcoholic solutions of the dibenzothiacyanines lay 150–200 Å, and the maxima of extra-sensitivity 250–300 Å, further into the region of longer wavelength than those of the unsubstituted thiacyanines (see Table VII). In all four groups the solubility decreased in the series chloride, bromide, iodide, and the melting point rose.[91] Thiacyanines having amino-groups, which might be substituted, were good sensitisers: e.g., the 6,6′-bis-diNEt$_2$-derivative of LIX (R=R′=Et, X=I) gave a sensitising maximum of 5600 Å.[38] The 6,6′-dichloro-derivative of LIX (R=R′=Et, X=Cl) and the 6,6′-dibromo-derivative of LIX (R=R′=Et, X=I) had the absorption maximum at 4300 Å and the sensitising maximum at 4500 Å.[73] The 5,6,5′,6′-dibenzo-derivative of LIX (R=R′=Et, X=I) had its absorption and sensitising maxima at 4950 Å and 4600 Å, respectively.[41] The 6,6′-dinitro-derivative of LIX (R=R′=Et, X=Cl) was prepared by heating 2-methyl-6-nitrobenzothiazole ethochloride with diphenylnitrosamine in acetic anhydride.[67]

D. Oxa- and Selena-cyanines

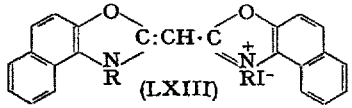
In preparing thiacyanines, chlorides were chosen as starting points, because nitrous acid does not liberate halogen from chlorides,[91] but in preparing oxacyanines the use of iodides was found to give some dyes which were inaccessible by use of chlorides; the purification of the crude dye then included treatment of its suspension in ice-cold alcohol

with sulphur dioxide. With six oxacyanines, LXI, LXII, and LXIII (R=Me or Et), the yields of recrystallised dye varied from 14–26%, being lowest for LXIII. The dibenzoxacyanines proved powerful sensitisers for chloride emulsions.[93,97]


(LXI)


(LXII)

Selenacyanines, LXIV, in the form of halides or alkylsulphates, improved photographic sensitivity in the region 4300–5200 Å. Sub-


(LXIII)

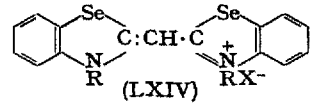

(LXIV)

TABLE VII. Some Properties of Symmetrical Methincyanines

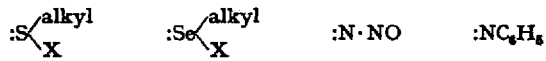
Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
I (R = Et cyanine)	green prisms	271–273	5900	5650, 6050	6350	5a, 98
XIX (R = Et 2,2′-cyanine)	bluish red	277	5250(and 4900)	5700	6000	56
XXIII (R = Et)	green and gold	310	5500(and 5100)	5700	6300	64
LVI (indocyanine)	greenish yellow	267	—	—	—	90
LIX (R=R′ =Et, X=I thiacyanine)	yellow prismatic needles	310–311	4230(and 4000)	between 4500 and 4600	4900	18
LX (R=R′=Et, X = I)	yellow	297	4450	4800	5300	91
LXI (R = Et oxacyanine)	pale yellow	301	3700	—	—	93
LXII (R = Et)	—	> 315	3950	—	—	93
LXIII (R = Et)	—	283	4020	—	—	93
LXIV (R = Et, X = I selenacyanine)	green shining needles	—	4200	4600	5000	92

stituents, such as methyl, methoxy-, or chloro-, might be introduced into the 5,5'-positions.[92] Substituted amino-groups were also introduced.[38]

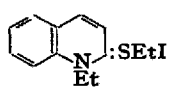
4. Alkyl-, or Aryl-thio- Method

A. General

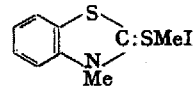
According to a patent of 1932, various types of methincyanines could be prepared by condensation of a quaternary heterocyclic salt, having a reactive methyl group, with an *N*-alkyldihydro heterocyclic base, of the quinoline or benzothiazole series, having in the 2-position one of the following four groups:



where X is an acid radical.[99] Consideration of the third and fourth types is relegated to Chapter II-5; the second is merely a possible variant of the first type, which is of great practical importance. Instances of compounds of this first type are in formulae LXV and LXVI. Application of this method would include 2,2'- and 2,4'-



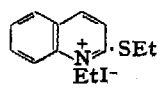
(LXV)



(LXVI)

cyanines, thiacyanines, oxa-2'-, thia-2'-, and selena-2'-cyanines, and thia-4'-cyanines, and out of these seven types there are examples of six.[99]

In an independent discovery in 1933, the reactant of the first type was formulated as the quaternary salt of a heterocyclic 2- or 4-alkylthio-compound, so that the above formulae would be written as LXVII and LXVIII, respectively. Instead of isolating such a salt



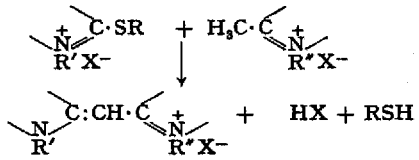
(LXVII)



(LXVIII)

and bringing about its reaction with a quaternary salt having a reactive methyl group, by heating with an acid-binding agent, a

modified procedure, which was said to give better yields, was to heat together a heterocyclic base having an alkylthio-group, one having a methyl group, and two mols. of an alkyl toluene-*p*-sulphonate, and to boil the melt with sodium acetate in alcohol, or with pyridine; boiling with benzene removed any thione by-product from the cyanine.[87,100] Alternatively, instead of using a base having an alkylthio-group for quaternary salt formation, the salt could be prepared from a thione. Formation of a methincyanine took place as indicated in equation 4.



(4)

The method had the advantage of cheapness and it made available many new types of dyes, including unsymmetrical types inaccessible by the nitrite method (see section 3). The unpleasant smell is a disadvantage. Some of these additional types are indoxa-, indothia-, and oxathia-cyanines, oxathiazolo-, oxazolothia-, and thiathiazolo-cyanines, also oxa-2′-pyrido- and 2-pyridothia-cyanines,[87,100,101] and oxazolo-, thiazolo-, and oxazolothiazolo-cyanines.[102] By means of the alkylthio-method, diazine and diazole nuclei were introduced into methincyanine molecules (see X-5-B).[103] By use of quaternary salts of 2-alkylthio-7,8-benzoquinoline, the method made possible the preparation of 2,2′-, thia-2′-, and selena-2′-cyanines having a 7,8-benzoquinoline nucleus.[104]

2-Arylthiopyridinium iodides and 2-arylthioquinolinium iodides were prepared by the action of arylmercaptans and triethylamine in alcohol on the corresponding 2-iodo-salts[105] and were used in the preparation of cyanine dyes.[106] So also a 4-arylthiopyridinium salt was used in preparing a 4,4′-pyridocyanine (see section 2-J).[62,107]

It was found in 1939 that when 2-methylthioquinoline was heated with ethyl iodide, the product was not the expected ethiodide but was 2-ethylthioquinoline methiodide: this was discovered through the anomalous analytical results on dyes prepared from the salt.[108] In the same way, 2-methylthiobenzothiazole, on heating with ethyl iodide, led to 2-ethylthiobenzothiazole methiodide: this was proved by examination of the product of the action of aqueous sodium sulphide on the salt.[109] Twelve years later it was pointed out that the action of alkyl iodide on 2-alkylthio-benzothiazole or -quinoline, having a dif-

ferent alkyl group, could lead to a mixture of four different quaternary salts, but the least soluble methiodides usually crystallised. 2-Alkylthiopyridines on heating with alkyl iodides gave quaternary salts without group interchange.[110] On heating with alkyliodides, 2-alkylthiobenzoxazoles did not lead to quaternary salts which could be isolated,[108,110] nor did the corresponding thiones,[110] yet oxacyanines can be prepared by the alkylthio-method. The fusion process involving alkyl toluene-*p*-sulphonates, in the benzothiazole and quinoline series, was found to lead to dyes formed without group interchange, whence it was inferred that these salts are more stable than alkiodides and indeed, unlike the alkiodides, they were not converted into thiones by heating with pyridine.[110] Nevertheless the possibility of group interchange does show the desirability of the simple precaution that the alkyl of the alkylthio-group should be identical with that of the ester used for salt formation.[108] Where this precaution has not been taken, published examples may not be what they purport to be, unless they are supported by analytical evidence.

B. 2,2′- and 2,4′-Cyanines

The 2,2′-cyanine, XIX (R=Et), was obtained by boiling quinaldine ethiodide with the ethiodide of 1-ethyl-2-thio-1,2-dihydroquinoline in pyridine; it was precipitated with water, washed with ether, and recrystallised.[99] The same dye was prepared by heating together quinaldine ethotoluene-*p*-sulphonate and 2-phenylthioquinoline ethiodide in pyridine[106] (see section 2-B). The 7,8-benzo-,5,6,7′,8′- and 7,8,7′,8′-dibenzo-derivatives of the bromides corresponding with XIX (R=Me) were prepared by condensing 2-methylthio-7,8-benzoquinoline methomethylsulphate with the appropriate quinaldinium salts.[104]

Dyes of the 2,4′-cyanine series are so readily available by other methods (sections 1-C and 2-C) that the alkylthio-method has found no application here.

C. Thia-4′- and Oxa-4′-cyanines

A thia-4′-cyanine, of type VIII, was prepared, in 30% yield, by heating together lepidine ethiodide, the methiodide of 3-methyl-2-thiobenzothiazoline, pyridine, and piperidine.[99] Another was prepared by fusing for 3·5 hours at 150° a mixture of lepidine, 2-methylthio-

benzothiazole, and ethyl toluene-*p*-sulphonate, then boiling with pyridine, and treating with aqueous potassium iodide; the *NN'*-dimethyl analogue was similarly made; to obtain an ethylmethyl analogue, a mixture of lepidine methiodide and 2-methylthiobenzothiazole ethiodide in ethanol was boiled with fused sodium acetate.[87]

A derivative of the oxa-4'-cyanine, XV, having a 4,5-benzo-group in the benzoxazole nucleus, was prepared from 2-methylthio-4,5-benzobenzoxazole, lepidine, and ethyl toluene-*p*-sulphonate.[100] XV itself was prepared by heating together 2-methylthiobenzoxazole, lepidine, and ethyl toluene-*p*-sulphonate, dissolving in ethanol, and treating with aqueous potassium iodide.[108]

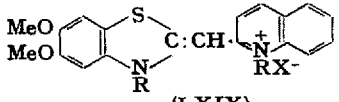
D. Indo-2'-cyanines

The indo-2'-cyanine, XXV (R=Me, R'=Et), was prepared by heating 2,3,3-trimethylindolenine methiodide with 2-phenylthioquinoline ethiodide in pyridine (see section 2-E).[108]

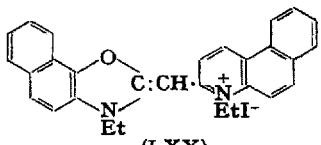
E. Thia-2'-, Oxa-2'-, and Selena-2'-cyanines

It is interesting that the original preparation of a thia-2'-cyanine, XXVI (R=Et), by this method comprised use of a seleno-compound, namely 1-ethyl-2-seleno-dihydroquinoline ethiodide, which was condensed with 2-methylbenzothiazole ethiodide, by heating in alcohol, with addition of pyridine.[99] Just as the thia-4'-cyanine, XI, having a 5,6-benzobenzothiazole nucleus, was claimed to be a useful sensitiser (section 1-D),[41] so also was the isomeric thia-2'-cyanine; this was made from 1-ethyl-6-methyl-2-thiodihydroquinoline ethiodide and 2-methyl-5,6-benzobenzothiazole ethoethylsulphate, by heating with piperidine in alcohol.[41] Again, just as the tetrahydrobenzothiazole nucleus imparted interesting photographic properties to the thia-4'-cyanine, XIV (section 1-D),[42] so it did to thia-2'-cyanines; to condense 1-ethyl-6-methyl-2-thiodihydroquinoline ethiodide with 2-methyltetrahydrobenzothiazole methomethylsulphate, they were boiled together in alcohol containing pyridine.[42] The thia-2'-cyanine, XXVI (R=Me), resulted in 65 % yield on boiling an alcoholic solution of 2-methylthio-quinoline methotoluene-*p*-sulphonate and 2-methylbenzothiazole methiodide with anhydrous potassium carbonate; according to the fusion method, whereby 1-methyl-2-thiodihydroquinoline, 2-methylbenzothiazole, and

methyl toluene-*p*-sulphonate were heated together at 150°, followed by treatment of the alcoholic solution with aqueous potassium iodide, the yield was only 32 %.[108] The arylthio-modification was applied to the preparation of four thia-2′-cyanines. Thus by boiling with triethylamine in alcohol, 2-methylbenzothiazole ethotoluene-*p*-sulphonate reacted with 2-phenylthioquinoline methiodide or ethiodide, or with 6-methyl-2-*β*-naphthylthioquinoline ethiodide, and 2-methyl-4,5-benzobenzothiazole methotoluene-*p*-sulphonate was condensed with 2-phenylthioquinoline ethiodide.[108] Six thia-2′-cyanine preparations were included in the original patent[100] and another in that concerning the thione modification.[101] To prepare XXVI (R=Me), the fusion method was applied to a mixture of 2-methylthiobenzothiazole, quinaldine, and methyl toluene-*p*-sulphonate, whilst to prepare XXVI (R=Et) it was applied to a mixture of 2-ethylthiobenzothiazole, quinaldine, and ethyl toluene-*p*-sulphonate: after 2 hours at 120°, each melt was boiled with pyridine for 45 minutes. LXIX (R=Me or Et) were



(LXIX)



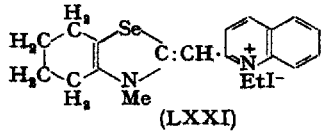
(LXX)

prepared by use of 2-alkylthio-5,6-dimethoxybenzothiazole: after its fusion with the other reactants at 140° for 4 hours, the resultant melt was boiled with fused sodium acetate in ethanol; the former dye was isolated as bromide and the latter as toluene-*p*-sulphonate.[87] Reaction of 2-alkylthio-7,8-benzoquinoline alkoalkylsulphate with a 2-methylbenzothiazolium quaternary salt led to three thia-2′-cyanines having a 7,8-benzoquinoline nucleus.[104]

The application of this method to oxa-2′-cyanines, e.g., XXXI, was claimed and an example given.[99] In preparing various oxa-2′-cyanines, the method consisted in heating together a 2-alkylthiobenzoxazole, quinaldine, and an alkyl toluene-*p*-sulphonate, boiling with fused sodium acetate in ethanol, and precipitating with potassium iodide.[100] In a patent on the sensitising action of these dyes for blue and blue-green light, condensation was effected by boiling the two quaternary salts with pyridine and piperidine.[111] Oxa-2′-cyanines having a 5,6-benzobenzoxazole nucleus were, like the corresponding oxa-4′-cyanines

(see section 1-D), photographically valuable,[44] as also were those having a 5-phenyl group in the benzoxazole nucleus.[112] The dibenzo-derivative, LXX, of the parent oxa-2′-cyanine, XXXI, was prepared by the fusion method, in which the melt was subsequently boiled with anhydrous potassium carbonate in alcohol, then treated with aqueous potassium iodide.[108] XXXI itself was prepared by heating the ethiodides of 2-methylbenzoxazole and 2-phenylthioquinoline in pyridine.[106] Its 5′,6′-benzo-derivative was obtained by fusion of 2-ethylthiobenzoxazole, 2-methyl-5,6-benzoquinoline, and ethyl toluene-*p*-sulphonate, and treatment of the product with iodide.[71]

The preparation of selena-2′-cyanines by this method was claimed and a 6-methyl derivative of XXXIII (R=Et) was prepared by heating the ethiodides of 2-methylbenzoselenazole and 1-ethyl-6-methyl-2-thiodihydroquinoline in ethanol containing piperidine.[99] The ethiodide of the latter base was condensed, by boiling in ethanol containing pyridine, with 2-methyltetrahydrobenzoselenazole methiodide to give LXXI, which, like thia-4′- and thia-2′-cyanines having a



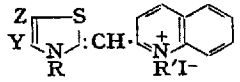
(LXXI)

tetrahydrobenzothiazole nucleus (see section 1-D and 4-E), was found to have useful sensitising properties.[42] A selena-2′-cyanine having a 7,8-benzoquinoline nucleus was prepared by the method used for such thia-2′-cyanines (see section 4-B).[104]

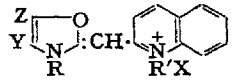
F. Thiazolo-2′-, Thiazolino-2′-, and Oxazolo-2′-cyanines

Of thiazolo-2′-cyanines, analogues of XXXIV were prepared, firstly, by heating together 1-methyl-2-thiodihydroquinoline (or its 6-methyl derivative), 2,4-dimethylthiazole, and alkyl toluene-*p*-sulphonate, heating the melt with pyridine, and treating with potassium iodide; alternatively, from 2,6-dimethylquinoline, 4-methyl-2-methylthiothiazole and methyl toluene-*p*-sulphonate.[87,101] XXXIV (R=Ph) was prepared by boiling 2-methyl-4-phenylthiazole ethotoluene-*p*-sulphonate and 2-phenylthioquinoline ethiodide with triethylamine in alcohol.[106] Five thiazolo-2′-cyanines, LXXII (Table VIII), were prepared by boiling together a quaternary salt of a 4,5-diarylthiazole, one

of 2-alkylthioquinoline, and triethylamine in ethanol, and treating the reaction mixture with potassium iodide. Introduction of substituents into the 4-aryl group had no effect on the absorption maximum.[113]



(LXXII)



(LXXIII)

The thiazolino-2′-cyanine, XXXVI, was prepared by heating 2-methylthiazoline ethotoluene-*p*-sulphonate, 2-phenylthioquinoline ethiodide, and triethylamine in alcohol.[106]

A series of oxazolo-2′-cyanines, LXXIII (Table VIII), materialised through the synthesis of 2-methyl-4- (or 4,5-di-) substituted oxazoles, each of which was converted into an alkotoluene-*p*-sulphonate. Equimolecular proportions of such a salt, of 2-alkylthioquinoline alkiodide, and of triethylamine were boiled together in ethanol for 15 minutes. 5-Aryl-substitution shifted the absorption maximum more than did 4-aryl-substitution, whilst introduction of substituents into the 4-aryl ring had little or no effect. Hence it was concluded that the 5-aryl group was coplanar with the oxazole ring but the 4-aryl group was not (see also section 2-G).[114]

G. 2-Pyrido-2′- and 4-Pyrido-4′-cyanines

The 2-pyrido-2′-cyanine, XLII (R=Me), was prepared by heating 2-picoline methiodide and 2-phenylthioquinoline methiodide with triethylamine in ethanol.[106]

The 4-pyrido-4′-cyanine, XLVI (R=Et), and its dimethyl analogue, were prepared in 16 % and 36 % yield, respectively, by heating together 4-phenylthiopyridine alkiodide, lepidine alkiodide, and triethylamine in n-propanol (see section 2-H).[63]

H. Oxa-2′-pyrido- and 2-Pyridothia-cyanines

The oxa-2′-pyridocyanine, XLVII (Y=O, R=Me), was prepared by heating together 3-methyl-2-thiobenzoxazoline, 2-picoline, and methyl toluene-*p*-sulphonate, followed by boiling with pyridine and treatment with aqueous potassium iodide (see section 2-I).[101]

To prepare the 2-pyridothiacyanine, XLVII (Y=S, R=Me), the reactants were 1-methyl-2-thiodihydropyridine, 2-methylbenzo-

TABLE VIII. Some Properties of Thiazolo-2′- and Oxazolo-2′-cyanines

Formula	Y	Z	R	R′	X⁻	Yield %	Appearance of crystals	M.p. (°C)	Absorption maximum (Å)	Ref.
LXXII	Ph	Ph	Et	Me	I	—	orange needles	271	4900	113
LXXII	*p*-MeO·C_6H_4	Ph	Et	Me	I	—	orange needles	267	4900	113
LXXII	Ph	PhO	Et	Me	I	—	orange threads	258	4800	113
LXXII	*m,p*-diMeO:C_6H_3	Ph	Et	Me	I	—	rust-red needles	258	4900	113
LXXII	Ph	*p*-Me·C_6H_4S	Me	Et	I	—	glossy red needles	227–228	4850	113
LXXIII	H	H	Et	Me	ClO_4	40	mustard-yellow prisms	235	4300 (infl. 4150)	114
LXXIII	Pr^n	Pr^n	Me	Me	ClO_4	—	orange needles	200	4350	114
LXXIII	Ph	Ph	Et	Me	I	76	orange needles	286[a]	4520	114
LXXIII	*p*-MeO·C_6H_4	Ph	Et	Et	ClO_4	27	orange prisms	227	4510	114
LXXIII	*p*-MeO·C_6H_4	Ph	Et	Me	ClO_4	45	orange prisms	270	4580	114
LXXIII	*p*-NMe_2·C_6H_4	Ph	Et	Me	I	—	red needles	290	4700	114
LXXIII	*p*-C_6H_4·NMe_3I	Ph	Et	Me	I	—	orange needles	271	4500	114

[a] Decomp.

thiazole, and methyl toluene-*p*-sulphonate, followed by pyridine and by potassium iodide.[101] It was also prepared from 2-picoline, 2-methylthiobenzothiazole, and methyl toluene-*p*-sulphonate; the *NN'*-diethyl analogue was similarly prepared, also derivatives of both having 5,6-dimethoxy- or 5,6-methylenedioxy-groups in the benzothiazole nucleus.[87,100] In preparing an ethyl–methyl dye of type XLVII (Y=S), 2-*β*-naphthylthiopyridine methiodide was condensed with 2-methylbenzothiazole ethotoluene-*p*-sulphonate by boiling with triethylamine in ethanol (see also sections 2-I and 6-C).[106]

I. 4,4'-Pyridocyanines

The 4,4'-pyridocyanines, L (R=Me or Et), were prepared by heating together 4-picoline alkotoluene-*p*-sulphonate, 4-phenylthiopyridine alkiodide, and triethylamine in n-propanol, followed by treatment with sodium perchlorate (see II-2-J).[62,107]

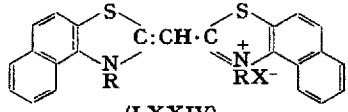
J. Thiazolo-2'- and Thiazolino-2'-pyridocyanines

The thiazolo-2'-pyridocyanine, LI (Y=S, R^1=Et, R^2=R^3=Me), was prepared by heating 2,4-dimethylthiazole ethiodide and 2-*β*-naphthylthiopyridine methiodide with triethylamine in ethanol.[106]

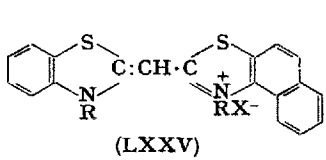
The thiazolino-2'-pyridocyanine, LII, was prepared by heating together 2-methylthiazoline methotoluene-*p*-sulphonate, 2-*β*-naphthylthiopyridine methiodide, and triethylamine in ethanol (see section 2-K).[106]

K. Thia-, Oxa-, Oxathia-, and Selenathia-cyanines

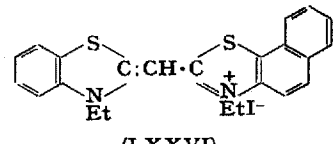
For preparing thiacyanines, the starting points for conversion into quaternary salts were either thiones[101] or alkylthio-compounds.[100] The latter were applied to the preparation of symmetrical thiacyanines such as LIX (R=R'=Me or Et, X=Br); also of 5,6,5',6'-bismethylenedioxy-derivatives of LIX (R=R'=Me, X=*p*-$SO_3C_6H_4Me$; or R=R'=Et, X=Br), and also of LX (R=R'=Me, X=*p*-$SO_3C_6H_4Me$; and R=R'=Et, X=Br). They were used in the preparation of LXXIV (R=Me, X=*p*-$SO_3C_6H_4Me$; or R=Et, X=Br)[87] (see section 6-D), whereas LXXIV was unobtainable by the nitrite method.[91] The alkylthio-method was further applied to unsymmetrical dyes, such as LIX (R=Et, R'=Me, X=I or Br),[71,87] and to dyes such as LXXV (R=Me or Et, X=Br)[87] or LXXVI.[108]



(LXXIV)



(LXXV)

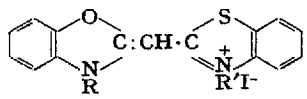


(LXXVI)

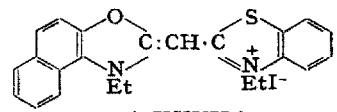
It was also used for unsymmetrical derivatives of LIX, in which one nucleus only carried substituents, such as 5,6-dimethoxy-, 5,6-methylenedioxy-, 5-dimethylamino-, or 6-diethylamino-.[87]

It is remarkable that the preparation of oxacyanines by the alkylthio-method has only been described in patents. The procedure of heating together a 2-methylbenzoxazole, a 2-methylthiobenzoxazole, and ethyl toluene-*p*-sulphonate, followed by treatment with potassium iodide, was applied to the preparation of LXI, to derivatives in which both nuclei had 5,6-dimethyl or 6-methyl substituents, and to LXIII. In addition, unsymmetrical oxacyanines were made.[100] LXI (R=Me) was also made by heating together 2-methylbenzoxazole, 3-methyl-2-thiobenzoxazoline, and methyl toluene-*p*-sulphonate, followed by heating with pyridine and treatment with potassium iodide; the 5,6,5′,6′-tetramethyl derivative of the corresponding bromide was similarly prepared.[101]

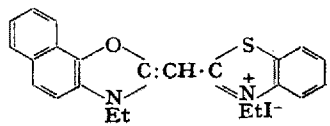
Dyes of the oxathiacyanine type were prepared either from an alkylthio-compound[100] or from a thione.[101] By heating together 2-methylbenzoxazole, 2-alkylthiobenzothiazole, and alkyl toluene-*p*-sulphonate, there were prepared LXXVII (R=R′=Me or Et),[100] also similarly LXXVIII and LXXIX.[87,108]



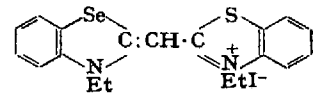
(LXXVII)



(LXXVIII)



(LXXIX)

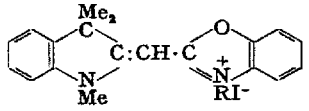


(LXXX)

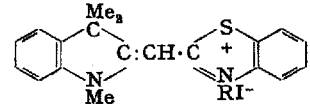
The selenathiacyanine, LXXX, was prepared, in 65% yield, by 20 minutes' boiling of 2-methylthiobenzothiazole ethiodide, 2-methylbenzoselenazole ethiodide, anhydrous potassium carbonate, and ethanol, followed by recrystallisation from methanol.[108]

L. Indoxa- and Indothia-cyanines

Four dyes of the indoxacyanine type, LXXXI, were made by heating together a 2-methylthiobenzoxazole, which might be substituted, 1,3,3-trimethyl-2-methyleneindoline, and ethyl toluene-*p*-sulphonate, followed by treatment with potassium iodide.[100] Alternatively, LXXXI (R=Me) was prepared by heating 3-methyl-2-thio-



(LXXXI)



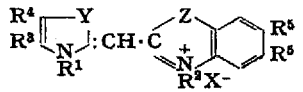
(LXXXII)

benzoxazoline with methyl toluene-*p*-sulphonate, adding 2,3,3-trimethylindolenine methiodide and pyridine, and heating further.[101]

The alkylthio-method also gave a dye of the indothiacyanine type.[100] Thus 2,3,3-trimethylindolenine methiodide, 2-methylthiobenzothiazole, and methyl toluene-*p*-sulphonate were fused together at 120° for 2 hours, the product was boiled with pyridine for 45 minutes, then treated with aqueous potassium iodide to give LXXXII (R=Me, X=I). Similarly use of 2-ethylthiobenzothiazole in conjunction with ethyl toluene-*p*-sulphonate gave LXXXII (R=Et, X=ClO_4).[87]

M. Oxaoxazolo-, Oxathiazolo-, Oxazolothia-, and Thiathiazolo-cyanines

A dye of the oxaoxazolocyanine class, LXXXIII (Y=Z=O, R^1=R^2=Et, R^3=R^4=Ph, R^5=H, X=I), was prepared by heating together 2-methylthiobenzoxazole, 2-methyl-4,5-diphenyloxazole,



(LXXXIII)

and ethyl toluene-*p*-sulphonate, boiling with anhydrous sodium acetate in ethanol, and treating with potassium iodide.[100]

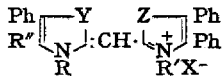
One of the oxathiazolocyanine type, LXXXIII (Y=S, Z=O, R^1=R^2=Et, R^3=R^5=Me, R^4=H, X=I), was made from 5,6-dimethyl-2-methylthiobenzoxazole, 2,4-dimethylthiazole, and ethyl toluene-*p*-sulphonate.[100]

A thione was the starting point for an oxazolothiacyanine.[101] Alternatively, LXXXIII (Y=O, Z=S, R^1=R^2=R^3=Me, R^4=R^5=H, X=I) was prepared by fusion of 2,4-dimethyloxazole, 2-methylthiobenzothiazole, and methyl toluene-*p*-sulphonate at 130–140° for 3 hours, followed by boiling with pyridine for 30 minutes, and treatment with aqueous potassium iodide.[87]

The thiathiazolocyanine, LXXXIII (Y=Z=S, R^1=R^2=R^3=Me, R^4=R^5=H, X=Br) was prepared either from 2-methylthiobenzothiazole, 2,4-dimethylthiazole, and methyl toluene-*p*-sulphonate, or, alternatively, from 2-methylbenzothiazole, 3,4-dimethyl-2-thiothiazoline, and methyl toluene-*p*-sulphonate, followed by heating with pyridine and conversion into bromide.[87] Another thiathiazolocyanine, LXXXIII (Y=Z=S, R^1=Et, R^2=Me, R^3=C_6H_4OMe, R^4=Ph, R^5=H, X=I), was prepared by boiling together 2-methylthiobenzothiazole methotoluene-*p*-sulphonate, 4-*p*-methoxyphenyl-2-methyl-5-phenylthiazole ethotoluene-*p*-sulphonate, and triethylamine in ethanol, and treating with potassium iodide (see section 6-C).[113]

N. Oxazolo-, Thiazolo-, and Oxazolothiazolo-cyanines

Symmetrical oxazolocyanines, LXXXIV (Y=Z=O, R=R′= Et or C_8H_{17}, R″=Ph, X=ClO_4) and LXXXIV (Y=Z=O, R= R′=R″=Ph, X=I) were synthesised[102] by condensation of a



(LXXXIV)

2-methylthio-4,5-diphenyloxazolium salt, obtained from a 2-thiooxazoline,[115] with a 2-methyl-4,5-diphenyloxazolium salt,[116] by heating with triethylamine in methanol. The former compound had its absorption maximum at 3810 Å. An unsymmetrical oxazolocyanine, LXXXIV (Y=Z=O, R=R′=Et, R″=*p*-C_6H_4OMe, X=ClO_4), was also described.[102]

An unsymmetrical thiazolocyanine, LXXXIV (Y=Z=S, R=Et, R′=Bu, R″=Ph, X=ClO_4), absorbed at 4380 Å.[102]

Oxazolothiazolocyanines, LXXXIV (Y=O, Z=S, R=R′=Et, R″=Ph, X=I) and LXXXIV (Y=O, Z=S, R=Et, R′=Bu, R″=Ph, X=ClO_4), were reached similarly. The former had its absorption maximum at 4200 Å.[102]

5. Condensations Depending on Reactive :N·R

A. General

In one of the original patents on the alkylthio-method (see section 4-A), it was claimed that various types of methincyanines could be prepared by condensing a quaternary heterocyclic salt, having a reactive methyl group, with an *N*-alkyldihydro heterocyclic base having a bivalent polyatomic group in the 2-position. Of four such groups formulated, the first, $:S<^{alkyl}_{X}$, was very fully exploited, and its applications have been discussed (see section 4). The second, $:Se<^{alkyl}_{X}$ is a variant which has no practical interest. For the third group, :N·NO, only one example was given in the patent, whilst for the fourth group, $:NC_6H_5$, there was no example.[100] It has, however, recently been claimed for the group :NH, that an *N*-alkyl-2-imino benzothiazoline is a valuable intermediate compound for synthesising methincyanines, and that such a base condenses with a quaternary salt, having a reactive methyl group, when they are heated together in a vacuum at 180–190°. It is said that these imines are more accessible than quaternary salts of 2-alkylthio-derivatives and that the method is a general one: so far it has been applied only to the synthesis of thiacyanines (cf. XII-9-A).[117]

B. Thia-2′-cyanines

According to the only example of its type in a patent, the thia-2′-cyanine, XXVI (R=Et), was prepared, in 30–35 % yield, by heating quinaldine ethiodide and 3-ethyl-2-nitrosoiminobenzothiazoline in pyridine containing piperidine for one hour.[99]

C. Thiacyanines

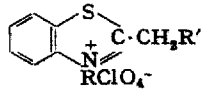
To prepare the thiacyanine, LIX (R=R′=Me, X=I), 3-methyl-2-iminobenzothiazoline and 2-methylbenzothiazole methomethyl-

sulphate were heated together in a vacuum at 180–190° for 15 minutes; the melt, on dissolving in ethanol, treatment with water, and then with aqueous potassium iodide, gave a 66% yield. Its 6-acetylamino-6′-methoxy-derivative was similarly obtained in 68% yield.[117] The method gave a 60% yield of a derivative having one 6-trifluoromethyl group.[118]

6. Other Methods

A. Use of Grignard Reagent for Thiacyanines

Whereas treatment of an *N*-ethyl-2-oxobenzothiazoline with ethyl, or benzyl, magnesium iodide, followed by acidification, led to a quaternary salt, LXXXV (R=Et, R′=Et or Ph), methyl magnesium



(LXXXV)

iodide behaved differently. Here gas was evolved in the cold and an oil was deposited, which on acidification gave a thiacyanine. In this way there were prepared LIX (R=R′=Me, X=I), the 6,6′-dimethyl derivative of LIX (R=R′=Et, X=I), and LX (R=R′=Et, X = I), which iodides were converted into perchlorates.[119]

B. Use of Ethyl Malonate for Synthesising Thiacyanines

The constitution of thiacyanines was established by the synthesis of LIX (R=R′=Et or Me) from *o*-aminothiophenol and ethyl malonate, via dibenzothiazolylmethane (see I-3-D).[18]

Twenty years later, an unsuccessful attempt was made to synthesise methincyanines from methanes substituted by two heterocyclic nuclei, of which at least one was a substituted quinoxaline. It failed because of the resistance of these methanes to quaternary salt formation (see X-5-B).[120]

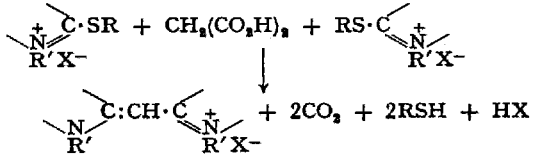
C. Disulphide Method for Thia-, Thia-2′-, Thia-4′-, 2-Pyridothia-, and Thiathiazolo-cyanines

It was discovered in 1923 that di-[*o*-*N*-alkylformanilido] disulphide fulfils two functions on heating in pyridine with a quaternary hetero-

cyclic ammonium salt having a reactive methyl group. One is to provide a 3-alkylbenzothiazolylidene residue, which enters into the molecule of a methincyanine. Thus with 2-methylbenzothiazolium salts such a disulphide gave thiacyanines, with a quinaldinium salt it gave a thia-2′-cyanine, and with lepidinium salts it gave thia-4′-cyanines, each accompanied by a trimethincyanine (see I-3-E).[69] So also with 2-picoline ethonitrate it gave the 2-pyridothiacyanine, XLVII (Y=S, R=Et), and with 2-methyl-4-phenylthiazole methiodide gave the thiathiazolocyanine, LXXXIII (Y=Z=S, X=I, $R^1=R^2=Me$, $R^3=Ph$, $R^4=R^5=H$); the trimethincyanine accompanying the last was also isolated.[69] Whilst of value in establishing the constitution of the dyes, the method has now no practical significance as a preparative one, since it gives a mixture of dyes, which have to be separated.

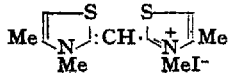
D. Malonic Acid Method for 2,2′-, Thia-, Oxa-, and Thiazolo-cyanines

By heating a heterocyclic alkotoluene-*p*-sulphonate, having a reactive 2-alkylthio-group, with malonic acid and pyridine, two mols. of salt condensed, as in equation 5, with one of acid to give a symmetrical methincyanine.



(5)

Thus the 2,2′-cyanine, XIX (R=Et) was prepared by heating 2-ethylthioquinoline with ethyl toluene-*p*-sulphonate at 130–140°, heating the salt with malonic acid and pyridine, then treating with aqueous potassium iodide; XIX (R=Me) was similarly prepared. The thiacyanine, LIX (R=R′=Me, X=*p*-$SO_3C_6H_4Me$), was prepared and converted into bromide; also the method was applied to the preparation of LIX (R=R′=Et, X=I) and of LXXIV (R=Me, X=*p*-$SO_3C_6H_4Me$). The oxacyanine, LXI (R=Me), was made by this method, as was also the thiazolocyanine, LXXXVI.[121]



(LXXXVI)

The method was applied to the preparation of symmetrical methincyanines having thiadiazole, pyrimidine, or quinazoline nuclei (see X-5-G and B) and to the synthesis of a 2,2′-cyanine in which the quinoline nuclei had a 1,8-bridge (see X-4-E). When glutaconic acid was used in place of malonic acid, the products were symmetrical trimethincyanines (see IV-14).

E. 4,4′-Cyanine by Cleavage of 4,4′-Carbocyanine with Lepidine Ethiodide

It was found in 1949 that the 4,4′-methincyanine, I (R=Et), was formed when the corresponding 4,4′-trimethincyanine was heated with lepidine ethiodide and acetic anhydride[122,123] but the yield was low (see V-12 and XIV-3-G).[124]

F. Thia-, Oxa-, and Selena-cyanines by Reaction of a Quaternary Salt, Having a Methylthio-Group, with Acetic Anhydride

Symmetrical methincyanines were obtained by heating a 2-methylthio-quaternary salt with acetic anhydride. Use of the anhydrides of other acids gave *meso*-substituted dyes (see III-A, E, and F), whilst by applying the method to the quaternary salt of a merocyanine, a tetranuclear dye resulted (see XV-6-B).[125]

The thiacyanine, LIX (R=R′=Me, X=SO_4Me), was prepared by heating 2-methylthiobenzothiazole methomethylsulphate with triethylamine in acetic anhydride, and precipitating with ether. The analogous oxacyanine and selenacyanine, LXIV (R=Me, X=SO_4Me), were made similarly.[125]

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CHAPTER III

Methincyanines with Substituents on the Chain

A. General

In a patent of 1931 there was put forward the idea of using a quaternary salt of, e.g., 2-ethylbenzothiazole, instead of one of 2-methylbenzothiazole, to give thia-2'-, thia-4'-, or thiacarbocyanines, with an α-methyl group on the chain.[1] The absorption maxima of the three examples of methincyanines—a thia-2'- and two selena-2'-cyanines—indicate that the chain-substituted dyes were in fact not obtained. The first were actually made in 1936. At that date 2-ethyl-5-phenylthiazole methiodide, 2-benzylbenzothiazole ethiodide, and 2-ethylbenzothiazole ethiodide, respectively, were condensed with 2-iodoquinoline methiodide: the products were so different in colour from the corresponding thiazolo-2'- and thia-2'-cyanines that, in spite of an analysis leading to the correct empirical formula for the dye from 2-ethylbenzothiazole ethiodide, they were concluded to be of an entirely different type. This last dye was violet, with its absorption maximum at 5300 Å. It was accompanied by an orange one which was, incorrectly, supposed to be the *meso*-methylthia-2'-cyanine,[2] but was subsequently shown to be the unsubstituted thia-2'-cyanine.[3] Besides the difference in colour, the violet dye was more soluble than the other, and more stable towards dilute sodium hydroxide solution, and it was devoid of sensitising properties.[2] It must be remembered that at this date chain-substituted trimethincyanines were known and were not so strikingly different from the parent dyes.

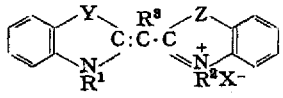
In 1947 the colour of chain-substituted methincyanines was discussed in a review on steric hindrance to planarity in dye molecules. Two scale drawings, reproduced in Figure I, of the molecule of a *meso*-alkyl-2,2'-cyanine, I (Y=Z=CH:CH) showed that there must be considerable crowding, and the effects of chain-substitution on the

TABLE I. Absorption Data for Chain-Substituted 2,2′- and Thia-cyanines (Formula I)

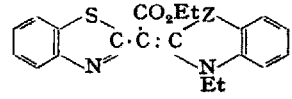
Nature of dyes	R^1	R^2	R^3	Absorption maximum Å	$\varepsilon \times 10^{-4}$	Ref.
2,2′- Series (I; Y=Z= CH:CH)	Me	Me	H	5200	7·2	4
	Me	Et	H	5225	7·0	4
	Et	Et	H	5235	7·6	4
	Me	Me	Me	5745	3·5	4
	Me	Et	Me	5770	2·7	4
	Et	Et	Me	5840	2·1	4
	Me	Me	Et	5760	3·1	4
	Me	Et	Et	5830	2·6	4
	Et	Et	Et	5910	2·0	4
	Me	Me	Pr^n	5750	3·2	4
	Me	Et	Pr^n	5830	2·7	4
	Et	Et	Pr^n	5900	2·1	4
Thia-Series (Y=Z=S)	Me	Me	H	4220	8·1	5
	Ph	Ph	H	4290	7·5	5
	Me	Me	Me	4650	6·0, 4·7	5, 6
	Et	Et	Me	4800	4·3	6
	Ph	Ph	Me	4600	3·5	5
	Me	Me	Et	4650	4·7	6
	Ph	Ph	Et	5010	2·1	5
	Me	Me	Pr^n	4660	4·5	6

absorption maximum of 2,2′-cyanine in methanol were tabulated. As seen in Table I, the bathochromic shift for the *NN*′-dimethyl dye was 545 Å on introduction of the *meso*-methyl group. Replacement of this methyl by an ethyl group had little further effect, and replacement of the ethyl by a propyl group practically none. The low values for the intensity indicated distortion of the molecule from planarity and it was considered that probably most of the bathochromic shift was also attributable to that.[4] Chain-substituted thiacyanines, I (Y=Z=S), likewise showed a considerable shift of the absorption maximum to a longer wavelength, decrease in intensity of absorption (Table I), and greater solubility; their melting points were lower than those of the unsubstituted dyes.[5,6] In contrast with these large bathochromic shifts

is the record that no change of absorption maximum occurred on passing from a thiacyanine to its *meso*-carbethoxy-derivative.[7] Whilst certain substituents in the chain give a bathochromic shift with methincyanines, they give a hypsochromic shift with styryl compounds (see XIII-1).[3,8]

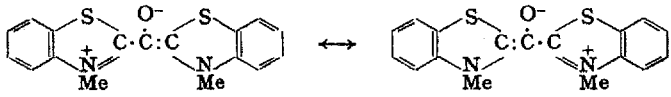


(I)



(II)

The preparation of thiacyanines with a methyl or phenyl group on the chain was described in the patent literature of 1949, by condensing a benzothiazolium quaternary salt, having a 2-alkylthio-group, with one having a 2-ethyl or a 2-benzyl group.[9] It was noted that the *meso*-methyl dye was accompanied by its analogue with an unsubstituted chain.[10] Thiacyanines having a *meso*-carbethoxy-group, were arrived at by heating the base, II (Z=S) (see XI-1 and 9-A), with methyl iodide or ethyl iodide.[7] By condensing a 2-hydroxymethyl with a 2-methylthio-benzothiazolium salt, there was prepared a thiacyanine having a *meso*-hydroxy-group. Its solution in ethanol was cerise, but changed to blue on addition of triethylamine, and this was attributed to the degenerate zwitterionic resonance system (III).[11]



(III)

In 1956 preparations of *meso*-methyl- and *meso*-phenyl-thia-2′-cyanines from 2-ethyl- and 2-benzyl-benzothiazolium salts were described. When 2-iodoquinoline ethiodide was used, the yields were comparable with those of unsubstituted thia-2′-cyanines (see II-2-F) and there was no dye by-product, but with 2-ethylthioquinoline ethiodide (see II-4-E), the *meso*-methylthia-2′-cyanine was accompanied by unsubstituted thia-2′-cyanine; similarly when 2-ethylthiobenzothiazole ethiodide (see II-4-K) reacted with 2-ethylbenzothiazole ethiodide, the *meso*-methylthiacyanine was accompanied by unsubstituted thiacyanine. Other *meso*-substituted thia-2′-cyanines prepared by use of 2-iodoquinoline ethiodide included one having a *meso*-

p-nitrophenyl group and one having a *meso*-2-benzothiazolyl group. Attempts to use 2-carbethoxymethylbenzothiazole ethiodide in the preparation of a *meso*-carbethoxy-thiacyanine or -thia-2′-cyanine were unsuccessful, but dyes of each type were made by the action of alkyl iodides on the bases, II (Z=S; or Z=CH:CH) (see XI-1 and 9-A), respectively. By use of 2-iodoquinoline ethiodide (see II-2-F), *meso*-methyl- and *meso*-phenyl-oxa-2′-cyanines were prepared but they were very unstable.[3]

Unlike the thia-2′-cyanine condensation, the thia-4′-cyanine condensation (see II-1-D) could not be extended to give chain-substituted dyes, and attempts to condense 2-ethylbenzothiazole ethiodide with quinoline ethiodide led only to apocyanines, which are formed by the action of alkali on quinoline ethiodide (see I-1 and 5). However by a modified ψ-cyanine condensation, in which 4-iodoquinoline ethiodide was one reactant (see II-2-D), and the other a 2-ethyl- or a 2-benzyl-benzothiazolium salt, a *meso*-ethyl- and a *meso*-phenyl-thia-4′-cyanine were prepared. A *meso*-methyloxa-4′-cyanine was similarly obtained.[3]

The synthesis of symmetrical methincyanines by reaction of a 2-methylthio-quaternary salt (see II-6-F) was extended to the preparation of *meso*-substituted thia- and selena-cyanines (see XV-6-B).[12]

Some properties of some of the chain-substituted methincyanines are shown in Table II. All of them show the decreased intensity of absorption which has been ascribed to non-planarity of the molecule. Most of them, like the dyes in Table I, show a large bathochromic shift of the absorption maximum. The two thiacyanines having a *meso*-carbethoxy-group show bathochromic shifts of smaller magnitude, whilst the two thia-2′-cyanines with that same substituent show hypsochromic shifts. These four dyes, and one other, differed from the rest in having extremely weak sensitising action, whereas none of the others sensitised.[3]

B. 2,2′-Cyanines

The absorption maxima of methanolic solutions of various *meso*-substituted 2,2′-cyanines, and the extinction coefficients[4] are given in Table I.

C. Thia-2′- and Oxa-2′-cyanines

When the ethiodide of pure 2-ethylbenzothiazole was condensed with that of 2-iodoquinoline by boiling with triethylamine in ethanol

TABLE II. Some Properties of Chain-Substituted Thia-2'-, Oxa-2'-, Thia-4'-, Oxa-4'-, and Thia-cyanines (Formulae I and IV; $R^1=R^2=Et$, X=I)

Nature of dyes	R^3	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Bathochromic shift on substitution (Å)	$\varepsilon \times 10^{-4}$	Ref.
Thia-2'-Series I; (Y=S, Z=CH:CH)	H	Scarlet needles	285	4860	—	5·1	3, 13
	Me	olive-green	148	5450	590	2·6	3
	Ph	—	—	5520	660	3·1	3
	p-$C_6H_4NO_2$	dark purple	216	5480 (4500)	620	2·4 (1·2)	3
	2-benzothiazolyl	purple	232	5470	610	1·2	3
	CO_2Et	orange	190	4780	—80	1·1	3
Oxa-2'-Series I; (Y=O, Z=CH:CH)	H	orange-yellow needles	290–292	4370	—	5·3	3, 14
	Me	maroon	133	4960	590	2·5	3
	Ph	dark maroon	227	5050 (infl. 4900)	680	3·0 (2·7)	3
Thia-4'-Series IV; (Y=S)	H	bright red needles	283	5030	—	5·3	3, 15
	Me	olive-green	185	5770	740	2·6	3
	Ph	—	222	5810	780	3·1	3
Oxa-4'-Series IV; (Y=O)	H	—	233	4700	—	6·4	3, 16
	Ph	maroon	224	5320	620	3·3	3
Thia-Series I; (Y=Z=S)	H	yellow prismatic needles	311	4220	—	8·7	3, 17
	Me	brick-red	214	4770	550	4·0	3
	CO_2Et	yellow	218	4370	150	1·2	3

for 1 minute, the *meso*-methylthia-2'-cyanine, I (Y=S, Z=CH:CH, $R^1=R^2=Et$, $R^3=Me$, X=I), resulted, after precipitation with ether and recrystallisation first from acetone and then from ethanol, in 54 % yield. This purple dye was unaccompanied by the orange by-

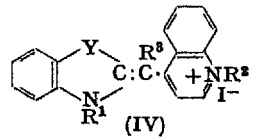
product[3] noted originally.[2] On the other hand, heating 2-ethylbenzothiazole ethiodide and 2-ethylthioquinoline ethiodide with triethylamine in ethanol gave a lower yield of the purple dye, together with the orange unsubstituted dye, I (Y=S, Z=CH:CH, R^1=R^2=Et, R^3=H, X=I). Condensation of 2-benzylbenzothiazole ethiodide with 2-iodoquinoline ethiodide by boiling with triethylamine in ethanol gave, after recrystallisation from ethanol, a 60 % yield of the *meso*-phenylthia-2′-cyanine. By use of 2-iodo-5,6-benzoquinoline ethiodide there were prepared derivatives of these two dyes, having a 5,6-benzo-group in the quinoline nucleus. To prepare a thia-2′-cyanine with a *meso*-*p*-nitrophenyl group, 2-*p*-nitrobenzylbenzothiazole and ethyl toluene-*p*-sulphonate were heated together at 165–175° for 4 hours, and the gum was dissolved in hot ethanol, treated with 2-iodoquinoline ethiodide and triethylamine, and boiled for 2 minutes. The washed product (40 % yield) after two purifications by chromatography gave a 6 % yield, and after recrystallisation from ethanol the yield was 3 %. The 2-benzothiazolyl group was introduced into the chain by boiling dibenzothiazolylmethane ethiodide and 2-iodoquinoline ethiodide with triethylamine in ethanol for 30 minutes. The product, precipitated by ether in 38 % yield, was homogeneous, and resulted in 20 % yield after two recrystallisations from methanol. To prepare the two *meso*-carbethoxythia-2′-cyanines, I (Y=S, Z=CH:CH, R^1=Me or Et, R^2=Et, R^3=CO_2Et, X=I), the base, II (Z=CH:CH), was heated at 100° for 24 hours with 1·5–2 mols. of methyl iodide or ethyl iodide, respectively. In each instance, the product was extracted with benzene, to remove unchanged base, and then shaken with benzene and aqueous sodium hydrogen carbonate, in order to remove hydriodide. The yields of recrystallised products were 25 % and 32 %.[3]

The *meso*-methyloxa-2′-cyanine, I (Y=O, Z=CH:CH, R^1=R^2=Et, R^3=Me, X=I), was prepared by boiling 2-ethylbenzoxazole ethiodide and 2-iodoquinoline ethiodide with triethylamine in ethanol for 1 minute. After precipitation with ether and washing, the crude dye (25 % yield) was twice purified by chromatography (17 % yield), and twice recrystallised from ethanol, the final yield being 3 %. It was very unstable. For preparing the *meso*-phenyl analogue, 2-benzylbenzothiazole ethotoluene-*p*-sulphonate was used; the red reaction mixture was treated with aqueous potassium iodide and the water-washed product recrystallised from ethanol, being obtained in 26 % yield. A derivative of the *meso*-phenyl dye with a 5,6-benzo-group in

the quinoline nucleus, was prepared through 2-iodo-5,6-benzoquinoline ethiodide, but the yield was only 2 % after protracted purification.[3]

D. Thia-4'- and Oxa-4'-cyanines

meso-Substituted thia-4'-cyanines were obtained by that modification of a 2'-cyanine condensation wherein 4-iodoquinoline ethiodide is used (see II-2-D). This salt was heated with 2-ethylbenzothiazole ethotoluene-*p*-sulphonate and triethylamine in ethanol for 2 minutes, and the product converted into iodide; the tar, by treatment with acetone, gave a 56 % yield of the *meso*-methylthia-4'-cyanine, IV



(IV)

(Y=S, R^1=R^2=Et, R^3=Me). Chromatography showed this blue dye to be the sole product and its recrystallisation from ethanol gave a 49 % yield. Its *meso*-phenyl analogue was prepared from 2-benzylbenzothiazole ethiodide with anhydrous potassium carbonate as condensing agent: the 99 % yield dropped to 56 % on one recrystallisation from ethanol and one from methanol.[3]

The *meso*-phenyloxa-4'-cyanine, IV (Y=O, R^1=R^2=Et, R^3=Ph), was made by heating 2-benzylbenzoxazole and ethyl toluene-*p*-sulphonate at 155–165° for 4 hours, adding 4-iodoquinoline ethiodide, ethanol, and triethylamine, and boiling for 3 minutes, then treating with aqueous potassium iodide. The resultant tar, after washing with water, crystallised from acetone in 16 % yield; three recrystallisations from ethanol resulted in a 4 % yield.[3]

E. Thiacyanines

Absorption data[5,6] for chain-substituted thiacyanines are given in Table I. The *meso*-methylthiacyanine, I (Y=S, R^1=R^2=R^3=Me, X=I), was prepared by condensing 2-ethylbenzothiazole methiodide either with 2-methylthiobenzothiazole methiodide, by boiling with sodium ethoxide or triethylamine in ethanol for 30 minutes,[9] or with 2-methylthiobenzothiazole methomethylsulphate by boiling with anhydrous sodium acetate in ethanol, whereby the yield before recrystallisation was 35 %.[5] In a preparation where a mixture of 2-ethyl-

and 2-methylthio-benzothiazole was heated with methyl toluene-*p*-sulphonate, and the salts were heated with pyridine, the product being converted into bromide, this *meso*-methyl dye was accompanied by the bromide of the unsubstituted thiacyanine.[10] A sensitising maximum of 4900 Å was recorded for the *meso*-methyl dyes;[9,10] the bromide, unlike its unsubstituted analogue, showed no fluorescence on filter paper.[10] A *meso*-methyl-*NN'*-diethylthiacyanine was prepared by condensing the ethiodides of 2-ethyl- and 2-methylthio-benzothiazole by means of ethanolic sodium ethoxide.[9] It was also prepared by condensing the ethiodides of 2-ethyl- and 2-ethylthio-benzothiazole by triethylamine in ethanol; the product precipitated by ether was washed with water and, from the dye residue (16 % yield), the more soluble *meso*-methyl dye was extracted with ethanol and obtained in 5 % yield after recrystallisation. It sensitised extremely weakly to 5400 Å. The less soluble residue was the analogous unsubstituted thiacyanine.[3] The orange *meso*-hydroxythiacyanine, I (Y = Z = S, $R^1 = R^2 = Me$, $R^3 = OH$, $X = p\text{-}SO_3C_6H_4Me$), m.p. 200°, was prepared by boiling the methotoluene-*p*-sulphonates of 2-hydroxymethyl- and 2-methylthio-benzothiazole with triethylamine in ethanol for 10 minutes. Its methanolic solution had its absorption maximum at 4900 Å but in the presence of triethylamine it lay at 5960 Å; the solutions slowly became colourless.[11]

The method of attaining a *meso*-carbethoxythiacyanine by addition of methyl iodide or ethyl iodide to the base, II (Z=S), was described in 1948.[7] The method of purification used for the corresponding thia-2'-cyanines (see section C) was applied here also, and the yields after recrystallisation were 25 % and 45 % respectively.[3]

The *meso*-substituted symmetrical thiacyanines, I (Y=Z=S, $R^1=R^2=Me$, $R^3=Me$ or Ph), were prepared by heating 2-methylthiobenzothiazole methomethylsulphate with propionic or phenylacetic anhydride, respectively, containing triethylamine, and precipitating with ether; the former dye was isolated as perchlorate and the latter as iodide.[12]

F. Selenacyanine

The *meso*-ethylselenacyanine, I (Y=Z=Se, $R^1=R^2=Me$, $R^3=Et$, $X=ClO_4$), was prepared from 2-methylthiobenzoselenazole methomethylsulphate, butyric anhydride, and triethylamine, followed by sodium perchlorate. Its absorption maximum was at 4680 Å.[12]

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CHAPTER IV

Symmetrical Trimethincyanines

1. From Certain Quaternary Salts, with Alkali

The colour of a trimethincyanine was first seen in 1887, when a mixture of the alkiodides of benzothiazole and 2-methylbenzothiazole was heated with ammonia.[1] Pyridine gave a better yield than ammonia and the purple dye was accompanied by a yellow one: the constitution of both was established in 1922, when it was proved that both nuclei of the purple dye were derived from the 2-methylbenzothiazole alkiodide and that the part played by benzothiazole alkiodide was to provide the central carbon atom of the three carbon chain (see I-3-D).[2] In a preparation of kryptocyanine by heating lepidine isopropyl halide in dilute solution with alkali,[3,4] the central carbon atom of the chain must arise by breakdown of the quaternary salt.

2. From a Quinolinium Salt, Having a Reactive Methyl Group, with Alkali and Formaldehyde

A. General

At the beginning of this century, an isocyanine preparation was carried out in the presence of formaldehyde: whereas heating a mixture of quinoline ethiodide and quinaldine ethiodide in alcohol with caustic alkali gave the purple colour of an isocyanine, formaldehyde led to a blue colour.[5] The blue dye was a sensitiser to red light and was known in Germany as Pinacyanol. In 1920 it was formulated[6] as I and its constitution was established (see I-3-C).[7] The quinolinium salt did not enter into the dye molecule[7,8] and its function may have been to take up the two hydrogen atoms, which, as in the 4′-cyanine condensation (see II-1-A) were eliminated as well as acid (equation 1). Addition of this salt was found to be of value, in certain instances, for increasing

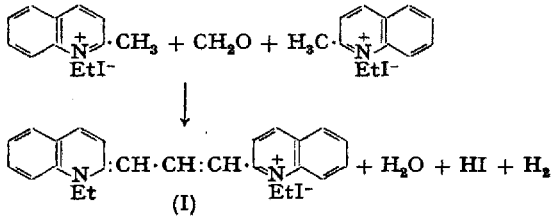
the yield.[6,7,9] The manufacturing process of the 1920's was to boil equimolecular quantities of quinoline alkiodide and quinaldine alkiodide in alcohol with formaldehyde (2·7 mols.) and sodium hydroxide (1·2 mols.); the dye crystallised and was recrystallised from methanol or ethanol:[6] this method gave at best a 21 % yield of pinacyanol. From a later study of the reaction, three conclusions were drawn[10] of which the last two need confirming: (a) potassium hydroxide gives better yields than does sodium hydroxide, (b) water is a better medium than alcohol, as it gives a higher yield of pure dye, (c) the yield of pure dye is not increased by use of quinoline ethiodide, provided that this salt and the alkali are proportionally increased (see section 5).

Whereas the absorption maximum of pinacyanol was at 6000 Å, the American kryptocyanine, prepared by the action of alkali and formaldehyde on a lepidinium alkyl halide, had its absorption maximum at 7000 Å. The corresponding sensitising maxima lay at slightly longer wavelengths, that of kryptocyanine being in the infrared.[3]

B. 2,2′-Carbocyanines

Patents were taken out for modifications in the method of producing the blue dye. Thus instead of alkyl halides of quinoline and quinaldine, alkyl sulphates and toluenesulphonates were proposed;[11] instead of sodium hydroxide, use of sodium sulphite was patented;[12] the part of formaldehyde could be played by glyoxylic acid, followed by oxidation.[13] The first modification is a useful one, as these salts are more soluble than iodides. In the early days, before it was realised that variations in the quinolinium salt did not affect the nature of the product, various pairs of quinolinium and quinaldinium salts were heated with alcohol, alkali, and formaldehyde; from such preparations there emerged pinacyanol analogues having 6,6′-dimethyl-[14] and 6,6′-bis-dimethylamino-groups.[15] When the constitution of pinacyanol was understood, various derivatives were prepared, with the object of correlating structure and sensitising action. The published wedge spectograms included those for I and the corresponding bromide; also I containing the groups 6,6′-dimethyl, 6,6′-diethyl, 6,6′-dibromo-, 5,5′-(or 7,7′-)dibromo-, 6,6′-diacetamino-, 6,6′-diamino-, 6,6′-diethoxy-, 5,5′-diethoxy-, or 6,7,6′,7′-dimethylenedioxy-; also the *NN*′-dimethyl-analogue of I and the corresponding chloride, the 6,6′-dimethyl-*NN*′-di-n-propyl analogue, and the 6,6′-dimethyl-*NN*′-di-n-butyl analogue.

In the 6,6′-dimethyl series, the sensitisation decreased as the size of the *NN′*-dialkyl groups increased, with the striking exception that the *NN′*-dimethyl dye was the weakest sensitiser of the series. 5,5′-Disubstitution depressed sensitisation.[6] The 5,5′-, 6,6′-, and 7,7′-diethoxy-derivatives of I each showed double-banded absorption and, at a



(I) (1)

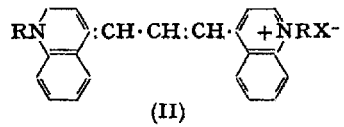
somewhat longer wavelength, there were two sensitising maxima; the extra-sensitisation induced by the 5,5′-isomeride was the least extensive.[16] Introduction of 5,5′- (or 7,7′-) or 6,6′-dibromo-groups into I caused a bathochromic shift of the sensitising maximum, with decrease of sensitising action.[17] The 5,6,5′,6′-dibenzo-derivative of I was prepared and converted into the more soluble nitrate; the principal sensitising maximum of this so-called Naphthacyanole was in the deep red at 6900 Å.[18]

A British Pinacyanol was called Sensitol Red and an analogue Sensitol Violet. Other German dyes of this type were Pinachrome and Pinachrome Blue; the name Quinaldine Blue was also used. I is 1,1′-diethyl-2,2′-carbocyanine iodide or [bis-2-(1-ethylquinoline)]trimethincyanine iodide.

C. 4,4′-Carbocyanines

An infrared sensitiser, kryptocyanine, was prepared in 9 % yield by heating a lepidinium alkyl halide with alkali and formaldehyde.[3,4] By using for sensitising only one-twentieth of the amount suitable for pinacyanol, kryptocyanine gave excellent results without fogging; the maximum was at 7600 Å.[18] It was proved in 1923 that such dyes are 4,4′-trimethincyanines, II (see I-3-F).[19]

In Germany, II was known as Rubrocyanine.

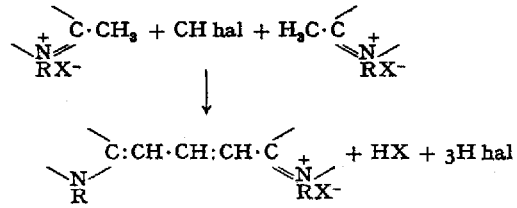


(II)

3. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Alkali and Trihalogenomethane

A. General

At the beginning of the century, a patented modification of the second method for preparing blue dyes (see section 2-A) consisted in replacing formaldehyde by a trihalogenomethane.[20] Thirteen years later, the method was applied to the synthesis of kryptocyanines.[3,4] In 1929 it was applied to the first synthesis of 2,2′- and 4,4′-pyridocarbocyanines[21] and in 1937 to a synthesis of symmetrical trimethincyanines of the benzimidazole series,[22] none of which types had been prepared by the ethyl orthoformate method (see section 6). Indocarbocyanines were obtainable from a 2-methylindolenine quaternary salt



(2)

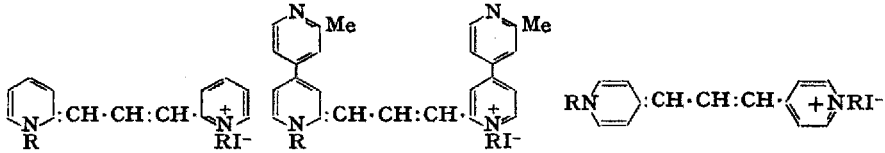
by use of iodoform, bromoform, or even chloroform, in acetic anhydride in the presence of sodium acetate.[23] In the method involving the use of trihalogenomethane, four mols. of acid are eliminated, as in equation 2.

B. 2,2′- and 4,4′-Carbocyanines

In the original patent, chloroform was added to a mixture of quinoline ethiodide and quinaldine ethiodide in alcohol, followed by 15 % sodium hydroxide solution;[20] in this straightforward reaction for preparing 2,2′-carbocyanines, the quinolinium salt is superfluous. The dimethyl-analogue of I was prepared by interaction of iodoform and the methylene base derived from a 1-methylquinaldinium salt;[24,25] similarly, the 4,4′-diphenyl derivative of this dye was obtained in 35 % yield by use of iodoform, but with chloroform the yield was lower.[25] In preparing a 4,4′-carbocyanine, a solution of lepidine methiodide in ethanol was boiled, then treated with chloroform and sodium ethoxide.[4]

C. 2,2′-Pyridocarbocyanines

The pyridocarbocyanines were decolorised by mineral acid and very sensitive to light; their sensitising action was weaker than that of Ethyl Red or Pinacyanol. To prepare III (R=Me), a boiling concentrated alcoholic solution of 2-picoline methiodide was treated with 20% alcoholic potassium hydroxide solution and then with chloroform, whereupon violent reaction occurred and a red colour developed. After some minutes' boiling, water was added to remove inorganic salts. The residue was purified with acetone and repeatedly recrystallised from water or alcohol. The corresponding picrate and bromide were made, also III (R=Et), and the 6,6′-diphenyl derivative of III (R=Me).[21]



(III) (IV) (V)

III (R=Me) is 1,1′-dimethyl-2,2′-pyridocarbocyanine iodide, or bis-[2-(1-methylpyridine)]trimethincyanine iodide.

By boiling 2,2′-dimethyl-4,4′-bipyridine alkiodide with chloroform and potassium hydroxide in ethanol, there were prepared IV (R = Me or Et), which had absorption maxima at 6060 Å and 6110 Å, respectively.[26]

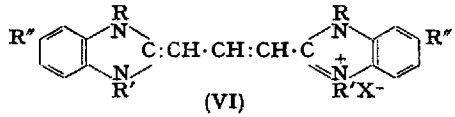
D. 4,4′-Pyridocarbocyanines

V (R=Me) was prepared by heating together 4-picoline methiodide, alcoholic potassium hydroxide, and chloroform, and was repeatedly recrystallised from methanol; the corresponding picrate was made.[21] V (R=Me) is 1,1′-dimethyl-4,4′-pyridocarbocyanine iodide, or bis-[4-(1-methylpyridine)]trimethincyanine iodide.

E. Benzimidazolocarbocyanines

Benzimidazolocarbocyanines, both symmetrical and unsymmetrical (see V-8-A), having substituted nuclei, were valuable orthochromatic sensitisers, with sensitising curves which fell away steeply at the long wavelength side. To prepare VI (R=R′=Et, R″=OEt, X=ClO_4), a mixture of 5-ethoxy-1,3-diethyl-2-methylbenzimidazo-

lium iodide and iodoform in methanol at 40° was treated with sodium methoxide; after boiling, the yellowish red solution was treated with sodium perchlorate.[22]

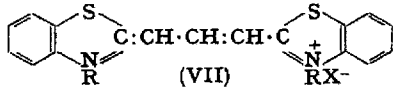


(VI)

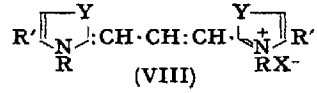
VI (R=R′=Et, R″=Me, X=ClO_4) is 1,3,1′,3′-tetraethyl-5,5′-dimethylbenzimidazolocarbocyanine perchlorate, or bis-[2-(1,3-diethyl-5-methylbenzimidazole)]trimethincyanine perchlorate.

4. From a Quaternary Salt, Having a Reactive Methyl Group, with a Disulphide in Pyridine, for 2,2′-, 4,4′-, Thia-, and Thiazolo-carbocyanines

It was discovered in 1923 (see I-3-E) that when di-[*o*-*N*-(alkylformanilido)] disulphide was heated in pyridine with a heterocyclic quaternary salt, having a reactive methyl group, it provided the central carbon atom of the chain of a trimethincyanine;[19] a second function was to provide the benzothiazole nucleus of a methincyanine (see II-6-C). Thus reaction with quinaldine ethonitrate, lepidine ethonitrate, and 2-methylbenzothiazole ethiodide, respectively, led to the 2,2′-carbocyanine, I, the 4,4′-carbocyanine, II (R=Et, X=I), and the thiacarbocyanine, VII (R=Et, X=I) (see I-3-E and F).[19] Reaction with 2-methyl-4-phenylthiazole methiodide led to the thiazolocarbocyanine, VIII (Y=S, R=Me, R′=Ph). With 2-picoline ethonitrate only the methincyanine was isolated (see II-6-C).[19]



(VII)

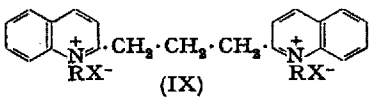


(VIII)

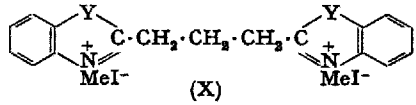
5. From Quaternary Salts of Diheterocyclyl-1,3-propanes, with Alkali, etc., for 2,2′-, Thia-, and Oxa-carbocyanines

When the constitution of pinacyanol was established as I, the unknown diethiodide, IX (R=Et, X=I), was postulated as a possible intermediate in the formaldehyde method of preparation (see

section 2).[7] Subsequently various methylenediquinaldine dialkylhalides, IX, were prepared by heating an alcoholic solution of quinaldine alkylhalide with formaldehyde, with piperidine as catalyst. Boiling an alcoholic solution of the dimethiodide, IX (R=Me, X=I) (1 mol.), with sodium ethoxide (3 mols.) gave only a 4 % yield of 2,2'-carbocyanine but if quinoline ethiodide (2 mols.) was amongst the reactants, the yield was 42 %. Similarly I was prepared from the diethiodide, IX (R=Et, X=I), and quinoline methiodide in 47 % yield, and its 6,6'-dimethyl derivative was obtained in 38 % yield. Although the function of the quinolinium salt must be the removal of two hydrogen atoms from the chain of IX, no oxidising agent was found to take its place.[27] However a different result was obtained in the benzothiazole series, where 1,3-di-2-benzothiazolylpropane was prepared by heating together *o*-aminothiophenol and glutaric acid at 165–170° for 12 hours, and was converted into the dimethiodide, X (Y=S), by heating with



(IX)



(X)

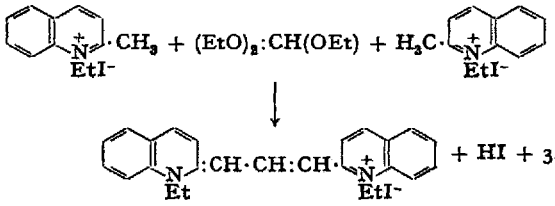
methyl sulphate, followed by potassium iodide; by treatment of an alcoholic solution of the dimethiodide with sodium hydroxide, followed by potassium ferricyanide, there was obtained a 70 % yield of pure thiacarbocyanine, VII (R=Me). From the dimethiodide, X (Y=O), there was similarly obtained a 17 % yield of oxacarbocyanine. Although from *o*-phenylenediamine and glutaric acid there was prepared a 1,3-disubstituted propane of the benzimidazole series and it was converted into the dimethiodide, X (Y=NH), this could not be converted into the corresponding carbocyanine.[28]

6. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of Ethyl Orthoformate

A. General

In 1922 the structure which had been established for pinacyanol[7] was supported by a synthesis from quinaldine ethiodide, acetic anhydride, and ethyl orthoformate (equation 3).[29] Two years later the new indocarbocyanine, XI (R=R'=Me, X=I), was similarly pre-

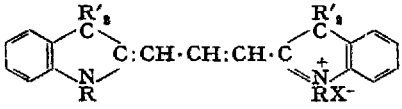
pared from 2,3,3-trimethylindolenine methiodide.[30] In 1925 the thiacarbocyanine, VII (R=Me, X=Br), was obtained by condensing 2-methylbenzothiazole methobromide with ethyl orthoformate in nitrobenzene: it was mentioned that acetic anhydride or pyridine might



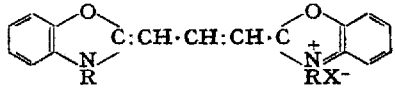
(3)

(I)

be used instead. At the same date the unknown oxacarbocyanines, XII (R=Me, X=I or SO_4Me), were synthesised by use of ethyl ortho, formate and acetic anhydride. For preparing VII (R=Me, X=Br)-sodium formate was said to be as good as ethyl orthoformate;[31] it was applied to the preparation of XI (R=R'=Me, X=I) and was said to have the advantage of enabling the reaction to be carried out at a

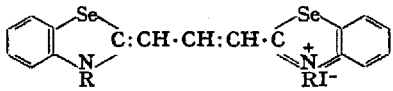


(XI)



(XII)

lower temperature.[32] The preparation of 2,2'-, 4,4'-, indo-, oxa-, and thia-carbocyanines by heating a quaternary salt with ethyl orthoformate and a suitable reagent in acid or neutral solution was patented: examples of such reagents were acetic anhydride, zinc chloride, nitrobenzene, and carbon tetrachloride.[23] In 1927, however, it was pointed out that the equation suggests that a basic solvent would be particularly suitable; anhydrous pyridine was used in conjunction with about four times the calculated amount of ethyl orthoformate in the preparation of 2,2'-, 4,4'-, thia-, oxa-, and indo-carbocyanines.[33] Subsequently this modification of the method was applied to the synthesis of the first selenacarbocyanines, XIII (R=Me or Et).[34] The pyridine



(XIII)

method has found widespread application, as indicated in the sections below, and it is indeed noteworthy when a solvent other than pyridine is proved preferable. It was for instance recorded that with indocarbocyanine an equally good yield was obtained with acetic anhydride or pyridine.[33] Benzimidazolocarbocyanines, VI (section 3-E, 6-F, and 13-F), could be prepared by the ethyl orthoformate method only when nitrobenzene was the medium.[35] It has been said that pyridine is inferior to such media as ethyl benzoylacetate, benzoylacetone, or ethyl benzoate, of the general formulae ArCOR or $ArCOCH_2COR$, as these media allow higher temperatures and shorter times of heating,[36] but no yields were quoted in support of the statement. Again, it has been claimed that in the preparation of oxa- and thia-carbocyanines, it is cheaper to replace pyridine by a slight excess of triethylamine in n-propanol and that this leads to a purer product in higher yield.[37] In preparing a couple of 2,2′-carbocyanines from quinaldine alkiodide and ethyl orthoformate, media such as 2-aminothiazole, formanilide, diphenylmethane, phenylacetonitrile, ethyl cyanoacetate, pyrocatechol, ethyleneglycol, and ammonium chloride were used;[38,39] these seem remarkable only for their diversity.

B. 2,2′-Carbocyanines

On boiling a solution of quinaldine ethiodide in acetic anhydride and gradually adding ethyl orthoformate, the yellow liquid became green and finally deep blue, and dye began to crystallise. Half the solvent was distilled off and the dye, I, was filtered off and recrystallised. Its dimethyl analogue was similarly prepared.[29] The yields, however, were not confirmed.[40] According to the modified method, quinaldine ethiodide (5 g.), ethyl orthoformate (5·5 c.c.), and pyridine (20 c.c.) were boiled under reflux for 3 hours: the 78 % yield dropped to 70 % on recrystallisation from dilute alcohol. The 6,6′-dimethyl derivative of the *NN*′-diallyl analogue was obtained in 71 % yield and the corresponding bromide in 79 % yield.[33] A 34 % yield of the 3,4,3′,4′-dibenzo-derivative of I was prepared by heating 2-methylphenanthridine ethotoluene-*p*-sulphonate with ethyl orthoformate and pyridine for 1·5 hours, converting into iodide, and recrystallising. Its absorption maximum lay at a shorter wavelength than that of the corresponding 5,6,5′,6′-dibenzo-derivative (see section 2-B). It did not sensitise.[41] After boiling 6-nitroquinaldine ethiodide with ethyl orthoformate in pyridine

for 40 minutes, the crude dye iodide was converted, in 33 % yield, to the 6,6′-dinitro-derivative of the chloride corresponding with I; after two recrystallisations the yield was 14 %.[42] Six symmetrical 2,2′-carbocyanines, having 5,5′- or 6,6′-dinitro-, 5,5′- or 6,6′-di(acetylamino)-, 5,5′-di(benzoylamino)-, and 6,6′-bis(dimethylamino)-groups, respectively, were prepared by heating a quinaldinium salt with ethyl orthoformate and pyridine. Ethotoluene-*p*-sulphonates were used for the first five preparations and the first two dyes were isolated as such, the third as perchlorate, and the rest as iodides; times of heating varied from 40–120 minutes, and yields from 12–27 %. By heating the 6,6′-di(acetylamino)-compound with concentrated hydrochloric acid, the corresponding 6,6′-diamino-dye resulted; after treatment with potassium iodide and recrystallisation, the yield was 43 %.[43]

C. 4,4′-Carbocyanines

By heating lepidine alkiodide with ethyl orthoformate and pyridine, three 4,4′-carbocyanines were prepared, namely II (R=Me, Et, or Allyl, X=I). In thus making II (R=Et), the reaction mixture was cooled and filtered to remove a less soluble by-product (see XV-3-A). On adding water to the filtrate, the 4,4′-carbocyanine resulted in 56 % yield; on recrystallisation from alcohol (67 c.c. per g.) the yield was 42 %.[33] The method was applied to the preparation of II (R=Et, X=I) having substituents such as 6,6′-dimethyl-, 6,6′-diethoxy-, or 7,8,7′,8′-dibenzo-, and these dyes were recorded as sensitising better than the parent dye, and with lower fog values.[44]

D. Indocarbocyanines

The first indocarbocyanine, XI (R=R′=Me, X=I), was prepared in 65 % yield by heating together 2,3,3-trimethylindolenine methiodide (4 g.), ethyl orthoformate (1·8 g.), and acetic anhydride (40 g.) for 0·5 hour. The dye was stable to alkali and also very stable to acids. Like cyanine, it had narrow absorption bands but, unlike cyanine, it was stable to light. It was only slowly decolorised by prolonged boiling with tin and hydrochloric acid. Its 5,5′-dichloro-derivative was also made.[30] By use of ethyl orthoformate in pyridine, the same yield of this dye was obtained; also XI (R=Et, R′=Me, X=I) was prepared, in 75 % yield after recrystallisation from dilute alcohol

acidified with hydriodic acid. Both were observed to be photographic sensitisers.[33] Indocarbocyanines having substituted amino-groups, such as 4,4′-bis(diethylamino)-, were prepared by the pyridine method and described as strong sensitisers to red light.[45] Acetic anhydride was the medium used in preparing indocarbocyanine methiodides having in the 3,3- and 3′,3′-positions the groups Et_2, EtMe, and MePh, and the ethiodide with Et_2. These groups had a bathochromic effect, which was greater the heavier the group.[46]

XI (R=R′=Me, X=I) was known as Indolenine Red.[47] As Astraphloxine FF it was described as dyeing a marvellous shade.[48] It may be called 1,3,3,1′,3′,3′-hexamethylindocarbocyanine iodide, or [bis-2-(1,3,3-trimethylindolenine)]trimethincyanine iodide.

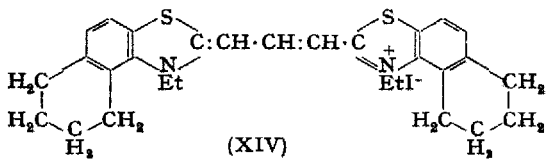
From alkiodides of 3-cyclohexanespirane-2-methylindolenine, by heating with ethyl orthoformate in pyridine, there were prepared XI (R=Me or Et, $R'_2=C_5H_{10}$) (see XIII-1-D).[49]

E. Thia-, Oxa-, and Selena-Carbocyanines

In preparing the thiacarbocyanine, VII (R=Me, X=Br), an 85 % yield was recorded by use of ethyl orthoformate in nitrobenzene.[31] The corresponding iodide was prepared by boiling together 2-methyl benzothiazole methiodide (4 g.), pyridine (40 c.c.), and ethyl orthoformate (4·6 c.c.) for an hour. The product, obtained in 95 % yield, gave a 74 % yield on recrystallisation from dilute alcohol. The diethyl analogue was similarly prepared, also VII (R=allyl, X=Br).[35] Thiacarbocyanines, VII (R=Me), having 5,5′-dichloro- or -dimethoxy-, 6,6′-dichloro- or -dibromo-, and 6,6′-dichloro-4,4′-dimethyl substituents, were prepared, with acetic anhydride as medium. It was recorded, on the one hand, that introduction of 6,6′-dichloro-, 6,6′-dibromo-, and 5,5′-dimethoxy-groups into VII (R=Me) caused bathochromic shifts of 170 Å, 160 Å, and 700 Å, respectively,[50] but, on the other hand, that with VII (R=Et) introduction of 6,6′-dichloro- or -dibromo-substituents did not affect the absorption maximum.[51] For comparison with *meso*-substituted thiacarbocyanines (see VI-3-A), there were prepared VII (R=Pr^n, Bu^n, or allyl).[52] Thiacarbocyanines having 6,6′-dimethyl or 6,6′-diethoxy-substituents were prepared and their absorption maxima compared with that of the unsubstituted dye.[53] As in other series (see II-1-D, 2-F, 3-C and D), so also here, improved sensitising by introducing substituted amino-,[54,55] alkylthio-, or alkylseleno-groups was

claimed.[56] In contradiction to this was the observation that the introduction of 6,6′-dimethylthio-groups into VII (R=Et, X=I) did not increase the sensitising action; nor did it increase the stabilising action, although the anti-fogging effect of other compounds havi g loosely bound sulphur was known. The dye was obtained in 75 % yield by the ethyl orthoformate and pyridine method.[57] Symmetrical thiacarbocyanines having two 4,5- or two 6,7-benzo-groups had their absorption maxima 350–400 Å and their sensitising maxima 500–600 Å nearer to the red than had the unsubstituted dyes; whereas the two new ethiodides were powerful sensitisers, the two new methiodides sensitised only feebly.[58] These photographic sensitisers were conveniently prepared by boiling a 2-methyl-4,5- (or 6,7-)benzobenzothiazole alkotoluene-*p*-sulphonate with pyridine and ethyl orthoformate for 2 hours, then treating with aqueous ammonium bromide solution.[59] Whereas these dibenzo-dyes sensitised to red light more powerfully than did the parent dye, they sensitised less strongly to green light.[60] The absorption maxima of thiacarbocyanines having two 5,6-benzobenzothiazole nuclei lay at a shorter wavelength than those of the corresponding dyes having two 4,5- or two 6,7-benzobenzothiazole nuclei, so also with the sensitising maxima.[61] Heating thiacarbocyanines with concentrated or fuming sulphuric acid made them water-soluble, so that they could be used as filter dyes.[62] A gap in the green in the sensitising curve of thiacarbocyanines was induced by the presence of 7,7′-dialkyl or -dialkoxy-groups, and such dyes were useful for colour photography.[63] When 4,4′- or 5,5′-dimethyl groups were introduced into VII (R=Et, X=I), the sensitisation was unaffected by their position; the bathochromic shift of the absorption maximum was slightly greater (by 20 Å) for 5,5′-substitution than for 4,4′- or 6,6′-substitution.[64] The 6,6′-dinitro-derivative of the chloride corresponding with VII was prepared, in 8 % yield after three recrystallisations, by boiling 2-methyl-6-nitrobenzothiazole ethochloride with ethyl orthoformate in acetic anhydride for 15 minutes.[42] The 5,5′-dinitro-derivative of the bromide corresponding with VII resulted, in 3 % yield, by boiling 2-methyl-5-nitrobenzothiazole ethotoluene-*p*-sulphonate with ethyl orthoformate in pyridine for 30 minutes, converting into bromide, and recrystallising.[65] As compared with the parent dye, VII, the 6,6′-dinitro-derivative had the absorption maximum of its methanolic solution at a longer wavelength by 260 Å,[42] whilst that of the 5,5′-dinitro-derivative was at a shorter wavelength by 15 Å than that of

the parent dye.[65] Symmetrical thiacarbocyanines having 4,5,6,7-tetrahydrobenzothiazole nuclei sensitised strongly and cleanly; the octahydro-derivative of VII (R=Et, X=I) was obtained in 8 % yield.[66] The 6,6'-dimethoxy-derivative of VII (R=Et, X=I) was prepared starting from 6-methoxy-2-methylbenzothiazole ethotoluene-*p*-sulphonate; by heating the dye with hydrobromic acid in a sealed tube at 120–130° for 5 hours, it gave a 21 % yield of 6,6'-dihydroxy-dye iodide and this, by heating with acetic anhydride, gave the 6,6'-diacetoxy-dye.[67] The method was applied to the preparation of thirteen new symmetrical thiacarbocyanines having electronegative substituents in the 6,6'-positions, such as sulphamino-, cyano-, carbethoxy-, and nitro- (see XVI-5-A-3).[68] Thiacarbocyanines having methoxy-groups in the 4,4'-, 5,5'-, 6,6'-, or 7,7'-positions were prepared by boiling methoxy-2-methylbenzothiazole ethotoluene-*p*-sulphonate with ethyl orthoformate in pyridine for 30–60 minutes, precipitating with ether, dissolving the dye in methanol, and treating with aqueous potassium iodide. Before recrystallisation, the yields were 62 %, 51 %, 76 %, and 65 %, respectively.[69] By condensing 2-methyl-4,5-tetramethylenebenzothiazole ethotoluene-*p*-sulphonate with ethyl orthoformate in pyridine, a 21 % yield of the dye iodide, XIV, was attained and the absorption



(XIV)

of this dye was compared with that of VII (R=Et) and of the 4,5,4',5'-dibenzo-derivative of VII (R=Et) (see XVI-5-A, 3).[70] It was more soluble than the latter.[70] Thiacarbocyanines having 4,4'-, 6,6'-, and 7,7'-dihydroxy-groups were also prepared by this method, the yields of recrystallised dyes being 13 %, 20 %, and 9 %, respectively. The last two were also prepared, in yields of 21 % and 34 %, respectively, by heating the corresponding dimethoxy-dyes with hydrobromic acid in sealed tubes. 4,4'-, 5,5'-, and 6,6'-diacetoxy-derivatives were prepared by the ethyl orthoformate and pyridine method, in yields of 13 %, 24 %, and 40 %, respectively: the 5,5'-dihydroxythiacarbocyanine was reached by saponification of the 5,5'-diacetoxy-derivative.[71] By use of ethyl orthoformate and pyridine, the 6,6'-di(acetylamino)- and 6,6-'

di(methylsulphamino)-derivatives of VII (R=Et, X=Br) were prepared in yields of 79 % and 49 %, respectively; by heating the toluene-*p*-sulphonate of the former with 25 % hydrochloric acid, followed by potassium iodide, the 6,6'-diamino-derivative of VII (R=Et, X=I) was obtained, and it was converted, by boiling with anhydrous formic acid, into the 6,6'-di(formylamino)-derivative (see XVI-5-A, 3).[72] 7,7'-Bis(dimethylamino)thiacarbocyanines were prepared from 7-dimethylamino-2-methylbenzothiazole methiodide, or its metho- or ethotoluene-*p*-sulphonate, and proved rather weak sensitisers.[73] The present method was applied to the synthesis of twenty-three tetramethylthiacarbocyanines[74] and eight tetramethoxythiacarbocyanines.[75] Four thiacarbocyanines having di(acetylamino)-groups were prepared, in 12–21 % yield, and hydrolysed to the diamino-analogues by boiling with 20 % sulphuric acid for 20–30 minutes. Thiacarbocyanines having di(tertiary butyl) groups were prepared in 44 % and 47 % yields. For obtaining four thiacarbocyanines having bis(dimethylamino)-groups, amino-2-methylbenzothiazole was heated with methyl sulphate at 100–110° for 4 hours, whereby methylation occurred as well as quaternary salt formation. After boiling with ethyl orthoformate and pyridine for 20 minutes, the solvent was distilled off and the residue was several times subjected to chromatography in order to isolate the dyes.[76] The 5,5'-diethyl derivative of VII (R=Me) and its 5,5'-diethyl-6,6'-dinitro-derivative, the former as iodide, the latter as methylsulphate, were obtained in yields of 50 % and 30 %, respectively, after washing. The 6,6'-dimethyl derivative of VII (R=Et) and its 5,5'-di(tertiary butyl)-6,6'-dinitro-derivative, both as toluene-*p*-sulphonates, were obtained in yields of 47 % and 69 %, respectively, after recrystallisation.[77] The observation that highly electronegative groups, such as 5,5'-dicarboxy-, increased sensitisation was surprising, but this was specific for substitution in those positions and did not occur in the 6,6'-positions.[78] Introduction of 5,5'-dicarbalkoxy-groups gave dyes which, unlike the parent dye VII, showed a sensitising gap in the green and were therefore useful for certain multi-layer photographic processes.[79] Symmetrical thiacarbocyanines having unsaturated groups, such as styryl, *p*-methoxystyryl, or *β*-thienylvinyl, in the 6,6'-positions were synthesised.[80] The dye, VII (R=Et), has been called Thiazole Purple.

The first oxacarbocyanine, XII (R=Me, X=I), was prepared by heating the methiodide or methomethylsulphate of 2-methyl-

benzoxazole with ethyl orthoformate and acetic anhydride for 5 minutes, and was recrystallised from chloroform or acetic anhydride. The name Oxazole Yellow indicates its colour.[81] By boiling 2-methylbenzoxazole methiodide (2 g.), ethyl orthoformate (3 c.c.), and pyridine (20 c.c.) for an hour, the dye was produced in 57 % yield, dropping to 40 % on recrystallisation from ethanol; with acetic anhydride as medium, the yield was only half as great. XII (R=Et, X=I) was similarly prepared by use of pyridine, and was recrystallised from pyridine. These dyes were found to be photographic sensitisers.[83] Certain substituted oxacarbocyanines sensitised more strongly and at a longer wavelength.[81] Those having 5,6,5',6'-dibenzo-groups were described as excellent sensitisers;[82] those with 4,5,4',5'- or 6,7,6',7'-dibenzo-groups were sensitisers to yellow-green light.[83] Oxacarbocyanines, XII (R=Me, X=I), having 5,5'- and 7,7'-diphenyl groups were obtained in practically theoretical yield by boiling the methiodide with ethyl orthoformate in pyridine for only 5 minutes. The 5,5'-diphenyl derivative showed a weakly bathochromic effect on absorption and sensitisation, but the 7,7'-disubstituted dye was very unstable.[84] Symmetrical oxacarbocyanines with branched-chain alkyl groups, such as $\cdot CMe_2Ph$ or $\cdot CMe_3$ in the 5,5'-positions, showed a steep cut-off of the sensitising curve.[85] 5,5'-Dibenzoyloxacarbocyanines[86] and those having 5,5'-dicarbalkoxy-groups[87] were claimed to give an extra range of sensitising.

The deep purple selenacarbocyanines, XIII (R=Me or Et), were prepared by boiling 2-methylbenzoselenazole alkiodide with ethyl orthoformate and pyridine for an hour, pouring the reaction mixture into water, and recrystallising from ethanol: the diethyl dye was far more soluble than the dimethyl dye. Both were photographic sensitisers.[34] Sensitising was improved by the introduction of substituents such as methyl, methoxy-, ethoxy-, acetylamino-, dimethylamino-, or halogeno-.[88]

F. Benzimidazolocarbocyanines

Only by use of nitrobenzene as medium, could quaternary salts of 2-methylbenzimidazole be condensed with ethyl orthoformate: the yields were better than by the iodoform method (see section 3-E). The benzimidazolocarbocyanines, VI (R=R'=Et, R''=H, X=I; R=Et, R'=benzyl, R''=H, X=Br; and R=Ph, R'=Et, R''=H, X=I) were made (see section 10).[35]

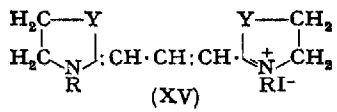
G. Thiazolo-, Oxazolo-, Thiazolino-, and Selenazolino-carbocyanines

Thiazolocarbocyanines, VIII (Y=S, R=R'=Me, X=I; and Y=S, R=Et, R'=Me, X=I), were prepared in 14 % and 27 % yields, respectively. Their absorption maxima lay only 100 Å nearer the blue end of the spectrum than did that of the thiacarbocyanine, VII, and their sensitising curves were very like that of the thiacarbocyanine.[89] Sensitisation by thiazolocarbocyanines was patented.[90] In preparing such dyes from a 2-methylthiazolium alkotoluene-*p*-sulphonate, with ethyl orthoformate and pyridine, it was noted that each was accompanied by another dye (see XV-3).[91]

2-Methyl-4-(phthalimidomethyl)thiazole was synthesised in 1952. By heating its ethiodide with ethyl orthoformate in pyridine there resulted VIII (Y=S, R=Et, R'=$C_9H_6O_2N$, X=I), with its absorption maximum at 5450 Å.[92] Five symmetrical thiazolocarbocyanines, VIII (Y=S, R=Me, R'=Ph, *p*-$C_6H_4NO_2$, *p*-C_6H_4OMe, *p*-C_6H_4OEt, or *p*-C_6H_4Br, X=I), were also described.[93] Three 4,4'-diarylthiazolocarbocyanines all showed their maximum absorption at 5600 Å, whether the aryl groups were α-$C_{10}H_7$, *p*-C_6H_4Ph or $C_{12}H_9$, but with β-naphthyl, *p*-biphenylyl, or 5-acenaphthyl groups in the 5,5'-positions the maxima were 6100 Å, 6080 Å, and 6060 Å, respectively. The corresponding 4,5,4',5'-tetra-arylthiazolocarbocyanines were also described,[94] and other thiazolocarbocyanines with 5,5'-di-(methoxyaryl)[95] or 5,5'-di-(α- or β-naphthyl) substituents.[96] The 4,4'-diaminothiazolocarbocyanines, VIII (Y=S, R=Me or Et, R'=NH_2, X=I), had their absorption maxima at 5160 Å and 5260 Å, respectively (see V-6-K and 7-C).[97]

Oxazolocarbocyanines with 5,5'-diphenyl, 5,5'-di-α-naphthyl, and 5,5'-di-β-naphthyl groups, had their absorption maxima at 5000 Å, 5420 Å, and 5580 Å respectively.[96]

Thiazolinocarbocyanines were discovered independently in Japan (see V-6-K)[98] and in America.[99] According to the latter process, XV



(XV)

(Y=S, R=Me or Et) were prepared, in 57 % and 58 % yields, respectively, by boiling 2-methylthiazoline methotoluene-*p*-sulphonate or its ethiodide for 2 hours with ethyl orthoformate and pyridine.[99,100]

TABLE I. Some Properties of Symmetrical Trimethincyanines

Nature of carbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
2,2′-	I	pleochroic green needles	287–288	6050 (and 5650)	6350	7000	6, 27, 102, 103
5,6,5′,6′-dibenzo-derivative	—	green needles	—	6350	6900	7300	18, 102
3,4,3′,4′-dibenzo-derivative	—	dark greenish	234–235	6125	—	—	41
4,4′-	II (R=Et, X=I)	prisms, golden and green lustre	253–254	7040	7600	8000	18, 19, 102
benzimidazolo-	VI (R=R′=Me, R″=H, X=I)	—	303	—	5300	—	104
indo-	XI (R=Et, R′=Me, X=I)	pleochroic, olive-green, steel-blue	260–263	5450	5800	6200	27, 33, 102
thia-	VII (R=Et, X=I)	steel-blue prisms	269	5570	5900 (and 5330)	6600	2, 102
4,5,4′,5′-dibenzo-derivative	—	green and gold	263	5970	6400	7200	57, 102
5,6,5′,6′-dibenzo-derivative	—	—	—	5700	6100	6400	63

(Table continued)

TABLE I *(continued)*

Nature of carbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
6,7,6′,7′-dibenzo-derivative	—	steely	294	5930	6350	6900	58, 102
oxa-	XII (R=Et, X=I)	red; blue reflex	277–279	4850	5150	5600	27, 33, 102
4,5,4′,5′-dibenzo-derivative[a]	—	reddish needles	—	5130	5550	6000	81, 102
5,6,5′,6′-dibenzo-derivative[b]	—	—	—	5080	5500	6100	82
6,7,6′,7′-dibenzo-derivative	—	garnet-red; blue reflex	—	5150	—	—	83, 102
selena-	XIII (R=Et)	dark green needles	270–271	5700	6200	6940	34, 102
2,2′-pyrido-	III (R=Et)	needles; green lustre	265	5650	—	—	21
4,4′-pyrido-	V (R=Me)	blue-green needles	226·5	6000	—	—	21
thiazolo-	VIII (Y=S, R=Et, R′=Me)	dark needles; greenish reflex	271–294	5500	5900 (and 5350)	6500	90, 98
thiazolino-	XV (Y=S, R=Et)	orange-brown needles; blue reflex	256–258	4435	4750	5200	100, 101
selenazolino-	XV (Y=Se, R=Et)	orange	—	—	4800	5400	101

[a] Bromide. [b] di-Me bromide.

The absorption maximum lay at a shorter wavelength than that of a thiazolocarbocyanine.

The selenazolinocarbocyanine, XV (Y=Se, R=Et), was prepared by heating 2-methylselenazoline ethiodide with pyridine and ethyl orthoformate: it was a sensitiser.[101]

Some properties of certain symmetrical carbocyanines are summarised in Table I.

Table II contains properties of some symmetrical thiazolo- and oxazolo-carbocyanines, which were prepared by a two-stage process (see V-7-C).[105, 106]

TABLE II. Some Properties of Symmetrical Thiazolo- and Oxazolo-carbocyanines (Formula VIII)

Y	X	R	R'	5,5'-Substituents	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum(Å)	Ref.
S	I	Et	Ph	Ph	gold threads	180[a]	5880	105
S	I	Et	*p*-$MeOC_6H_4$	Ph	purple threads	181	5900	105
S	I	Et	3,4-di$MeOC_6H_3$	Ph	green	179	5900	105
S	ClO_4	Et	*p*-xylyl	Ph	mauve powder	225	5920	105
S	ClO_4	Me	*p*-$MeOC_6H_4$	PhO	bronze powder	240	5800	105
S	I	Me	Ph	*p*-tolylthio-	bronze needles	224	5850	105
S	I	Et	β-naphthyl	*p*-tolylthio-	bronze	194	5850	105
O	ClO_4	Et	Ph	H	orange needles; purple reflex	226	4600	106
O	ClO_4	Et	H	Ph	crimson leaflets	221	5000	106
O	ClO_4	Et	H	*p*-$MeOC_6H_4$	orange	260	5100	106
O	ClO_4	Et	Ph	Ph	brown prisms; green reflex	242	5040	106
O	ClO_4	Et	*p*-$MeOC_6H_4$	Ph	orange-brown	220	5070	106
O	ClO_4	Et	3,4-di$MeOC_6H_3$	Ph	orange leaflets; gold reflex	237	5100	106

[a] Decomp. not recorded for thiazolocarbocyanines.

7. From a Base, Having a Reactive Methylene Group, with Formaldehyde or Formic Acid

When the indocarbocyanine, XI (R=R'=Me), was prepared by the ethyl orthoformate method (see section 6-D) in 1924, it was detected spectroscopically that the dye is also formed by the action of formaldehyde on 1,3,3-trialkyl-2-methyleneindoline, even without added alkali; as with the formation of pinacyanol (see section 2), so also here, oxidative elimination involving formaldehyde must take place.[30] When the methylene base, dissolved in alcohol, reacted with 38 % formaldehyde at 30–35°, a white crystalline product was formed and this, on exposure to air, gave a red dye.[107] So also, by heating the methylene base with formic acid and acetic anhydride, making alkaline, and treating the product with hydrochloric acid and sodium chloride, XI was produced; a dimethyl and a tetramethyl derivative were similarly made. The formic acid method, involving a methylene base, was recommended for the smooth preparation of 8,8'-disubstituted-2,2'-carbocyanines.[108]

8. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Ethyl Formimino Ether Hydrochloride

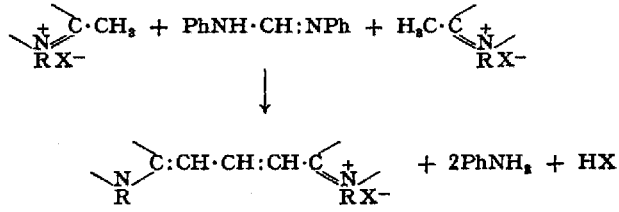
According to a process patented in 1929, compounds such as the hydrochloride of ethyl formimino ether, EtO·CH:NH, HCl, covered by the general formula, X·CH:NH, were applicable to the preparation of both unsymmetrical (see V-5) and symmetrical carbocyanines. In the examples given, this compound (> 1 mol.) was heated with 6-chloro-1-methyl-2-methylene-1,2-dihydroquinoline (2 mols.) in pyridine to give a 2,2'-carbocyanine chloride; also it was heated with 1,3,3-trimethyl-2-methyleneindoline, in pyridine or in acetic anhydride, followed by treatment with hydrochloric acid, to give an indocarbocyanine chloride.[109] No yields were quoted. The method has not been found useful.

9. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Diphenylformamidine

The importance of diphenylformamidine in cyanine chemistry was discovered in 1929 and lay in the fact that one mol. could be

condensed with one mol. of a heterocyclic quaternary ammonium salt, having a reactive methyl group, to give an intermediate compound: this could then be condensed with one mol. of another such salt to give a trimethincyanine in which the two nuclei were different.[110] A procedure, favoured in Japan, for preparing symmetrical trimethincyanines, consisted in carrying out such a two-stage reaction, but with the same quaternary salt at both stages[88,104,111] and it gave, for example, a quantitative yield of thiacarbocyanine, VII.[104] This is essentially the method considered in the next chapter (see V-6). In the present chapter we are concerned with a one-stage process, also described in 1929, according to which two mols. of quaternary salt are condensed with one of diphenylformamidine, to give a symmetrical trimethincyanine. Thus the 2,2′-carbocyanine, I, was prepared by heating together quinaldine ethiodide, diphenylformamidine, and anhydrous sodium acetate, in acetic anhydride; the thiacarbocyanine, VII (R=Et, X=I), was similarly prepared from 2-methylbenzothiazole ethiodide; the indocarbocyanine, XI (R=R′=Me, X=Cl), was prepared from 1,3,3-trimethyl-2-methyleneindoline, either by heating it with diphenylformamidine (or its hydrochloride) in acetic anhydride, or by fusion with diphenylformamidine hydrochloride, followed by treatment with hydrochloric acid. As a recommendation of the method, it was said that diphenylformamidine was cheaper and more accessible than ethyl orthoformate.[110] Nevertheless this one-stage method for preparing symmetrical trimethincyanines is definitely inferior to the ethyl orthoformate method. For instance, by heating together 2-methylbenzothiazole ethiodide, diphenylformamidine, and piperidine at 65°, the yield of recrystallised dye was only 20 %.[104] Apart from the original patent, the method has scarcely been used.

The net result of the reaction of a quaternary salt with diphenylformamidine is the elimination of two mols. of aniline and one of acid and may be indicated as in equation 4.



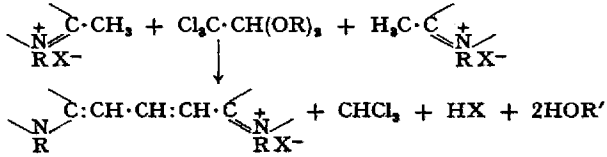
(4)

10. From a Quaternary Salt, Having a Reactive Methyl Group, with Chloral Hydrate, or Alcoholate, and Alkali, for Benzimidazolo-, 2,2′-, 4,4′-, and 2,2′-Pyrido-carbocyanines

It was recorded in 1933 that to prepare a trimethincyanine from 2,3-dimethylbenzimidazole methiodide neither the dianil method (section 9) nor the ethyl orthoformate method (section 6) was applicable. The then unknown benzimidazolocarbocyanine, VI (R=R′=Me, R″=H, X=I), was prepared in 13 % yield by heating the quaternary salt with chloral hydrate and sodium ethoxide in ethanol for 30 minutes, treating with water, and recrystallising from methanol. Its sensitising action was recorded.[104] Subsequently, in 1937, such dyes were prepared by use of iodoform and sodium alkoxide (section 3-E) and, in 1949, by the ethyl orthoformate method under special conditions (see section 6-F and 13-F). The original method, modified in that chloral alcoholate was used instead of chloral hydrate, was applied to the preparation of VI (R=R′=Et, R″=H, X=I), which resulted in 14 % yield.[65] In 1956 the modified method was applied to the preparation of benzimidazolocarbocyanines having one or two chlorine atoms in each nucleus. For instance, by heating 5-chloro-3-ethyl-2-methylbenzimidazole ethiodide (2 mols.), chloral alcoholate (1 mol.), and a solution of sodium (3 atoms) in ethanol for 30 minutes, and recrystallising from ethanol, there was obtained a 29 % yield of VI (R=R′=Et, R″=Cl, X=I), whilst 5,6-dichloro-3-ethyl-2-methylbenzimidazole ethiodide similarly gave a 32 % yield of the 5,6,5′,6′-tetrachloro-derivative. The dyes had sharp sensitising bands in the blue-green.[112]

The chloral hydrate method was also applied to the preparation of the 2,2′-carbocyanine, I, of the 4,4′-carbocyanine, II (R = Et, X = I), and of the 2,2′-pyridocarbocyanine, III (R=Me).[113]

The course of the reaction may be formulated as in equation 5.



(5)

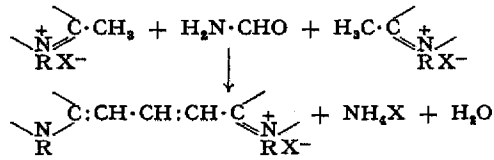
11. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of Ethyl Orthothioformate

When a quaternary salt, having a reactive methyl group, condenses with ethyl orthoformate to give a trimethincyanine, that dinuclear

dye may be accompanied by a trinuclear one (see XV-3-A). It was pointed out in 1937 that formation of the trinuclear dyes was favoured by use of an acidic medium and of ethyl orthothioformate, $CH(SEt)_3$. This reagent was therefore not recommended for the preparation of dinuclear carbocyanines. Thus when 2-methylbenzothiazole ethiodide was heated with it for an hour at 140°, in either pyridine or acetic anhydride solution, the yield of dye was slight; it is, however, interesting that with pyridine containing a little acetic anhydride (5 drops in 3 c.c.), the yield of thiacarbocyanine was 49 %. With the same mixed solvents, the yield of oxacarbocyanine was 31 %.[114]

12. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of Formamide, Thioformamide, or Thioformanilide

For this kind of synthesis, alkotoluene-*p*-sulphonates seemed best. By fusion of quinaldine ethotoluene-*p*-sulphonate and formamide at 160° for an hour, followed by treatment with potassium iodide, the 2,2′-carbocyanine, I, was prepared.[115] Subsequently quinaldine ethotoluene-*p*-sulphonate and formamide, on fusion for 4 hours at 130°, gave a 10 % yield of I. By heating 2-methylbenzothiazole ethotoluene-*p*-sulphonate and formamide at 130° for 2 hours, the thiacarbocyanine, VII (R=Et, X=I), resulted in 64 % yield, whilst its 6,7,6′,7′-dibenzo-derivative was obtained in 30 % yield by 4 hours' heating. Formamide was recommended for recrystallising the dyes, as they are more readily soluble in it than in the usual solvents. Dimethylformamide, but not acetamide, could also be used in this synthesis and, on 8 hours' heating with 2-methylbenzothiazole ethotoluene-*p*-sulphonate, led to a 49 % yield of VII (R=Et, X=I). Formamide was not applicable to the preparation of oxa-, indo-, benzimidazolo-, or selena-carbocyanines.[116] The reaction with formamide was reversible.[117] The synthesis must consist in elimination of water and ammonium salt, as indicated in equation 6.

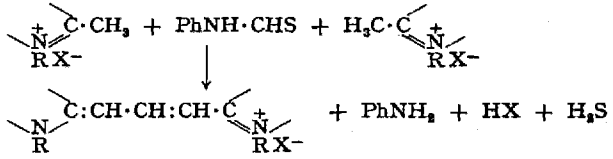


(6)

Thioformamide was more reactive than formamide and condensation was best induced by heating it and the salt with triethylamine, or

sodium ethoxide, in ethanol for 30 minutes; thus VII (R=Me, X=I) was prepared from 2-methylbenzothiazole methotoluene-*p*-sulphonate in 66 % yield.[115] Here hydrogen sulphide was eliminated instead of water.

Thioformanilide was still more reactive and pyridine was a suitable medium, or sodium acetate in acetic anhydride. I was prepared by heating together quinaldine ethiodide and thioformanilide in pyridine for an hour.[115] In this reaction aniline, acid, and hydrogen sulphide are removed (equation 7) (see V-11).

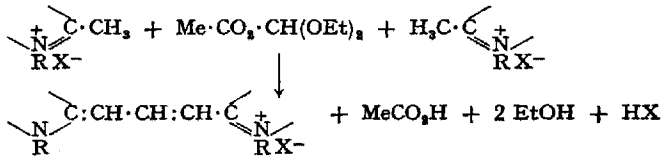


(7)

13. From a Quaternary Salt, Having a Reactive Methyl Group, with Diethoxymethyl Acetate

A. General

According to a method patented in 1951, the preparation of trimethincyanines, by condensing a quaternary heterocyclic ammonium salt (having a reactive methyl group) with diethoxymethyl acetate, was successful with salts with which ethyl orthoformate in pyridine failed: such were 2-picoline alkiodide and 1-methylisoquinoline alkiodide.[118] The course of the reaction is indicated in equation 8.



(8)

Trinuclear dyes were also formed (see XV-3-A).[118]

B. 2,2'- and 4,4'-Carbocyanines

The 7,7'-dihydroxy-derivative of the 2,2'-carbocyanine, I, was prepared by boiling 7-hydroxy-2-methylquinoline ethobromide and diethoxymethyl acetate in pyridine for an hour, precipitating with

ether, and treating with sodium iodide in methanolic acetic acid. The 7,7′-dihydroxy-derivative of the dimethyl analogue of I was similarly made. They were purified by dissolving in alcoholic sodium hydroxide solution and precipitating with acetic acid.

The 6,6′-dihydroxy-derivative of the 4,4′-carbocyanine, II (X=Br), was prepared from 6-hydroxylepidine ethobromide and the ester by heating in pyridine.[118]

C. Thia- and Oxa-carbocyanines

The 4,5,4′,5′-dibenzo-6,6′-dihydroxy-derivatives of the thiacarbocyanine, VII (R=Me or Et, X=Br), were prepared by condensing 4,5-benzo-6-hydroxy-2-methylbenzothiazole metho-, or etho-, bromide with the ester in pyridine.

The oxacarbocyanine, XII (R=Et, X=I), was prepared in 68 % yield by heating 2-methylbenzoxazole ethiodide (2 mols.) and diethoxymethyl acetate (1 mol. + 100 % excess) first at 85°, at which stage the evolution of ethyl iodide occurred, and then at 105°; the reaction mixture was treated with hot water, and the product was washed with acetone and ether, and recrystallised.[118]

D. 2,2′- and 4,4′-Pyridocarbocyanines

By heating 2-picoline methiodide (2 mols.) and diethoxymethyl acetate (1 mol.) in piperidine at 120° for 3 hours, and recrystallising the product from ethanol (200 c.c. per g.), the 2,2′-pyridocarbocyanine, III (R=Me), was obtained in 9 % yield.

Similarly, from 4-picoline methiodide, with 3 hours' heating, there resulted, after three recrystallisations, a 27 % yield of V (R=Me).[118]

E. Thiazolocarbocyanines

By heating two mols. of 2,4-dimethylthiazole methiodide and one of the ester in piperidine at 120° for 5 minutes, washing, and recrystallising twice from ethanol (100 c.c. per g.), there was obtained a 29 % yield of the thiazolocarbocyanine, VIII (Y=S, R=R′=Me).[118]

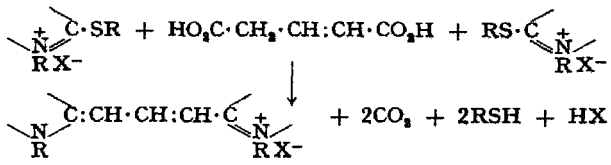
F. Benzimidazolocarbocyanines

The benzimidazolocarbocyanine, VI (R=R′=Et, R″=Cl, X=I), was prepared in 4 % yield by heating 5-chloro-3-ethyl-2-methylbenzimidazole ethiodide and diethoxymethyl acetate in pyridine for

2 hours, but the yield by use of chloral alcoholate (section 10) was 29 %. The yield of the 5,6,5′,6′-tetrachloro-derivative was 18 % by the present method and 32 % by the chloral alcoholate method.[112]

14. From a Quaternary Salt, Having a Reactive Alkylthio-Group, with Glutaconic Acid or Crotonic Anhydride

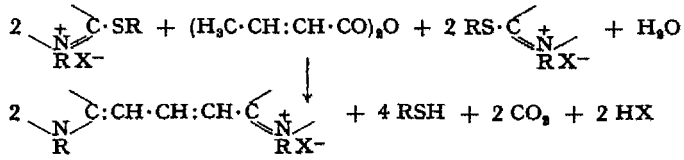
This method differs from the preceding ones in that the whole of the trimethin chain is supplied by glutaconic acid, which is condensed with a heterocyclic alkotoluene-*p*-sulphonate, having a reactive alkylthio-group, by heating in pyridine. Thus a 2,2′-carbocyanine was prepared by heating 2-methylthioquinoline with methyl toluene-*p*-sulphonate at 130–140° for 2·5 hours, adding glutaconic acid and pyridine and heating for 15 minutes, then treating with potassium bromide; alternatively, the starting point could be 1-methyl-2-thiodihydroquinoline. Thiacarbocyanines, such as VII (R=Me, X=Br), and the toluene-*p*-sulphonate of its 4,5,4′,5′-dibenzo-derivative were similarly prepared, also the oxacarbocyanine, XII (R=Me, X=I).[119] The reaction may be formulated as in equation 9.



(9)

It is the counterpart of the method in which the methin group of the symmetrical methincyanines is supplied by malonic acid (see II-6-D).[120]

Crotonic anhydride might be used instead of glutaconic acid. Thiacarbocyanines and an oxacarbocyanine were thus prepared.[119] The chemistry of the modified reaction has not been explained. The following formulation is not altogether satisfactory because of the introduction of water into equation 10.



(10)

Although the glutaconic acid method is interesting theoretically, there is no evidence that it has had practical application.

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CHAPTER V

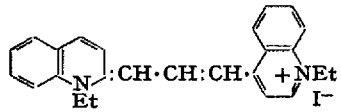
Unsymmetrical Trimethincyanines

1. Early Work

As long ago as 1886, a blue dye was obtained by the action of alkali and air on a solution of 2,4-dimethylquinoline methiodide.[1] The preparation of such sensitising dyes was patented in 1903,[2] and subsequently the conditions of their formation were studied.[3] These dicyanines were prepared, together with pinacyanol analogues, by the action of alkali on 2,4-dimethyl- or on 2,4,6-trimethyl-quinolinium salts, and it was realised in 1918 that their molecule must have a 2,4'-linking.[4] The dyes sensitised to infrared light, as far as 9000 Å.[5] An alternative method, which was said to give twelve times as much dicyanine, together with cyanine, consisted in heating a 2,4-dimethylquinolinium iodide with sodium sulphide and chloroform in ethanol.[6]

2. Syntheses by Use of a Disulphide

The first unsymmetrical trimethincyanine to be obtained pure was the 2,4'-carbocyanine, I. Although its nuclei are identical, their positions of linking are different, and that makes the compound unsymmetrical. It was synthesised in 1924 by the method which had been



(I)

used for symmetrical trimethincyanines (IV-4), but in this instance it was a mixture of quinaldine ethonitrate and lepidine ethonitrate which was heated with di-[*o*-*N*-methylformanilido] disulphide in pyridine. Comparison of its absorption spectrum with that of a sample of dicyanine prepared by the empirical method[5] led to the conclusion

that dicyanine was a 2,4′-carbocyanine (I-3-G).[7] As establishing the constitution of dicyanine, this was very important but it is clear that any process involving a mixture of salts must be unsatisfactory as a preparative method, because the unsymmetrical dye is liable to be contaminated by two symmetrical ones.

3. 2,2′-Carbocyanines from a Quinaldinium Salt, a Methylene Base and Formaldehyde

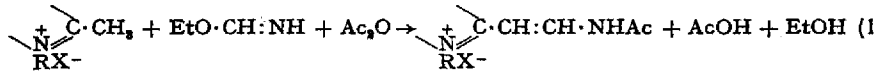
In 1925, crude 1-ethyl-2-methylene-1,2-dihydroquinoline, prepared from quinaldine ethiodide, was condensed with 2,6-dimethylquinoline ethiodide and formaldehyde, by heating for 20 minutes in alcoholic solution, to give the first unsymmetrical 2,2′-carbocyanine; another such was obtained by condensation of the base with 2-methyl-5,6-benzoquinoline ethobromide and formaldehyde.[8]

4. 2,2′-Carbocyanine from a Quinaldinium Salt, a Methylolquinaldinium Salt, and Alkali

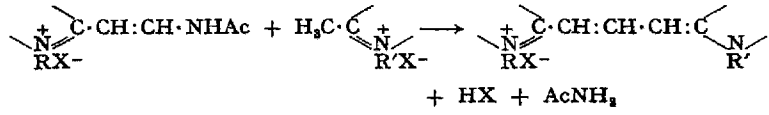
Another unsymmetrical 2,2′-carbocyanine was described in 1927 as being prepared by heating an alcoholic solution of 6-ethoxyquinaldine ethiodide and methylolquinaldine ethiodide with alkali.[9]

5. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Ethyl Formimino Ether Hydrochloride

Besides giving symmetrical carbocyanines (IV-8), the hydrochloride of ethyl formimino ether, or, more generally, X·CH:NH, could be condensed by heating in acetic anhydride with a quaternary salt having a reactive methyl group, to give an intermediate compound, as in equation 1.



This intermediate compound could then be condensed with a second such quaternary salt, as in equation 2, to give a trimethincyanine.



In the examples given, ethyl formimino ether hydrochloride (> 1 mol.) and 1,3,3-trimethyl-2-methyleneindoline (1 mol.) were heated in acetic anhydride containing acetic acid at 120–130° for 20 minutes, then treated with aqueous potassium iodide. By heating the intermediate compound with the same methylene base in acetic anhydride, the product was a symmetrical indocarbocyanine. On the other hand by treating the intermediate compound with alkali, it gave a base, having the group



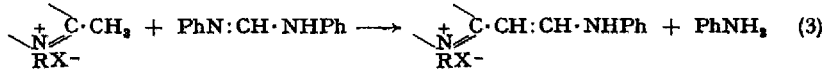
and that base, when heated in acetic anhydride with 1-methyl-2-methylene-1,2-dihydroquinoline, gave an unsymmetrical carbocyanine,[10] an indo-2′-carbocyanine.

The method has not been used, possibly because the following one, patented in the same year, proved so satisfactory.

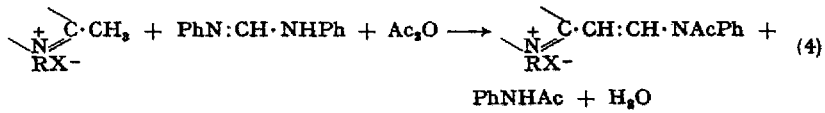
6. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Diphenylformamidine

A. General

It was discovered in 1929 that, whilst one mol. of diphenylformamidine can condense with two of a quaternary salt having a reactive methyl group to give a symmetrical trimethincyanine (see IV-9), on the other hand equimolecular quantities can react to give an intermediate compound. If condensation is effected by fusion at 180–200°, the methyl is converted into an anilinovinyl group (equation 3), but if by refluxing with acetic anhydride, it is converted into an acetanilidovinyl group (equation 4):



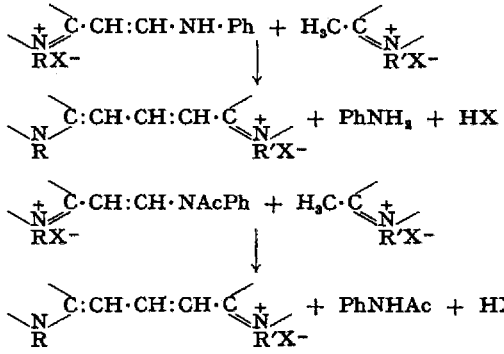
(3)



(4)

The former type of compound is converted into the latter by heating with acetic anhydride; the reverse change may be effected by heating

the acetanilidovinyl salt with concentrated hydrochloric acid. Either type of intermediate compound proved capable of condensation with another molecule of quaternary salt having a reactive methyl group and in this way various unsymmetrical trimethincyanines, possessing photographic sensitising properties, were prepared (equations 5 and 6).[11]



(5)

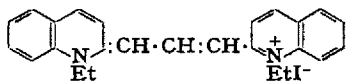
(6)

It was noted in 1934 that although an anilinovinyl compound condensed smoothly, by use of potassium acetate in acetic anhydride, with a salt having a reactive methyl group, the corresponding acetanilidovinyl compound was better. A dye prepared from quinaldine ethiodide and diphenylformamidine, followed by heating with lepidine ethiodide and potassium acetate in acetic anhydride, was compared with one prepared from lepidine ethiodide and diphenylformamidine, followed by similar condensation with quinaldine ethiodide; three other dyes also were prepared by such alternative routes and compared, leading to the conclusion that the same dye is arrived at by either route.[12] Many types of unsymmetrical trimethincyanines were prepared by the diphenylformamidine method, as indicated in the sections below. Some workers found it convenient to prepare symmetrical trimethincyanines by condensing a salt with diphenylformamidine and then condensing the product with more of the same salt,[13–15] which method was also used in the original patents.[11] An improved method for preparing the intermediate 2-β-anilinovinyl compounds consisted in heating together, e.g., at 100° for 30 minutes, equimolecular quantities of a heterocyclic quaternary salt having a reactive methyl group, ethyl orthoformate, and aniline. The yields of acetone-washed salts from 2-methylbenzoxazole alkotoluene-p-sulphonates were 78–81 % and from 2-picoline methiodide 65 %. Other primary amines could be used instead of

aniline, as could also piperidine.[16] Another variation consisted in heating an alkotoluene-*p*-sulphonate, having a reactive methyl group, with diphenylformamidine in the presence of alkyl ortho-ester. Thus, by boiling in n-amyl alcohol, such a 2-picolinium salt and diphenylformamidine, the yields were 61 % and 58 %, respectively, in the presence of ethyl orthoformate or ortho-acetate, but only 23 % without the ortho-ester. Similarly, on heating quinaldine ethotoluene-*p*-sulphonate with diphenylformamidine at 100° for an hour, the yield of 2-*β*-anilinovinyl salt was 70 % if ethyl orthoformate or ortho-acetate was present but only 43 % without it, and similarly in the benzoxazole series.[17]

B. 2,2′-, 2,4′-, and 4,4′-Carbocyanines

The diphenylformamidine method was used for preparing unsymmetrical 2,2′-carbocyanines. Thus II was prepared, firstly by condensing quinaldine ethiodide with diphenylformamidine, followed by reaction with 6-ethoxyquinaldine ethiodide, and, alternatively, by



(II)

condensing 6-ethoxyquinaldine ethiodide with diphenylformamidine, followed by reaction with quinaldine ethiodide.[12] The absorption maximum of an unsymmetrical 2,2′-carbocyanine having one 5,6-benzo-group was compared with those of the two related symmetrical carbocyanines.[18] A two-stage process for preparing a symmetrical 2,2′-carbocyanine[15] was applied to one having 5,6,5′,6′-dibenzo-groups and consisted in condensing the appropriate anilinovinyl ethiodide with 5,6-benzoquinaldine ethiodide by heating with acetic anhydride and sodium acetate.[19]

The 2,4′-carbocyanine, I, was reached by alternative routes.[12] It was obtained in 12 % yield by boiling 2-*β*-anilinovinylquinoline ethiodide and lepidine ethiodide in pyridine for 30 minutes.[20] Its absorption maximum, and that of a derivative prepared from a 5,6-benzoquinaldinium salt, were compared with those of the corresponding 2,2′- and 4,4′-carbocyanines.[18]

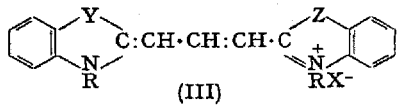
A symmetrical 4,4′-carbocyanine was prepared from lepidine ethiodide by the two-stage process.[15]

C. Benzimidazolo-2′-, Indo-2′-, Thia-2′-, Oxa-2′, and Selena-2′-Carbocyanines

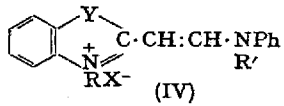
It seems convenient to group together unsymmetrical trimethincyanines in which a quinoline nucleus is linked in the 2-position to another heterocyclic nucleus.

The first benzimidazolo-2′-carbocyanine, III (Y=NMe, Z=CH:CH, R=Me, R′=Et, X=I), was prepared in 1934, as one of a series in which the sensitising maximum of an unsymmetrical dye was compared with the maxima of its two symmetrical parent dyes.[21]

By heating together quinaldine ethiodide and diphenylformamidine at 180°, there resulted 2-β-anilinovinylquinoline ethiodide, IV (Y=CH:CH, R=Et, R′=H, X=I). When this salt was heated



(III)



(IV)

with 1,3,3-trimethyl-2-methyleneindoline in acetic anhydride, it gave the indo-2′-carbocyanine, III (Y=CMe_2, Z=CH:CH, R=Me, R′=Et, X=I).[11] It was also prepared by condensing 2,3,3-trimethylindolenine methiodide with diphenylformamidine and reaction of the anilinovinyl product with quinaldine ethiodide by heating with sodium acetate in acetic anhydride.[12] An analogue, III (Y=CMe_2, Z=CH:CH, R=R′=Et, X=ClO_4), was obtained in 13 % yield by boiling 2,3,3-trimethylindolenine ethiodide and 2-β-acetanilidovinylquinoline ethiodide in pyridine for 20 minutes, converting to perchlorate, and recrystallising; the observed and calculated values of the absorption maximum were compared.[20] Five derivatives of the indo-2′-carbocyanine, III (Y=CMe_2, Z=CH:CH, R=Me, R′=Me or Et, X=I or ClO_4), were prepared by boiling IV (Y=CMe_2, R=Me, R′=Ac) with a substituted quinaldinium salt in pyridine for 40–60 minutes; substituents were 5- or 6-nitro- or -acetylamino-, or 5-benzoylamino-, and the yields were 27–60 %. The 6-acetylamino-derivative was hydrolysed to the 6-amino-derivative.[22]

Diphenylformamidine was used for preparing the thia-2′-carbocyanine, III (Y=S, Z=CH:CH, R=R′=Et, X=I), and its sensitising maximum was compared with those of the corresponding symmetrical thiacarbocyanine and 2,2′-carbocyanine.[21] A similar comparison of absorption maxima was made with this dye, as well as with four others, having a 4,5- or 6;7-benzobenzothiazole nucleus in

conjunction with a quinoline or with a 5,6-benzoquinoline nucleus.[18] To prepare III (Y=S, Z=CH:CH, R=Pr^n, R'=Me, X=I), it was satisfactory to boil IV (Y=S, R=Pr^n, R'=Ac, X=I) with quinaldine methotoluene-*p*-sulphonate in pyridine for 15 minutes, the yield of recrystallised dye being 54 %, but for III (Y=S, Z=CH:CH, R=R'=Et, X=I) an intermediate compound less reactive than the acetanilidovinyl salt was recommended; thus quinaldine ethotoluene-*p*-sulphonate was boiled for 30 minutes in pyridine either with 2-*β*-methylanilinovinyl- or with 2-*β*-piperidylvinyl-benzothiazole ethiodide (yields 40 % and 21 %, respectively).[23] A derivative of III (Y=S, Z=CH:CH, R=R'=Et, X=I), having a 6-nitro-group in the benzothiazole nucleus, was prepared, in 50 % yield after recrystallisation, by boiling 2-methyl-6-nitrobenzothiazole ethochloride and IV (Y=CH:CH, R=Et, R'=Ac, X=I) in pyridine for 10 minutes. Its isomer, having a 6-nitro-group in the quinoline nucleus, was similarly prepared, in 38 % yield, from IV (Y=S, R=Et, R'=Ac, X=I) and 6-nitroquinaldine ethiodide. The absorption maxima of their methanolic solutions lay at longer wavelengths, by 20 Å and 220 Å, respectively, than that of the unsubstituted dye.[24] Condensation of 2-methyl-4,5-benzobenzothiazole ethiodide with IV (Y=CH:CH, R'=H, X=I), by boiling in pyridine for 30 minutes, gave a 30 % yield of dye; the observed and calculated values of its absorption maximum were compared, as also for III (Y=S, Z=CH:CH, R=R'=Et, X=I).[20] Four thia-2'-carbocyanines were made by condensing an alkyl halide having a *β*-anilinovinyl group with one having a methyl group, by heating with sodium acetate in acetic anhydride; substituents were 6-chloro- or 4,6-dichloro- in the benzothiazole nucleus or else 6-bromo- or 5,6-benzo- in the quinoline nucleus.[19] Five thia-2'-carbocyanines were prepared by condensing IV (Y=S, R=Et, R'=Ac) with a substituted quinaldinium salt, by boiling in pyridine for 30–50 minutes. The substituents were 5- or 6-nitro- or -acetylamino-, or 5-benzoylamino-, and the yields were 20–30 %. The 5-amino-compound was prepared by hydrolysis of the 5-acetylamino-compound.[22]

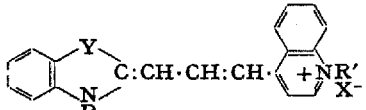
The sensitising maximum[21] and the absorption maximum[18] of the oxa-2'-carbocyanine, III (Y=O, Z=CH:CH, R=R'=Et, X=I), were compared with those of the corresponding symmetrical dyes. It was prepared in 25 % yield by boiling IV (Y=O, R=Et, R'=Ac, X=I) and quinaldine ethiodide for 30 minutes with sodium acetate

in ethanol.[20] A similar comparison of absorption maxima was made with four derivatives having a 4,5- or a 6,7-benzobenzoxazole nucleus together with a quinoline or 5,6-benzoquinoline nucleus.[18]

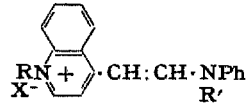
The absorption maximum of the selena-2'-carbocyanine, III (Y=Se, Z=CH:CH, R=R'=Et, X=I), and of its analogue having a 5,6-benzoquinoline nucleus, were compared with those of the corresponding symmetrical carbocyanines.[18]

D. Indo-4', Thia-4'-, Oxa-4'-, and Selena-4'-carbocyanines

The indo-4'-carbocyanine, V (Y=CMe_2, R=R'=Et, X=ClO_4), was prepared in 34 % yield by heating VI (R=Et, R'=Ac, X=I) and 2,3,3-trimethylindolenine ethiodide together in pyridine for 15 minutes, converting the dye to perchlorate, and recrystallising. The observed and calculated values of its absorption maximum were compared.[20]



(V)



(VI)

The absorption maximum of the thia-4'-carbocyanine, V (Y=S, R=R'=Et, X=I), and of its derivatives having a 4,5- or 6,7-benzobenzothiazole nucleus, were compared with those of the corresponding symmetrical dyes.[18] Thia-4'-carbocyanines prepared by heating 2-methyl-4,5- or -6,7-benzobenzothiazole ethiodide with diphenylformamidine at 100–150° for 10 minutes, and condensing the recrystallised salt with a lepidinium salt, were valuable sensitisers to red light; the condensation was effected either by heating the two salts in pyridine or with sodium acetate in acetic anhydride, and the lepidinium salts included ones with a 5,6- or 7,8-benzo-group.[25] The thia-4'-carbocyanine, V (Y=S, R=R'=Et, X=I), was prepared in 12 % yield by boiling in pyridine for 10 minutes a mixture of lepidine ethiodide and IV (Y=S, R=Et, R'=Ac, X=I), and recrystallising; its analogue, having a 4,5-benzobenzothiazole nucleus, resulted in 10 % yield by boiling a mixture of 2-methyl-4,5-benzobenzothiazole ethiodide and VI (R=Et, R'=H, X=I) in pyridine.[20] A thia-4'-carbocyanine, V (Y=S, R=R'=Et, X=I), having a 6-nitro-group in the benzothiazole nucleus, was obtained in 31 % yield by

boiling 2-methyl-6-nitrobenzothiazole ethochloride with VI (R=Et, R′=Ac, X=I) in pyridine for 10 minutes. The absorption maximum of its methanolic solution lay at a wavelength shorter by 880 Å than that of the unsubstituted dye.[24]

The absorption maximum of the oxa-4′-carbocyanine, V (Y=O, R=R′=Et, X=I), and of its derivatives having a 4,5- or 6,7-benzobenzoxazole nucleus, were compared with those of the parent symmetrical dyes.[18] The first of these three was obtained in 12 % yield by boiling lepidine ethiodide with IV (Y=O, R=Et, R′=Ac, X=I) in pyridine for 10 minutes, and recrystallising.[20]

The absorption maximum of the selena-4′-carbocyanine, V (Y=Se, R=R′=Et, X=I), was compared with those of the parent dyes.[18]

E. Indo-, Thia-, and Oxa-carbocyanines

In the original patents, the intermediate compound, IV ($Y=CMe_2$, R = Me, R′ = H, X = I), was prepared by 20 minutes' heating at 200° of 2,3,3-trimethylindolenine methiodide and diphenylformamidine, followed by treatment with alcohol; alternatively, its acetyl derivative, IV ($Y=CMe_2$, R=Me, R′=Ac, X=I), was prepared by heating the same reactants in acetic anhydride.[11] The symmetrical indocarbocyanine, III ($Y=Z=CMe_2$, R=R′=Me, X=I), resulted in 71 % yield by a two-stage process, in which the anilinovinyl salt prepared from 2,3,3-trimethylindolenine methiodide was heated with that salt and sodium acetate in acetic anhydride.[15]

The absorption maxima of four unsymmetrical thiacarbocyanines, III (Y=Z=S, R=R′=Et, X=I), in which one nucleus had a 4,5- or a 6,7-benzo-substituent, or in which one had a 4,5- and the other a 6,7-benzo-group, were compared with those of the corresponding symmetrical thiacarbocyanines.[18] The dyes having a 4,5- or 6,7-benzo-group were patented as good sensitisers.[26] One of the former was obtained in 33 % yield by 10 minutes' boiling in pyridine of 2-methyl-4,5-benzobenzothiazole ethiodide and IV (Y=S, R=Et, R′=Ac, X=I).[20] A thiacarbocyanine with a 5,6-benzo-group in one nucleus was described.[27] Thiacarbocyanines having one 4,5,6,7-tetrahydrobenzothiazole nucleus were also patented.[28] By heating one 2-methylbenzothiazolium salt with diphenylformamidine in acetic anhydride and condensing the acetanilidovinyl salt with another 2-methylbenzothiazolium salt in boiling pyridine, there were prepared unsymmetrical

thiacarbocyanines in which one nucleus had a 6-hydroxy-, -methoxy-, -nitro-, or -dimethylamino-substituent: also others in which the nuclei were substituted thus: 6-hydroxy-6′-nitro-, 6-acetoxy-6′-nitro-, 6-dimethylamino-6′-nitro-, or 6′-nitro-6-(tolyl-*p*-sulphonamido)-; hydrolysis of the last gave a 6-amino-6′-nitrothiacarbocyanine.[29] By use of diphenylformamidine there were prepared three thiacarbocyanines having a 4-, 5-, or 6-hydroxy-group, and also one having 4-hydroxy-6′-nitro-substituents.[30] By heating a suitable 2-methylbenzothiazolium salt and a 2-*β*-anilinovinylbenzothiazolium salt with sodium acetate in acetic anhydride, two thiacarbocyanines having a 6-chloro- or -bromo-substituent were made.[19] Thiacarbocyanines having one 5-carbalkoxy-substituent were patented as good sensitisers and two examples were given.[31] The symmetrical thiacarbocyanine from 2-methylbenzothiazole ethiodide was prepared by a two-stage process.[15] The introduction of an unsaturated group, such as styryl, *p*-methoxystyryl, or 2-thienylvinyl into the 6′-position of a 4,5-benzothiacarbocyanine, or of either of the first two unsaturated groups into the 6′-position of a 5-methoxythiacarbocyanine, led to a bathochromic shift of absorption.[32]

Unsymmetrical oxacarbocyanines having a 5-carbalkoxy-group were likewise good sensitisers. Two were prepared by heating the 5-carbomethoxy- or 5-carbethoxy-derivative of IV (Y=O, R=Et, R′=Ac, X=I) with 2-methyl-4,5-benzobenzoxazole ethiodide in pyridine containing acetic anhydride, and a third by similar heating of the former salt with 2,5,6-trimethylbenzoxazole ethiodide.[33] The two-stage process was applied to the preparation of a symmetrical oxacarbocyanine from 2-methylbenzoxazole methiodide.[15] Condensation of 2-methyl-4,5,6,7-tetrahydrobenzoxazole ethotoluene-*p*-sulphonate with 2-*β*-acetanilidovinylbenzoxazole ethiodide gave an unsymmetrical dye with its absorption maximum at 4740 Å.[34]

F. Benzimidazoloindo-, Benzimidazolo-oxa-, Indoxa-, Indothia-, Oxaselena-, Oxathia-, and Selenathia-carbocyanines

The 5-acetyl, 5-bromo-, and 5-ethylcarbamyl derivatives of the benzimidazoloindocarbocyanines, III (Y=NEt, Z=CMe_2, R=Et, R′=Me, X=ClO_4), were prepared by use of IV (Y=CMe_2, R=Me, R′=Ac, X=I).[35]

The same derivatives of the benzimidazolo-oxacarbocyanines, III (Y=NEt, Z=O, R=R′=Et, X=I), were similarly prepared.

Carbocyanines with an alkyl- or alkylcarbamyl-benzimidazole nucleus had unusually sharp sensitising bands (see IV-3-E).[35]

The indoxacarbocyanine, III (Y=CMe_2, Z=O, R=Me, R'=Et, X=I), was prepared by heating IV (Y=CMe_2, R=Me, R'=Ac, X=I) with 2-methylbenzoxazole ethiodide and potassium acetate in acetic anhydride.[11] In 1933 indoxacarbocyanines having an alkyl or alkoxy-group in one or both rings were claimed to be better than any orthochromatic sensitisers that were then known: their sensitising curves fell off sharply on the long wavelength side. In one example 2-methylbenzoxazole ethotoluene-*p*-sulphonate was heated with diphenylformamidine in acetic acid; the product was heated with 2,3,3,5,6-pentamethylindolenine methiodide in pyridine, and the dye was isolated as perchlorate (see also section 8-E).[36] By boiling for 5 minutes in pyridine a mixture of IV (Y=O, R=Et, R'=Ac, X=I) and 2,3,3-trimethylindolenine ethiodide, there resulted a 45 % yield of III (Y=CMe_2, Z=O, R=R'=Et, X=I), for the absorption of which observed and calculated values were compared.[20] Indoxacarbocyanines in which the benzoxazole nucleus had a 5-carbomethoxy- or -carbethoxy-group were good sensitisers and were prepared in the same way as unsymmetrical oxacarbocyanines with these substituents (see section 6-E).[33]

The indothiacarbocyanine, III (Y=CMe_2, Z=S, R=Me, R'=Et, X=I), was prepared by heating the acetanilidovinyl salt, IV (Y=S, R=Et, R'=Ac, X=I), with 2,3,3-trimethylindolenine methiodide and anhydrous sodium acetate in acetic anhydride, then treating with water.[11] The analogue, III (Y=CMe_2, Z=S, R=R'=Et, X=I), was obtained in 52 % yield by boiling the same acetanilidovinyl salt with 2,3,3-trimethylindolenine ethiodide in pyridine for 10 minutes, and recrystallising. The 4,5-benzo-derivative of the acetanilidovinyl salt gave rise to a 33 % yield of the corresponding indothiacarbocyanine having a 4,5-benzobenzothiazole nucleus. For each dye the observed and calculated values of the absorption maximum were compared.[20]

For the oxaselenacarbocyanine, III (Y=O, Z=Se, R=R'=Et, X=I), and for derivatives having a 4,5- or 6,7-benzobenzoxazole nucleus, the absorption maximum was compared with those of the related symmetrical carbocyanines.[18] Amongst unsymmetrical carbocyanines having a 5-carbalkoxybenzoxazole nucleus (see section 6-E and below) were three oxaselenacarbocyanines, in which the benzoxazole

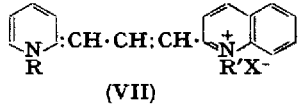
nucleus had a 5-carbomethoxy-group, and the benzoselenazole nucleus was unsubstituted or had a 5-methyl or 6,7-benzo-substituent.[33]

The oxathiacarbocyanine, III (Y=O, Z=S, R=R'=Et, X=I), was prepared by heating IV (Y=S, R=Et, R'=Ac, X=I) with 2-methylbenzoxazole ethiodide and potassium acetate in acetic anhydride.[11] Its absorption maxima and those of eight of its derivatives were compared with those of the related symmetrical dyes; the derivatives had a 4,5- or a 6,7-benzo-group in one or both nuclei.[18] The first dye was prepared in 40 % yield, and its derivative having a 4,5-benzobenzothiazole nucleus in 25% yield, by boiling IV (Y=O, R=Et, R'=Ac, X=I) with the appropriate 2-methylbenzothiazole ethiodide in pyridine for 10 minutes.[20] The same acetanilidovinyl compound was similarly condensed with 2-methyl-4,5,6,7-tetrahydrobenzothiazole ethotoluene-*p*-sulphonate (cf. section 6-E).[28] Amongst unsymmetrical carbocyanines having a 5-carbalkoxybenzoxazole nucleus were a couple of oxathiacarbocyanines.[33]

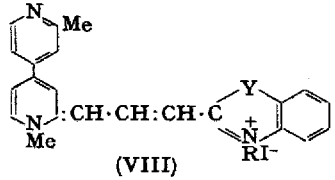
The absorption maxima of the selenathiacarbocyanine, III (Y=Se, Z=S, R=R'=Et, X=I), and of its derivatives having a 4,5- or 6,7-benzobenzothiazole nucleus, were compared with those of the related symmetrical carbocyanines.[18] Derivatives having a 5-carbalkoxybenzothiazole nucleus were, like the corresponding thiacarbocyanines (see section. 6-E), patented as good sensitisers.[31]

G. 2-Pyrido-2'- and 2-Pyrido-4'-carbocyanines, Oxa-2'-pyrido- and 2-Pyridothia-carbocyanines

The 2-pyrido-2'-carbocyanine, VII (R=Me, R'=Et, X=I), is another unsymmetrical trimethincyanine for which alternative preparative routes were described.[12] By heating 2-*β*-anilinovinyl-2'-methyl-4,4'-bipyridine methiodide with quinaldine alkiodide, potassium acetate, acetic anhydride and pyridine, there resulted VIII (Y=CH:CH, R=Me or Et); of which the former had its absorption maximum at 6000 Å; *p*-toluquinaldine methiodide was also used.[37]



(VII)



(VIII)

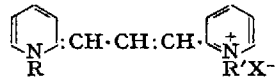
A 2-pyrido-4′-carbocyanine analogous to VIII (R=Me), obtained by condensing the preceding anilinovinyl salt with lepidine methiodide, had its absorption maximum at 7010 Å.[37]

The oxa-2′-pyridocarbocyanine, VIII (Y=O, R=Me), was prepared by fusing 2,2′-dimethyl-4,4′-bipyridine methiodide, 2-β-acetanilidovinylbenzoxazole methiodide, and potassium acetate: it had its absorption maximum at 5250 Å.[37]

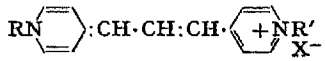
The 2-pyridothiacarbocyanines, VIII (Y=S, R=Me or Et), of which the former absorbed at 5800 Å, were prepared by heating 2-β-anilinovinyl-2′-methyl-4,4′-bipyridine methiodide and 2-methylbenzothiazole alkiodide in pyridine.[37]

H. 2,2′- and 4,4′-Pyridocarbocyanines

By use of 2- or 4-β-acetanilidovinyl-, but not 2- or 4-β-anilinovinyl-, pyridine methiodides (see section 7-A), it was possible to prepare the symmetrical 2,2′- and 4,4′-pyridocarbocyanines, IX and X (R=R′=Me, X=I); the condensing agent for the former was potassium acetate in butanol and for the latter alcoholic potassium hydroxide.[38]



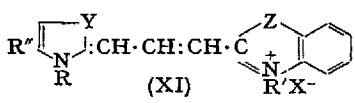
(IX)



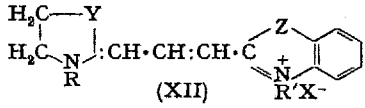
(X)

I. Thiazolo-2′- and Thiazolino-2′-carbocyanines

The thiazolo-2′-carbocyanine, XI (Y=S, Z=CH:CH, R=R″=Me, R′=Et, X=I), was prepared and its sensitising maximum compared with those of the related symmetrical dyes;[21] XI (Y=S, Z=CH:CH, R=Allyl, R′=Et, R″=Me) was similarly made.[19]



(XI)



(XII)

A thiazolino-2′-carbocyanine, XII (Y=S, Z=CH:CH, R=R′=Et, X=I), was prepared by boiling a 2-methylthiazolinium salt with IV (Y=CH:CH, R=Et, R′=Ac, X=I) in pyridine for 10 minutes but was accompanied by the symmetrical 2,2′-carbocyanine (see section 8-G).[39]

J. Thiathiazolo-, Oxathiazolo-, Oxathiazolino-, Selenathiazolino-, and Thiathiazolino-carbocyanines

Three thiathiazolocarbocyanines, XI (Y=Z=S, R″=Me, R=Me, Bu, or iso-Amyl, R′=Et, X=I), were prepared by condensing a quaternary salt having an anilinovinyl with one having a methyl group, by boiling with sodium acetate in acetic anhydride.[19]

The oxathiazolocarbocyanines, XI (Y=S, Z=O, R=R′=Me or Et, R″=NH_2, X=I), were reached through 4-amino-2-methylthiazole alkiodides.[40] A tetrahydro-derivative of XI (Y=S, Z=O, R=R′=Et, R″=Me, X=I) was obtained through 2-methyl-4,5,6,7-tetrahydrobenzoxazole ethiodide.[34]

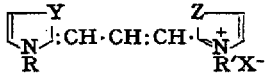
Oxathiazolinocarbocyanines, XII (Y=S, Z=O), were recommended for sensitising to blue and green light. They were prepared from a 2-methylthiazolinium alkotoluene-*p*-sulphonate by boiling with IV (Y=O, R′=Ac) in pyridine for 10 minutes and separating from the symmetrical oxacarbocyanine.[39] Sensitising was improved by the presence of a 5-carbalkoxy-group in the benzoxazole nucleus.[33]

A selenathiazolinocarbocyanine, XII (Y=S, Z=Se, R=Et, R′=Me, X=I), was prepared by boiling 2-methylthiazoline methotoluene-*p*-sulphonate with IV (Y=Se, R=Et, R′=Ac, X=I) in pyridine for 10 minutes and separating from the selenacarbocyanine.[39]

A thiathiazolinocarbocyanine, XII (Y=Z=S, R=Et, R′=Me, X=I) was similarly made.[39]

K. Thiazolo-, Oxazolo-, and Thiazolino-carbocyanines

A symmetrical thiazolocarbocyanine, XIII (Y=Z=S, R=R′=Et, X=I), was prepared in 33 % yield by boiling 2-methylthiazole ethiodide and 2-*β*-acetanilidovinylthiazole ethiodide in ethanol for 10 minutes.[41]



(XIII)

Two other symmetrical thiazolocarbocyanines, the 4,4′-dimethyl derivatives of XIII (Y=Z=S, R=R′=Me, X=I)[15] and of XIII (Y=Z=S, R=R′=Allyl, X=Br)[19] were prepared by the method in which a 2-*β*-anilinovinylthiazolium salt was condensed with the original 2-methylthiazolium salt by boiling with sodium acetate in acetic

anhydride; so also was the unsymmetrical 4,4'-dimethyl derivative of XIII (Y=Z=S, R=Allyl, R'=Me, X=Br).[19]

A symmetrical oxazolocarbocyanine, the 4,5,4',5'-tetraphenyl derivative of XIII (Y=Z=O, R=R'=Me, X=I) was similarly made.[19]

Cyanine dyes containing a thiazoline nucleus were discovered independently in America (see IV-6-G) and in Japan. According to the Japanese workers, a symmetrical thiazolinocarbocyanine was prepared by boiling 2-methylthiazoline methiodide, 2-β-anilinovinylthiazoline methiodide, and sodium acetate in acetic anhydride.[15]

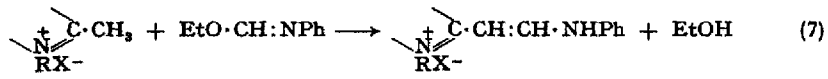
L. Benzimidazolocarbocyanines

An unsymmetrical benzimidazolocarbocyanine, the 5,6,5'-trichloro-derivative of III (Y=Z=NEt, R=R'=Et, X=I) was prepared by heating together 2-β'-anilinovinyl-5,6-dichlorobenzimidazole ethotoluene-*p*-sulphonate, 5-chloro-2-methylbenzimidazole ethiodide, pyridine, acetic anhydride, and triethylamine: it sensitised powerfully, with the maximum at 5750 Å.[42]

7. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of Ethylisoformanilide

A. General

Although diphenylformamidine did give anilinovinyl compounds with 2- or 4-methylpyridinium salts (see section 6-H), it was found in 1946 that ethyl(or methyl)isoformanilide is a more satisfactory reagent for preparing the intermediate compounds of these series. It reacted according to equation 7.



(7)

The yields rose with the temperature: thus when reaction was carried out in boiling ethanol, butanol (or pyridine), or n-amyl alcohol, they were 30 %, 50 %, and 60 %, respectively, whilst fusion of the reactants at 160° gave a yield of over 70 %. The 2-β-anilinovinylpyridinium salts were acetylated by dissolving in acetic anhydride.[43,44]

B. Thiathiazolo- and Oxaoxazolo-carbocyanines

Ethylisoformanilide was used in the preparation of two derivatives of the thiathiazolocarbocyanine, XI (Y=Z=S, R=R'=Et); in the first, a perchlorate, the thiazole nucleus had 4-β-naphthyl-5-*p*-tolylthio-substituents and in the second, an iodide, it had 4-phenyl-5-*p*-tolylthio-substituents.[45]

Similarly it was used for preparing eleven oxaoxazolocarbocyanines, XI (Y=Z=O, R=R'=Et, X=I or ClO_4), in ten of which the oxazole nucleus was substituted. The method consisted in heating each 2-methyloxazole with ethyl toluene-*p*-sulphonate at 120–170° for 1–6 hours, heating the salt with ethylisoformanilide at 130–150° for ⅓ to 2 hours, purifying the resultant anilinovinyl salt, acetylating with acetic anhydride, removing excess of solvent, and condensing with the 2-methylbenzoxazolium salt. Mono-substituted dyes carried 4- or 5-phenyl or -*p*-methoxyphenyl, whilst di-substituted dyes carried 4,5-diphenyl, or else 5-phenyl together with 4-*p*-methoxyphenyl, 4-*p*-dimethylamino-phenyl, or its methotoluene-*p*-sulphonate, and 4-*m*,*p*-dimethoxy-phenyl.[46]

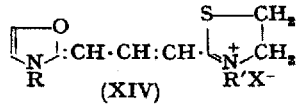
C. Thiazolo-, Oxazolo-, and Oxazolothiazolino-carbocyanines

Eight symmetrical thiazolocarbocyanines, XIII (Y=Z=S), substituted in the 4,5,4',5'-positions, were prepared by use of ethylisoformanilide. The method consisted in fusing equimolecular quantities of 2-methylthiazole base and alkyl ester at 150–170° until the maximum water-solubility of the product was reached: 1·5–2 hours for methyl toluene-*p*-sulphonate or ethyl sulphate, but 5–6 hours for ethyl toluene-*p*-sulphonate were required; some of the anilinovinyl salts crystallised, whilst others were converted into iodides. Each anilinovinyl compound was acetylated by boiling with acetic anhydride for half an hour. The solvent was removed and the oily acetanilidovinyl salt was condensed with an equimolecular quantity of the original 2-methylthiazolium salt by heating with triethylamine in alcohol. Whilst introduction of substituents into the 4-phenyl groups had little or no effect on the absorption maximum, replacement of the 5-phenyl groups by 5-*p*-tolylthio- or 5-phenoxy- caused hypsochromic shifts (see IV-6-G, Table II).[45]

Six symmetrical oxazolocarbocyanines, XIII (Y=Z=O), either di- or tetra-substituted (see IV-6-G, Table II), were similarly prepared,

also an unsymmetrical oxazolocarbocyanine, XIII (Y=Z=O, R=R'=Et, X=ClO_4), having 4-*p*-methoxyphenyl-5-phenyl in one nucleus and 4,5-diphenyl in the other.[45]

Similarly there were prepared four derivatives of the oxazolothiazolinocarbocyanine, XIV (R=Et, R'=Me, X=I or ClO_4), in which the



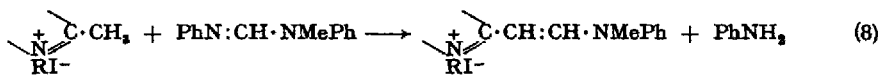
(XIV)

oxazole nucleus was di-substituted: by 4,5-di-(2-furyl), 4,5-diphenyl, 4-*p*-methoxyphenyl-5-phenyl, and 4-*p*-dimethylaminophenyl-5-phenyl groups, respectively.[46]

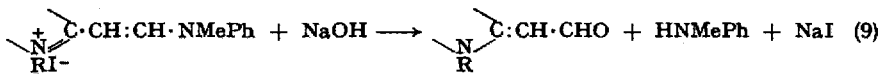
8. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with a Heterocyclic Base Having the Group: CH.CHO

A. General

It was found that by condensing a substituted formamidine, such as PhN:CH·NAlkPh, with a quaternary salt, having a reactive methyl group, or with the corresponding methylene base, and by hydrolysing the resultant alkylanilinovinyl salt, there resulted an aldehyde, as in equations 8 and 9.



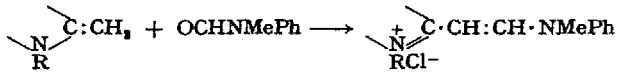
(8)



(9)

Conversion of the methyl into the methylanilinovinyl group was effected by heating the quaternary salt with the substituted formamidine in acetic anhydride for an hour; the product was hydrolysed by pouring into water, adding sodium hydroxide, and steam-distilling. The aldehydes described included those derived from 2-methylbenzothiazole, 2-methylindolenine, and quinaldine quaternary salts.[47] In the indolenine series the aldehydes were also prepared by treating the

appropriate methylene base and formylmethylaniline with phosphorus oxychloride and chloro- or dichloro-benzene, as in equation 10,

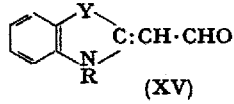


(10)

followed by hydrolysis with sodium hydroxide.[48] These aldehydes were condensed with quaternary salts having a reactive methyl group, in the presence of an acid or basic reagent, to give symmetrical or unsymmetrical carbocyanines: four types of the latter were given in the original patent.[49] Subsequently the sensitising action of trimethincyanines having a benzimidazole nucleus was patented: the seventy-seven examples, for each of which sensitising data were recorded, comprised two symmetrical (see IV-3-E) and seventy-five unsymmetrical dyes. The method of preparing the latter was to condense a 2-methylbenzimidazolium salt with the aldehyde of another heterocyclic series, in the presence of pyridine or piperidine; the aldehydes were derived from 2-methyl-quinolinium, -benzothiazolium, -benzoxazolium, -benzoselenazolium, -indoleninium, and -thiazolinium salts.[50] As semicarbazones and thiosemicarbazones of the aldehydes crystallised well, they were recommended for making dyes in place of the aldehydes themselves.[51] Di-ionic carbocyanines, prepared from 1-alkyl-2-methylbenzimidazolium salts, having a $3\text{-}(CH_2)_3NR^1R^2R^3X^-$ group, were sensitisers of high water-solubility (see sections 8-F and H).[52]

B. Benzimidazolo-2'- and Indo-2'-carbocyanines

The benzimidazolo-2'-carbocyanine, III (Y=NPh, Z=CH:CH, R=R'=Et, $X=SO_4Et$), containing a 6-chloro-group in the benz-



(XV)

imidazole nucleus, was prepared by condensing the appropriate benzimidazolium ethoethylsulphate with 1-ethyl-2-formylmethylenedihydroquinoline, XV (Y=CH:CH, R=Et).[50]

The indo-2'-carbocyanine, III ($Y=CMe_2$, Z=CH:CH, R=Me, R'=Et, X=I), was prepared by boiling 1,3,3-trimethyl-2-formyl-

methyleneindoline, XV (Y=CMe_2, R=Me) and quinaldine ethiodide in pyridine for 9 hours; substituted quinaldinium salts could also be used.[49]

C. Indo-4'-carbocyanines

The indo-4'-carbocyanine, V (Y=CMe_2, R=Me, R'=Et, X=I), was similarly prepared by use of lepidine ethiodide.[49]

D. Indocarbocyanines

The method was applied to the preparation of the symmetrical indocarbocyanine, III (Y=Z=CMe_2, R=R'=Me, X=Cl): a solution of the aldehyde, XV (Y=CMe_2, R=Me), and 1,3,3-trimethyl-2-methyleneindoline in benzene was treated with phosphorus oxychloride.[49]

E. Indoxa- and Indothia-carbocyanines

Some of the substituted indoxacarbocyanines described as good orthochromatic sensitisers (see section 6-F) were prepared by the aldehyde method. Thus 2-formylmethylene-1,3,3,5-tetramethylindoline was heated in pyridine for 1·5–2 hours, either with 6-methoxy-2-methylbenzoxazole ethiodide or with 2,5,6-trimethylbenzoxazole methomethylsulphate, to give derivatives of III (Y=CMe_2, Z=O, R=Me).[36]

In the original patent, the indothiacarbocyanine, III (Y=CMe_2, Z=S, R=Me, R'=Et, X=I) was prepared by boiling a solution of the aldehyde, XV (Y=CMe_2, R=Me), with 2-methylbenzothiazole ethiodide in pyridine for 1·5 hours. Three other dyes of this type resulted by using derivatives of the salt having 5,6-dimethoxy-, 6-dimethylamino-, or 4,5-benzo-substituents; another was made by condensing the 5,6-dimethyl derivative of the aldehyde with the 5,6-dimethyl derivative of the salt.[49]

F. Benzimidazoloindo-, Benzimidazolothia-, Benzimidazolo-oxa-, and Benzimidazoloselena-carbocyanines

Benzimidazoloindocarbocyanines, of which the simplest member was III (Y=NPh, Z=CMe_2, R=Et, R'=Me, X=I), were represented in the patent by thirty-two examples, comprising analogues and dyes with substituents in one or both nuclei.[50] Through 2-formylmethylene-1,3,3-trimethylindoline there was prepared the 6-chloro-derivative of

the di-ionic benzimidazoloindocarbocyanine, III (Y=NMe, Z=CMe_2, R=$(CH_2)_3\overset{+}{N}Me_3ClO_4^-$, R'=Me, X=$ClO_4$); the 6-chloro-5'-methyl derivative of III (Y=NEt, Z=CMe_2, R=$(CH_2)_3\overset{+}{N}EtMe_2ClO_4^-$, R'=Me, X=$ClO_4$) was made similarly.[52]

For preparing a benzimidazolothiacarbocyanine, III (Y=NEt, Z=S, R=R'=Et, X=I), having a 6-ethoxy-group in the benzimidazole nucleus, the substituted benzimidazolium salt was condensed with the aldehyde, XV (Y=S, R=Et); two others were also made.[50]

In two benzimidazolo-oxacarbocyanines, III (Y=NPh, Z=O, R=R'=Et, X=SO_4Et), the benzoxazole nucleus had a 5,6-benzo-substituent, and in one of them the benzimidazole nucleus had a 6-chloro-substituent.[50] Dyes of this kind, in which the benzimidazole nucleus had one or more chloro-substituents, were claimed to be especially useful orthochromatic sensitisers. The two examples were prepared by condensing *NN'*-di-substituted-5,6-dichloro-2-methylbenzimidazolium salts with the anil of 3-ethyl-2-formylmethylene-5-phenylbenzoxazoline by heating in pyridine containing piperidine or triethylamine.[53]

The patent contained twelve examples of benzimidazoloselenacarbocyanines, including III (Y=NPh, Z=Se, R=R'=Et, X=SO_4Et) and various analogues; either nucleus, or both, could be substituted.[50] The di-ionic benzimidazoloselenacarbocyanine, III (Y=NMe, Z=Se, R=$(CH_2)_3\overset{+}{N}Me_3ClO_4^-$, R'=Et, X=$ClO_4$), and the 6-chloro-derivatives of it and of III (Y=NEt, Z=Se, R=$(CH_2)_3\overset{+}{N}EtMe_2ClO_4^-$, R'=Et, X=$ClO_4$) were described.[53]

G. Thiazolino-2'-carbocyanines

The thiazolino-2'-carbocyanine, XII (Y=S, Z=CH:CH, R=Me, R'=Et, X=I), was prepared by boiling 2-formylmethylene-3-methylthiazolidine and quinaldine ethiodide in acetic anhydride for 7 minutes (see section 6-I).[39]

H. Benzimidazolothiazolino- and Indothiazolo-carbocyanines

The patent contained twenty-five examples of benzimidazolothiazolinocarbocyanines, of which the simplest were XII (Y=S, Z=NMe, R=Et, R'=Me or Et, X=SO_4Et); others had one or more sub-

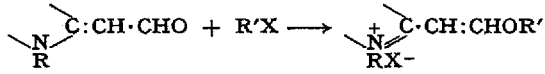
stituents in the benzimidazole nucleus, with various acid radicals.[50] The di-ionic XII (Y=S, Z=NMe, R=Et, R′=$(CH_2)_3\overset{+}{N}Me_3ClO_4^-$, X=$ClO_4$), and the 6-chloro-derivatives of it and of XII (Y=S, Z=NEt, R=Et, R′=$(CH_2)_3\overset{+}{N}EtMe_2ClO_4^-$, X=$ClO_4$) were described.[53]

The indothiazolocarbocyanine, XI (Y=S, Z=CMe_2, R=R′=Me, R″=NH_2, X=I) was arrived at through 4-amino-2-methylthiazole methiodide.[40]

9. From a Quaternary Salt, Having a Reactive Methyl Group, and a Quaternary Salt, Having the Group ·CH:CHOR

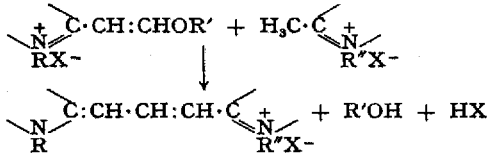
A. General

It was noted[54] in 1946 that a heterocyclic compound having the group :CH·CHO (section 8) was converted by heating with an ester into a quaternary salt having the group ·CH:CHOR, as in equation 11.



(11)

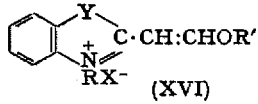
These salts crystallised well, whereas the compounds from which they were derived tended to be oily. Salts belonging to the benzothiazole and benzoselenazole series were prepared by heating a formylmethylene compound with alkyl sulphate in benzene; heating with methyl iodide in a sealed tube also effected salt formation. Such a salt could be condensed with another, having a reactive methyl group, to give a carbocyanine, as in equation 12.



(12)

B. Thia-4′-carbocyanine

The thia-4′-carbocyanine, V (Y=S, R=R′=Et, X=I), was prepared by heating XVI (Y=S, R=Et, R′=Me, X=SO_4Me) with



(XVI)

lepidine ethiodide and triethylamine in acetic anhydride at 100° for 10 minutes, followed by potassium iodide.[54]

C. Oxaselena- and Oxathia-carbocyanines

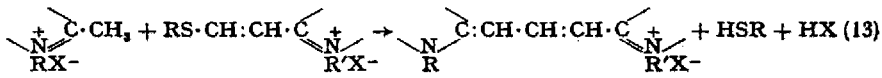
The oxaselenacarbocyanine, III (Y=O, Z=Se, R=R′=Et, X=SO_4Me), was similarly prepared from XVI (Y=Se, R=Et, R′=Me, X=SO_4Me) and 2-methylbenzoxazole ethoethylsulphate.[54]

The oxathiacarbocyanine, III (Y=O, Z=S, R=R′=Et, X=I), was prepared from XVI (Y=S, R=Et, R′=Me, X=SO_4Me) and the same 2-methylbenzoxazolium salt, followed by potassium iodide.[54]

10. From a Quaternary Salt, Having a Reactive Methyl Group, and a Quaternary Salt, Having the Group ·CH:CH·SR

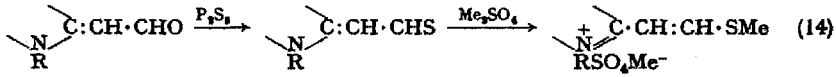
A. General

The observation that a quaternary salt having a reactive methyl group could be condensed with one having the group ·CH:CH·SR to give unsymmetrical trimethincyanines was made independently in Germany and in England.[55,56] The course of the reaction is indicated in equation 13.



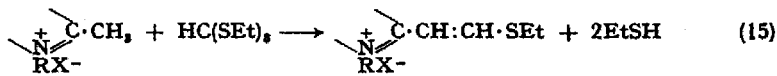
(13)

The German chemists prepared the β-alkylthiovinyl salts by boiling a heterocyclic base, having a formylmethylene group, with phosphorus pentasulphide in benzene and subsequently treating the thioaldehyde with an ester such as methyl sulphate, as in equation 14.



(14)

The resultant salts included members of the indolenine, benzothiazole, benzoselenazole, and thiazoline series.[57] The alternative method was to prepare them by heating a quaternary salt, preferably alkotoluene-*p*-sulphonate, with alkyl orthothioformate in acetic anhydride for 30 minutes; further series included benzoxazole and 2- and 4-linked quinoline.[58,59] The reaction is as in equation 15.



(15)

The examples of the German work covered six types of trimethincyanines and those of the British patent nine, of which only one type was duplicated.

B. 2,4′-Carbocyanines

To prepare the 2,4′-carbocyanine, I, quinaldine and ethyl toluene-*p*-sulphonate were heated together at 140–150° for 3 hours, the salt was dissolved in acetic anhydride containing ethyl orthothioformate and boiled for 30 minutes; after adding lepidine ethiodide and triethylamine, heating was continued for 20 minutes; the dye was recrystallised from methanol.[56, 59]

C. Indo-2′-, Oxa-2′-, and Thia-2′-carbocyanines

An indo-2′-carbocyanine, III (Y=CMe_2, Z=CH:CH, R=Me, R′=Et, X=I), but having a 5-methyl group in the indolenine nucleus, was prepared by this method.[55]

To prepare the oxa-2′-carbocyanine, III (Y=O, Z=CH:CH, R=Et, R′=Me, X=I), the ethylthiovinyl salt, XVII (Y=CH:CH, R=Me, R′=Et, X=I), was condensed with 2-methylbenzoxazole ethiodide.[56]

A thia-2′-carbocyanine, III (Y=S, Z=CH:CH, R=Me, R′=Et, X=I), but having a 6-methyl group in the quinoline nucleus, was prepared by heating 2-methylbenzothiazole methotoluene-*p*-sulphonate with ethyl orthothioformate in acetic anhydride, followed by condensation with *p*-toluquinaldine ethiodide.[56, 59]

D. Thia-4′-carbocyanines

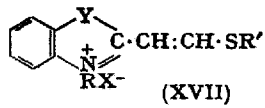
Condensation of the same ethylthiovinyl salt with lepidine ethiodide, by boiling with triethylamine in acetic anhydride, gave the thia-4′-carbocyanine, V (Y=S, R=Me, R′=Et, X=I).[56]

E. Thiacarbocyanines

The symmetrical thiacarbocyanine, III (Y=Z=S, R=R′=Et, X=I), was prepared by heating together first 2-methylbenzothiazole and ethyl toluene-*p*-sulphonate, further with addition of ethyl orthothioformate and acetic anhydride, and finally with 2-methylbenzothiazole ethiodide.[56]

F. Benzimidazoloindo-, Indoselena-, Indothia-, Indoxa-, Oxaselena-, and Oxathia-carbocyanines

In preparing three derivatives of the benzimidazoloindocarbocyanine, III (Y=NEt or NMe, Z=CMe_2, R=Me, X=ClO_4), a 2-methylbenzimidazolium salt was heated with XVII (Y=CMe_2, R=R'=Me, X=ClO_4) in pyridine containing triethylamine.[55]



(XVII)

An indoselenacarbocyanine and an indothiacarbocyanine, III (Y=CMe_2, Z=Se or S, R=Me, R'=$\cdot CH_2CH_2CO_2H$, X=ClO_4), were prepared by use of XVII (Y=CMe_2, R=R'=Me, X=ClO_4),[55] and another dye of the latter type was prepared by the alternative route through XVII (Y=S, R=Me, R'=Et, X=I).[56]

For preparing two indoxacarbocyanines of type III (Y=CMe_2, Z=O, X=ClO_4), the methylthiovinyl salt of the indolenine series, XVII (Y=CMe_2, R=R'=Me, X=ClO_4), and its 5-methyl derivative, respectively, were condensed with substituted 2-methylbenzoxazolium salts.[55]

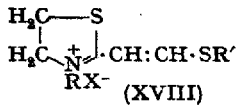
The oxaselenacarbocyanine, III (Y=O, Z=Se, R=R'=Et, X=I), was prepared by boiling 2-methylbenzoselenazole ethotoluene-*p*-sulphonate with ethyl orthothioformate in acetic anhydride for 30 minutes, adding 2-methylbenzoxazole and triethylamine, and heating for another 15 minutes; the yield before recrystallisation was 20 %.[56, 59]

The oxathiacarbocyanine, III (Y=O, Z=S, R=R'=Me, X=I), was obtained crude in 58 % yield by boiling together XVII (Y=S, R=Me, X=I) and 2-methylbenzoxazole methiodide in pyridine for one hour. An analogue was prepared by heating 2-methylbenzothiazole methotoluene-*p*-sulphonate with ethyl orthothioformate in acetic anhydride, followed by addition of 2-methylbenzoxazole ethiodide and triethylamine and further heating; another was made by an alternative route in which the ethylthiovinyl salt was of the benzoxazole series.[56, 59]

G. Oxa- and Thia-thiazolinocarbocyanines

A methylthiovinyl salt of the thiazoline series, XVIII (R=Et, R'=Me, X=ClO_4), was used for preparing the 5,6-dimethyl derivative

of the oxathiazolinocarbocyanine, XII (Y=S, Z=O, R=Et, R'=·$CH_2CH_2CO_2H$, X=ClO_4), by heating it with the 2,5,6-trimethylbenzoxazolium salt in pyridine at 100° for 45 minutes.[55]

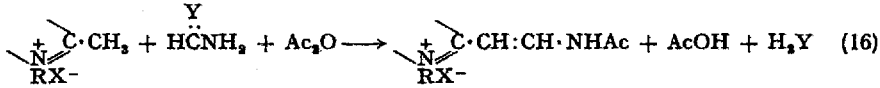


(XVIII)

The thiathiazolinocarbocyanine, XII (Y=Z=S, R=R'=Me, X=I), was prepared in 37 % yield by boiling 2-methylthiazoline methotoluene-*p*-sulphonate with ethyl orthothioformate in acetic anhydride for 30 minutes, adding 2-methylbenzothiazole methiodide and triethylamine to the solution of the ethylthiovinyl salt, boiling for 10 minutes, and recrystallising the dye from methanol.[56, 59]

11. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of Formamidoxime, Formamide, or Thioformamide

The best quaternary salts for this reaction were alkotoluene-*p*-sulphonates. By heating such a salt, having a reactive methyl group, with formamidoxime, formamide, or thioformamide, for 45 minutes, in acetic anhydride solution, a salt with an acetamidovinyl group was produced, as in equation 16 (where Y=NOH, O, or S).



(16)

These salts are the same as those prepared by use of ethyl formimino ether hydrochloride or diphenylformamidine (see sections 5 and 6). Quinaldinium, 2-methylbenzoxazolium, or 2-methylbenzothiazolium salts were used in their preparation. With thioformanilide, which was better than formamide or thioformamide for giving symmetrical trimethincyanines (see IV-12), an intermediate salt of this type was not isolated.[60]

12. 4'-Carbocyanines by Cleavage of Carbocyanines with Quaternary Salts

A. General

The first observation of the cleavage of the chain of a trimethincyanine by means of a quaternary salt was made when heating a 4,4'-tri-

methincyanine and lepidine ethiodide in acetic anhydride led to a 4,4′-methincyanine (see II-6-E). On the other hand, higher yields of 4′-carbocyanines were obtained by heating this 4,4′-carbocyanine with various quaternary salts in pyridine. Other media could also be used. It was concluded that the $\alpha\beta$-linking of the trimethin chain was more easily broken than the linking between the α-carbon atom and the nucleus. A thiacarbocyanine and a 2,2′-pyridocarbocyanine were also disrupted, by heating with lepidine ethiodide in pyridine, to give unsymmetrical 4′-carbocyanines, as also were a couple of unsymmetrical carbocyanines (see also XIV-3-G).[61] As the reaction temperatures, 160–170°, were considerably above the boiling points of the media used, the reactions must presumably have been carried out in sealed tubes.

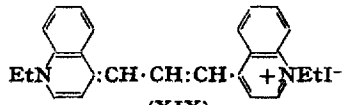
B. 2,4′-Carbocyanine

The unsymmetrical 2-pyrido-2′-carbocyanine, VII (R=Me, R′=Et, X=I) (1 mol.), was heated for 1 hour at 155–160° with lepidine ethiodide (2 mols.) in pyridine (10 c.c. per g. of dye). The product was washed with ether. By treatment with methanol, the less soluble starting-point was removed and evaporation of the filtrate gave the 2,4′-carbocyanine, I (R=R′=Et, X=I), which, after two recrystallisations from methanol, resulted in 4 % yield.[61]

C. Indo-4′-, Selena-4′-, and Thia-4′-carbocyanines

The indo-4′-carbocyanine, V (Y=CMe_2, R=Me, R′=Et, X=I), was prepared by heating the 4,4′-carbocyanine, XIX, and 2,3,3-trimethylindolenine methiodide with acetic acid at 160–170° for 1 hour, and was obtained in 13 % yield after recrystallisation. Acetic anhydride or pyridine could also be used.[61]

The selena-4′-carbocyanine, V (Y=Se, R=R′=Et, X=I), was prepared by heating XIX and 2-methylbenzoselenazole ethiodide in

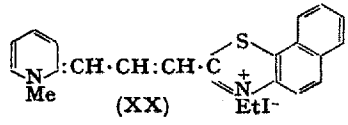


(XIX)

acetic anhydride at 160–165° for 8 minutes. After washing with ether, and repeated recrystallisation from ethanol, it was obtained in 15 %

yield. Other possible media were acetic acid, pyridine, or alcohol containing piperidine.[61]

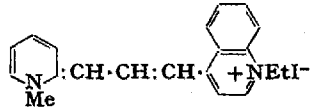
The thia-4'-carbocyanine, V (Y=S, R=R'=Et, X=I), was obtained in two ways. According to the first, XIX (1 mol.) and 2-methylbenzothiazole ethiodide (2 mols.) were heated with pyridine (10 c.c. per g. of dye) at 160–165° for 8 minutes; the yield of recrystallised product was 24 %: thiacarbocyanine was a by-product. Here again, acetic anhydride, acetic acid, or piperidine in ethanol could be used. According to the second method, the symmetrical thiacarbocyanine, III (Y=Z=S, R=R'=Et, X=I), lepidine ethiodide, and pyridine were heated at 160–165° for 1 hour. The ether-washed product was treated with ethanol to remove thiacarbocyanine; the more soluble thia-4'-carbocyanine was isolated by concentration of the filtrate, washing with chlorobenzene, and recrystallising from ethanol, in 13 % yield. Acetic anhydride could not be used as medium. The 6,7-benzo-derivative of the thia-4'-carbocyanine, V (Y=S, R=R'=Et, X=I), was one of two dyes which resulted on heating XX with lepidine ethiodide and pyridine.[61]



(XX)

D. 2-Pyrido-4'-carbocyanine

The 2-pyrido-4'-carbocyanine, XXI, was obtained, in 10 % yield after recrystallisation, by heating 1,1'-dimethyl-2,2'-pyridocarbocyanine iodide with lepidine ethiodide and pyridine at 160–170° for 30 minutes. The ether-washed product was treated with ethanol, the less-soluble 4,4'-carbocyanine was removed, and concentration of the filtrate gave XXI.[61]



(XXI)

Some of the physical properties of various typical unsymmetrical trimethincyanines have been summarised in Tables I and II. Table I is of necessity composite, because sometimes patents give sensitising data without other properties, whilst scientific papers may omit sensitising properties: it has only occasionally been possible to find all the data for a particular dye.

TABLE I. Some Properties of Some Unsymmetrical Trimethincyanines

Nature of carbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum(Å)	Sensitising (Å) Maximum	Extent	Ref.
2,4′-	I	needles, green lustre	240–241	6560	6950	7500	7, 18, 62
Benzimidazolo-2′-	III (Y=NPh, Z=CH:CH, R=R′=Et, X=SO_4Et[a])	—	—	—	6000	6500	50
Indo-2′-	III (Y=CMe_2, Z=CH:CH, R=R′=Et, X=ClO_4)	black	247–248	5610	—	—	20
Oxa-2′-	III (Y=O, Z=CH:CH, R=R′=Et, X=I)	dull bluish	248–250	5450	5800	—	18, 20, 21
Selena-2′-	III (Y=Se, Z=CH:CH, R=R′=Et, X=I)	—	—	5820	—	—	18
Thia-2′-	III (Y=S, Z=CH:CH, R=R′=Et, X=I)	lustrous green	276–277	5780	6100	—	21, 23
Indo-4′-	V (Y=CMe_2, R=R′=Et, X=ClO_4)	dull with greenish reflex	226–227	6040	—	—	20
Oxa-4′-	V (Y=O, R=R′=Et, X=I)	blue needles, green reflex	260–262	5960	—	—	18, 20
Selena-4′-	V (Y=Se, R=R′=Et, X=I)	—	—	6320	—	—	18
Thia-4′-	V (Y=S, R=R′=Et, X=I)	green needles	262–265	6300	—	—	18, 20
Indoselena-	III (Y=CMe_2, Z=Se, R=Me, R′=$CH_2CH_2CO_2H$, X=ClO_4)	—	—	5500	—	—	55
Indothia-	III (Y=CMe_2, Z=S, R=R′=Et, X=I)	blue	252–253	5420	—	—	20
Indoxa-	III (Y=CMe_2, Z=O, R=R′=Et, X=I)	green reflex	266–267	5080	5500[b]	5950[b]	20, 36

(Table continued)

TABLE I *(continued)*

Nature of carbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
Oxaselena-	III (Y=O, Z=Se, R=R′=Et, X=I)	purple[c]	257–258[c, d]	5270	5700[c]	6000[c]	18, 31
Oxathia-	III (Y=O, Z=S, R=R′=Et, X=I)	blue	260–262	5200	—	6400	11, 18, 20
Selenathia-	III (Y=Se, Z=S, R=R′=Et, X=I)	green[e]	254–255[d, e]	5620	6500[e]	6720[e]	18, 33
Benzimidazoloindo-	III (Y=NPh, Z=CMe_2, R=Et, R′=Me, X=I)	—	—	—	5400	—	51
Benzimidazolo-oxa-	III (Y=NPh, Z=O, R=R′=Et, X=SO_4Et[f])	—			5250	5500	51
Benzimidazolo-selena-	III (Y=NPh, Z=Se, R=R′=Et, X=SO_4Et[g])	—	—	—	5670	6000	51
Benzimidazolothia-	III (Y=NPh, Z=S, R=R′=Et, X=SO_4Et)	—	—	—	5550	5850	51

[a] 6-Cl in benzimidazole nucleus.

[b] Sensitising data for VII (R=Me, R′=Et).

[c] Appearance, m.p., sensitising for dye with 5-CO_2Me in benzoxazole nucleus.

[d] Decomp. not recorded.

[e] Appearance, m.p., sensitising for dye with 5-CO_2Me in benzoxazole and 5-Me in benzoselenazole nucleus.

[f] 5,6-benzo in benzoxazole nucleus.

[g] 5-Cl in benzimidazole nucleus.

TABLE II. Some Properties of Some Unsymmetrical Trimethincyanines Having One or Two Monocyclic Nuclei

Nature of carbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
2-Pyrido-2'-	VII (R=Me, R'=Et, X=I)	—	269	—	—	—	12
Thiazolo-2'-	XI (Y=S, Z=CH:CH, R=R''=Me, R'=Et, X=I)	—	—	—	6100	—	21
Thiazolino-2'-	XII (Y=S, Z=CH:CH, R=R'=Et, X=I)	brownish needles	—	—	5550	6050	39
Oxaoxazolo-	XI (Y=Z=O, R=R'=Et, R''=H, X=ClO_4)	orange-brown leaflets	236	4600	—	—	46
Thiathiazolo-	XI (Y=Z=S, R=R'=Et, X=I[a])	bronze needles	195[b]	5600	—	—	45
Oxathiazolino-	XII (Y=S, Z=O, R=R'=Et, X=I)	orange	—	—	4900	5300	39
Selenathiazolino-	XII (Y=S, Z=Se, R=Me, R'=Et, X=I)	blue and green	—	—	5450	6000	39
Thiathiazolino-	XII (Y=Z=S, R=Me, R'=Et, X=I)	garnet-red needles	—	—	5400	5800	39
Oxazolothiazolino-	XIV (R=Et, R'=Me, X=I[c])	orange-red needles	241	—	4610	—	46

[a] Thiazole nucleus has 4-Ph-5-*p*-tolylthio-substituents.

[b] Decomp. not recorded.

[c] Oxazole nucleus has 4,5-diPh.

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CHAPTER VI

Trimethincyanines with Substituents on the Chain

1. General Survey

The first instance of a trimethincyanine with a substituted chain was recorded in 1920. When a solution of pinacyanol nitrate in dilute nitric acid was warmed to 60°, an orange-red colour suddenly appeared and, on cooling, red crystals separated: they were converted to bromide. The product was identified as a derivative in which two nitro-groups were attached to the chain of the 2,2′-carbocyanine, probably, because of the stability of the compound, by substitution rather than by addition.[1] This type of compound remains an isolated instance.

In 1923 it was found that the method for preparing symmetrical carbocyanines that involved the use of a trihalogenomethane (see IV-3) could be modified and, through benzotrichloride, there was prepared a 2,2′-carbocyanine with a *meso*-phenyl group on the chain,[2,3] a method which has been developed a little (section 2).

In 1928 the preparation of symmetrical carbocyanines by condensing a quaternary salt having a reactive methyl group with ethyl orthoformate in the presence of pyridine (see IV-6) was extended, by means of ethyl orthoacetate, to give *meso*-methylthiacarbocyanines, which were sensitisers to green light.[4] In the following year, *meso*-methyl-6,7,6′,7′-dibenzothiacarbocyanines were prepared by reaction of ethyl orthoacetate and pyridine with the appropriate alkiodides; the method failed with the 2-methyl-4,5-benzobenzothiazole alkiodides[5] but by use of quaternary salts other than iodides the dyes were obtained.[6] The scope of the method was enormously extended by use of ortho-esters other than ortho-acetates, so that various alkyl groups, which might be substituted, and also phenyl groups, were introduced into the *meso*-position of the thiacarbocyanine chain. It was noted that replacement of the *meso*-hydrogen atom by a methyl group caused a hypsochromic shift of 150 Å in the absorption maximum. Replace-

ment of the methyl by an ethyl group caused a bathochromic shift of 50 Å but higher groups produced no further shift. Replacement of the *meso*-hydrogen by a benzyl group caused a hypsochromic shift of 75 Å and by a phenyl group a bathochromic shift of 25 Å. The results were similar in the 4,5,4',5'- and 6,7,6',7'-dibenzo-series and also with selenacarbocyanines. The *meso*-substituted dyes sensitised[6] and the extensive patent literature testifies to the usefulness both of the method and of the dyes (see section 3).

By use of a mixture of solvents, a *meso*-methyloxacarbocyanine was attained by the ortho-ester method. Thus a 2-methylbenzoxazolium salt (2 mols.) and excess of ethyl orthoacetate (4 mols.) were boiled in pyridine containing triethylamine (1 mol.);[7] this method was applied to analogues.[6] Another recommended solvent mixture consisted of pyridine and acetic anhydride; thus whilst a 75 % yield of washed thiacarbocyanine resulted on heating a 2-methylbenzothiazolium salt with pyridine and ethyl orthoacetate, the addition of a few drops of acetic anhydride led to a 92 % yield.[8] In a paper published in 1952, acetic anhydride with a few drops of pyridine was used for one thiacarbocyanine preparation and pyridine with a few drops of acetic anhydride for another[9] but without control experiments.

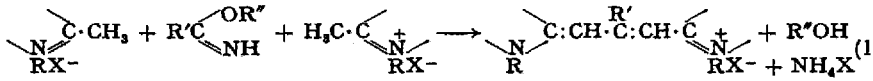
Oxacarbocyanines differed from thia- and selena-carbocyanines in that introduction of a *meso*-methyl group caused a bathochromic shift of the absorption maximum.[6] In 1953 it was suggested that the hypsochromic shifts caused by the introduction of *meso*-alkyl groups into thia- and selena-carbocyanines might be due to the hyperconjugative effect of the alkyl, whilst the corresponding bathochromic shift in oxacarbocyanines might be caused by hydrogen-bonding.[10]

A patent of 1930 described the preparation of *meso*-substituted carbocyanines by heating two molecular proportions of a quaternary salt having a reactive methyl group with at least two of an acid anhydride, in the presence of an acid-binding agent, such as sodium acetate. The dye which resulted from 2-methylbenzothiazole ethiodide, sodium acetate, and acetic anhydride was identified with the *meso*-methylthiacarbocyanine prepared by the use of ethyl orthoacetate (see section 3). It was supposed that the *meso*-methyl group was derived from the acetic anhydride (cf. section 9). In one example sodium formate took the place of sodium acetate and benzoic anhydride the place of acetic anhydride. The method was applied to series other than thiacarbocyanines.[11]

According to another early patent, dye formation occurred when a methylene base derived from, e.g., a 2-methyl-indoleninium or -benzothiazolium salt was heated with carbon tetrachloride or tetrabromide at 100–110° for 8 hours,[12] but the nature of the products was not determined.

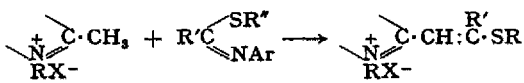
The same applies to a sensitising dye made by heating 2-methylbenzoselenazole ethiodide with ethyl orthocarbonate and piperidine in ethanol.[13] Subsequently 2-methylbenzothiazole ethiodide, also its 6-methyl and 6-ethoxy-derivatives, were heated with methyl orthocarbonate in pyridine, and the three products were formulated as having a *meso*-methoxy-group,[14] but the absorption maxima could well be those of the *meso*-methyl dyes. It has been stated that *meso*-alkoxy-dyes (see section 15) are not thus obtainable.[15] This was confirmed in 1950 when the four products, obtained by condensing each of four 2-methylbenzothiazolium salts with methyl orthocarbonate in pyridine, were identified with the *meso*-methylthiacarbocyanines prepared by interaction of ethyl orthoacetate in pyridine on the same four salts.[16]

According to a patent of 1932, a quaternary salt having a reactive methyl group could be condensed with an imino ester, HN:CR′(OR″), to give *meso*-substituted symmetrical carbocyanines, as in equation 1.



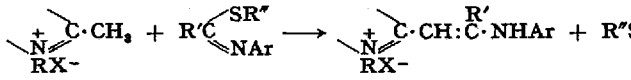
(1)

The examples and samples were all thiacarbocyanines, whilst substituents included *meso*-alkyl and -phenyl groups.[17] The method was later used to introduce *meso*-(alkylthio)methyl groups (see section 4).[18] Use of an iminothio-ester, ArN:CR′(SR″), to give similarly *meso*-substituted symmetrical carbocyanines was also patented in 1932; these esters could further be used to form intermediate compounds and hence *meso*-substituted unsymmetrical carbocyanines,[19] the formation of the intermediate salts being indicated by equation 2.



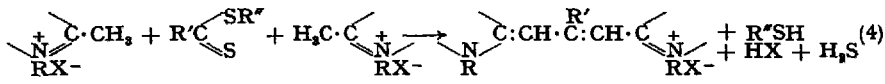
(2)

In a patent of 1946, however, it was stated that improved yields resulted if the anilo-group of the ester ArN:CR′(SR″) contained a *p*-halogen atom[20] and the formation of the intermediate salts was represented as in equation 3 (see section 5).

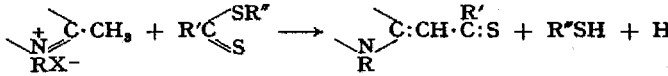


(3)

In 1949 it was recorded that reaction of a dithiocarboxylic ester, S:CR′(SR″), with a 2-methyl-benzothiazolium or -thiazolinium quaternary salt gave symmetrical *meso*-alkylcarbocyanines of these two series (equation 4); at the same time thioketones having the group :CH·CR′:S were formed[21] (equation 5) (see section 6):



(4)



(5)

In instances where a quinaldinium, a lepidinium, or a 4-phenylthiazolium salt, respectively, were treated with methyl dithioacetate and triethylamine in ethanol, only the corresponding thioketone was isolated.[21]

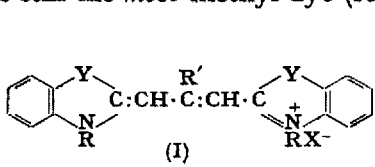
By heating a quaternary salt having a reactive methyl group with an alkyl imino-carbonate or -dithiocarbonate, i.e., $HN:C(OR)_2$ or $HN:C(SR)_2$, in the presence of a solvent, there resulted, according to a patent of 1932, carbocyanines with a *meso*-alkoxy- or a *meso*-alkylthio-group. The examples included 2,2′-, thia-, and selena-carbocyanines.[22] Later work, however, led to the conclusion that the products were mainly *meso*-alkyl dyes.[23]

A considerably later patent claimed the preparation of *meso*-(alkylthio)carbocyanines from 2 mols. of a heterocyclic base, having a reactive methyl group, at least 3 mols. of alkyl toluene-*p*-sulphonate, and not more than 1 mol. of alkyl dithiocarbamate, S:CNRR′(SAlk); the examples comprised oxa- and thia-carbocyanines (see section 7).[24]

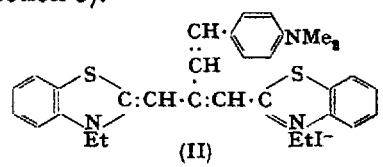
According to an interesting publication in 1935, a *meso*-methylthiacarbocyanine resulted in 4 % yield when 2-methylbenzothiazole ethiodide was heated in pyridine, but when triethylamine or piperidine was also present, the yield was 56 %. The method was applied also to salts of 2-methylbenzoselenazole and, in a modified form, to salts of 2-methylbenzoxazole. In this reaction, part of the salt decomposes to give the CMe group which forms the centre of the chain (see section 8).[7,25] Many years later, there was described the preparation of two *meso*-

methylthiacarbocyanines, in 32 % and 53 % yields, by heating a 2-methylbenzothiazolium salt with diphenylacetamidine in 2-picoline or in a mixed pyridine base,[26] this being a modification of the method (see IV-9) in which diphenylformamidine was used, generally in conjunction with acetic anhydride. There were also described similar preparations of *meso*-methylthiacarbocyanines having 6,6'-dimethoxy-, 6,6'-dichloro-, or 4,5,4',5'-dibenzo-substituents, in yields varying from 7–30 %, and of a *meso*-methylselenacarbocyanine in 16 % yield.[26] In view of the method of 1935, it would seem that further work is needed in order to establish whether, in the later method, the diphenylacetamidine does in fact contribute the central CMe group of the chain.

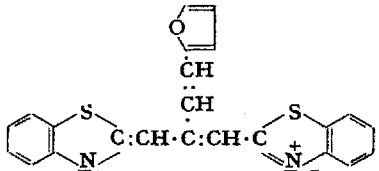
Just as sodium formate could be used instead of ethyl orthoformate (see IV-6-A), so, in 1936, the use of potassium acetate in place of ethyl orthoacetate was described: certain *meso*-methylthiacarbocyanines were made by heating a 2-methylbenzothiazolium salt with potassium acetate in acetic anhydride.[27] When potassium propionate or potassium benzoate was used, in conjunction with acetic anhydride, the product was still the *meso*-methyl dye (see section 9).[28]



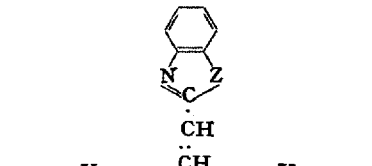
(I)



(II)



(III)

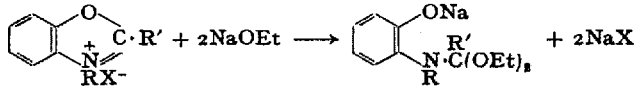


(IV)

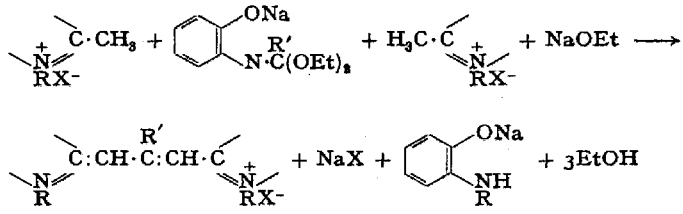
A very important observation was that of the reactivity of the *meso*-methyl group of a thiacarbocyanine such as I (Y=S, R=Et, R'=Me, X=I), as evidenced by its condensation with various aldehydes, whereby derivatives such as II and III were obtained.[27] The method was later improved and extended (see section 10). Certain meso-methylcarbocyanines were condensed with heterocyclic aldehydes, or their anils, to give dyes such as IV, but these could not be converted

into quaternary salts, so that an attempt thus to synthesise di-ionic trinuclear dyes with the chain ·CH:C<CH:/CH:CH· (see XV-3-A) was unsuccessful.[29]

Certain methods of preparing cyanines are of intrinsic interest. One such, patented in 1933, was the preparation of *meso*-substituted symmetrical thiacarbocyanines by heating an alcoholic solution of a 2-methylbenzothiazolium salt and of a 2-substituted benzoxazolium salt with alkali, whereby the 2-substituent of the benzoxazole salt appeared in the *meso*-position of the resultant thiacarbocyanine. The benzoxazolium salt was split by the alkali to give the acetal of a substituted amide (equation 6), and this acetal reacted with the 2-methylbenzothiazolium salt (equation 7). The same method was applied to

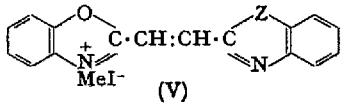


(6)



(7)

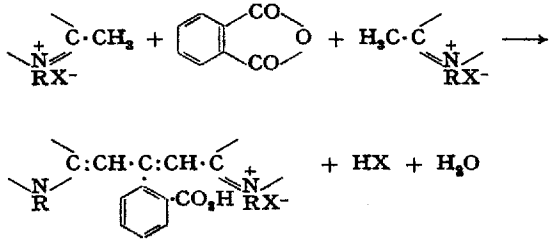
the preparation of *meso*-substituted selenacarbocyanines.[30] In the original patent, the molecular proportions of benzoxazolium salt to benzothiazolium salt to sodium ethoxide were in the ratio 1:2:2, whereas in fact they should be 1:2:3, since 2 mols. of sodium ethoxide are required for the fission (equation 6) and 1 mol. for the condensation (equation 7). With these proportions, the *meso*-pentadecylthiacarbocyanine was obtained in 26 % yield after recrystallisation and the *meso*-undecyl analogue in 40 % yield, but nuclear substituted derivatives of both resulted in poorer yields. Through a 2-*p*-dimethylaminostyrylbenzoxazolium salt, there was obtained the *meso*-substituted thiacarbocyanine, II; through the 2-substituted benzoxazolium salts, V



(V)

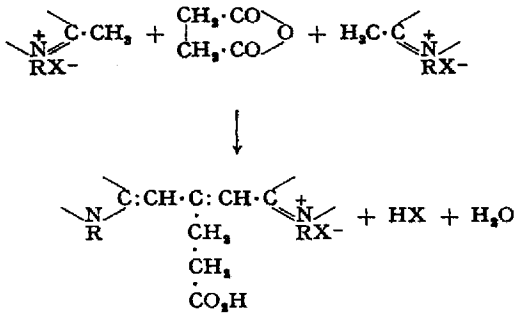
(Z=S or CH:CH), there resulted the *meso*-substituted thiacarbocyanines, IV (Y=S, Z=S or CH:CH), but in very low yields (see section 11).[29]

Another interesting method, patented in 1940, consisted in heating a 2-methylbenzothiazolium salt with a large excess of phthalic anhydride in pyridine, and this gave a symmetrical thiacarbocyanine with a *meso*-*o*-carboxyphenyl group (equation 8). The carboxy-group



(8)

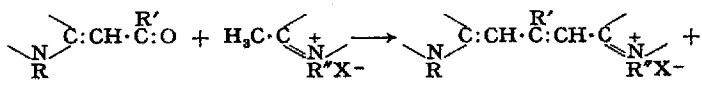
could be esterified. The method was also applied in other series, whilst use of succinic anhydride, instead of phthalic anhydride, gave a *meso*-*β*-carboxyethylthiacarbocyanine (equation 9).



(9)

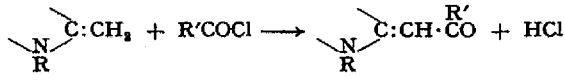
Some of the dyes were photographic sensitisers (see section 12).[31]

By condensation of heterocyclic ketones, possessing an acylmethylene group, with quaternary salts, having a reactive methyl group, unsymmetrical, as well as symmetrical *meso*-substituted carbocyanines were obtained (equation 10) (see section 13):



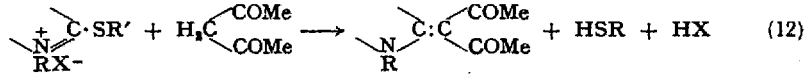
(10)

Such ketones were prepared, firstly, by treating the methylene base from a heterocyclic quaternary salt, having a reactive methyl group, with an acid halide or anhydride (equation 11).[32]



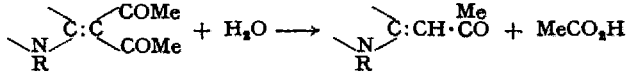
(11)

Those of the benzothiazole or benzoselenazole series were made by reaction, at a low temperature, of an acyl chloride and a 2-methyl quaternary salt in the presence of pyridine.[33] A later method, which was applied to the preparation of ketones of the 2- and 4-quinoline, as well as of the benzothiazole, series consisted in condensing a quaternary salt having a reactive alkylthio-group with acetylacetone, by



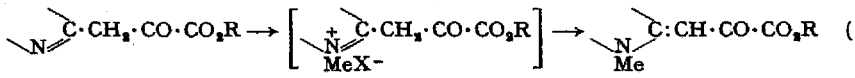
(12)

heating with triethylamine in ethanol (equation 12) and hydrolysing the diacetyl product by heating with concentrated hydrochloric acid, and then making alkaline (equation 13).



(13)

Yields of 67–89 % were quoted, dropping to 28–52 % on recrystallisation.[34] In the benzothiazole series, ketones with the group $:CH\cdot CO\cdot CO_2Et$ or $:CH\cdot CO\cdot CO_2H$ were obtained by alkylation of bases with the group $\cdot CH_2\cdot CO\cdot CO_2R$ (equation 14).



(14)

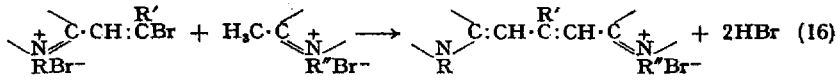
The ketone with the group $:CH\cdot CO\cdot CO_2Et$ could be condensed with salts having a reactive methyl group to give *meso*-carbethoxycarbocyanines.[35]

By the action of phosphorus oxyhalide in benzene on the ketones, there were obtained β-halogenovinyl salts (equation 15).[36]



(15)

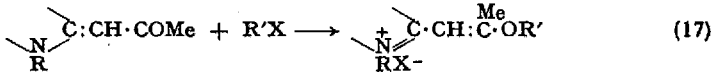
Such salts could be condensed with salts having a reactive methyl group to give *meso*-substituted carbocyanines (equation 16).[36]



(16)

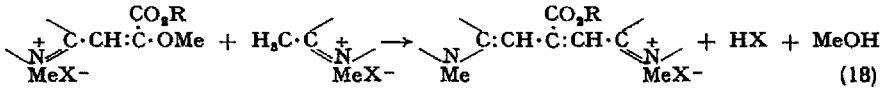
The method was applied to the preparation of thiacarbocyanines having a *meso*-*p*-hydroxyphenyl group.[37]

By heating ketones, of the benzothiazoline or indoline series, having the group :CH·COMe, with alkyl toluene-*p*-sulphonate, they were converted into salts (equation 17),



(17)

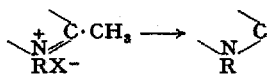
from which halides could be made.[38] Such salts, through their reactive methyl group, were used for preparing *meso*-alkoxycarbocyanines (see section 15). On the other hand, ketones with the group :CH·CO·CO_2R were converted into quaternary salts with the group ·CH:C(CO_2R)(OMe) and these were used, in virtue of the reactivity of the alkoxy-group, to prepare carbocyanines with a *meso*-carbethoxy- or -carboxy-group (see section 13) (equation 18).[35]



(18)

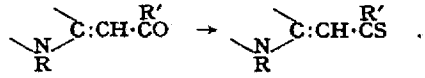
A thiacarbocyanine with an α-carbethoxy-group was prepared by treating the corresponding base (see XI-10-B) with alkyl iodide.[39]

Unlike the heterocyclic ketones, thioketones comprising the group :CH·CSR′ and belonging to the benzothiazoline and benzoselenazoline series, were not used directly in the synthesis of *meso*-substituted carbocyanines, but were useful indirectly. The thioketones were prepared in the following ways. The first consisted in heating a quaternary salt, having a reactive methyl group, with an acyl chloride and phosphorus pentasulphide in pyridine,[40] whereby

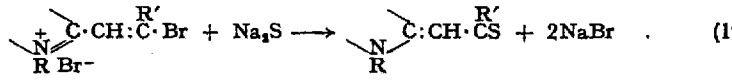


The same result could be effected by heating with a thio-acid, R′·CO·SH, in pyridine.[41] In a third process, thioketones were obtained directly from

the ketones by heating with phosphorus pentasulphide in pyridine,[42] whereby



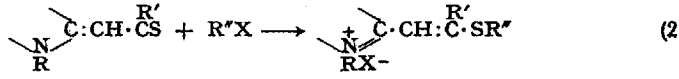
Fourthly, they were prepared from halogenovinyl salts by the action of alkali sulphide (equation 19) or thiosulphate[43] or of a thioamide.[44]



(19)

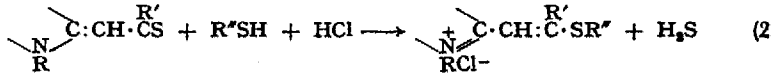
They included compounds in which the substituent R′ was a cycloalkyl group.[45]

Quaternary salts, prepared from thioketones by heating with such compounds as benzyl bromide, were first described in 1940 and formulated as having the group $:CH\cdot\overset{R'R''}{\overset{|}{C}}:SX$.[46] The reaction is better represented as in equation 20.



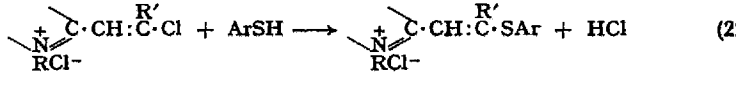
(20)

The thioketones prepared by the use of thio-acids, R′·CO·SH (preceding paragraph), were forthwith converted to such salts by means of alkyl iodides at room temperature.[41] Salts of this type were also prepared, in yields varying from 23–93 %, by the protracted action of alkyl mercaptan and dry hydrochloric acid on the thioketones in methanol,[47] as in equation 21.



(21)

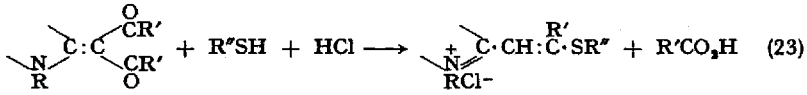
2-β-Arylthiovinyl salts of the benzothiazole and benzoselenazole series were prepared from salts having a 2-β-halogenovinyl group, by the action of aryl mercaptan and triethylamine in alcohol,[48] as in equation 22.



(22)

A method, which was applied to the preparation of salts of the benzothiazole, 2-linked quinoline, and indolenine series, consisted in the

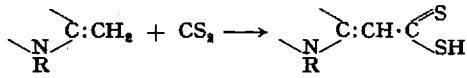
reaction of a heterocyclic base, having a diacylmethylene group, with alkyl mercaptan and a strong acid in an alcohol. Less soluble by-products were filtered off.[49] The net result may be represented as in equation 23.



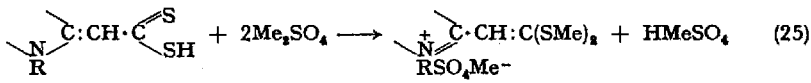
(23)

The higher vinylene homologues of salts of this type were similarly made (see VII-8-A).

Heterocyclic quaternary salts having the group $\cdot CH{:}C(SR')_2$ and representative of the benzothiazole, benzoselenazole, and 2-quinoline series, were described in 1940.[23] They were obtained by the action, over several days, of a heterocyclic methylene base with carbon disulphide, in ethanol or benzene, and heating the product with alkyl sulphate (equations 24 and 25).

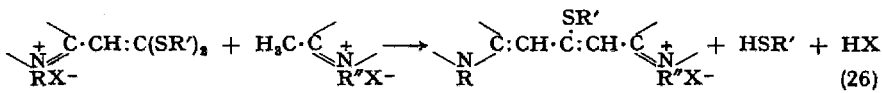


(24)



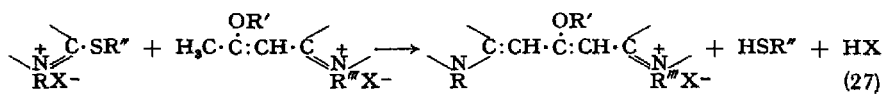
(25)

Such salts, by heating with a salt having a reactive methyl group, and with a condensing agent (see section 14), gave various types of *meso*-(alkylthio)carbocyanines, both symmetrical and unsymmetrical (equation 26).



(26)

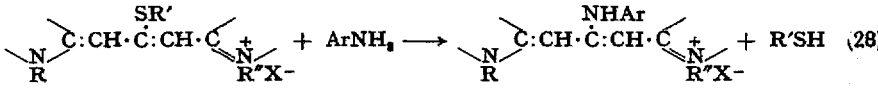
Increased sensitising action was claimed for the *meso*-(alkylthio)thiacarbocyanines.[23] Another type of reaction (see section 15), whereby a benzothiazolium salt having an alkylthio-group was condensed with one having the group $:CH{:}CMe(OR')$ or $\cdot CH{:}CMe(SR')$, gave *meso*-substituted thiacarbocyanines (equation 27).[50,51]



(27)

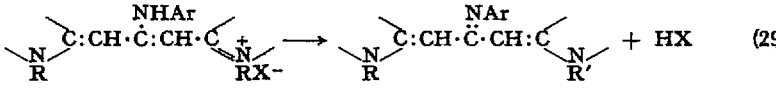
Benzoxazoles and benzothiazoles with a 2-CH:CMe_2 or 2-CH:CMeEt, and 2-CH:CMePh-benzothiazole, were synthesised and, unlike 2-propenylbenzothiazole, could be converted into quaternary salts,[52] which were used to synthesise dyes with a *meso*-alkyl or -phenyl substituent, but the products required repeated recrystallisation.[53] Carbocyanines with a *meso*-alkoxy-group sensitised at a shorter wavelength than those with a *meso*-alkyl group.[15] Pentamethincyanines with β-(alkylthio)- and β-alkoxy-substituents were also made (see VII-8-A).

The *meso*-alkoxy- and -alkylthio-groups of trimethincyanines proved to be reactive, giving *meso*-NRR′-trimethincyanines, and also compounds of new types (see section 16): the same applies to β-alkoxy- and β-(alkylthio)pentamethincyanines (see VII-8-A). Thus by heating a carbocyanine having a *meso*-(alkylthio)-group with a primary amine, a *meso*-arylamino-group was introduced (equation 28).[54,55]



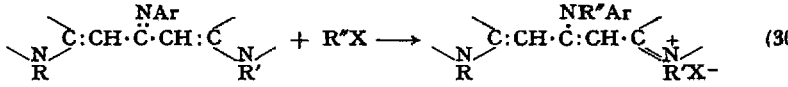
(28)

Treatment of the arylamino-compound with a base gave a new type of coloured compound (equation 29).[55,56]



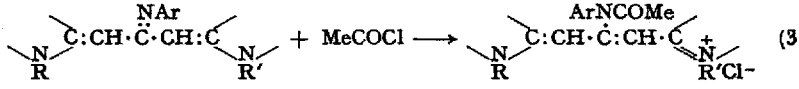
(29)

Treatment with an ester, R″X, converted such a compound to a carbocyanine having a *meso*-NR″Ar group (equation 30).[56]



(30)

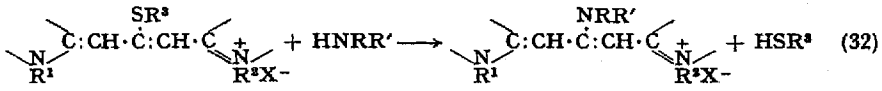
On the other hand, treatment with acetyl chloride converted it into a carbocyanine with an acetylated amino-group (equation 31).[55]



(31)

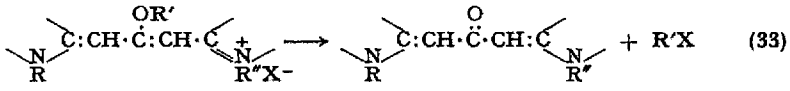
These acetylamino-carbocyanines showed sensitising properties. They were also obtainable by acetylation of those having a *meso*-arylamino-group.[57] Other carbocyanines with a di-substituted amino-group were

prepared from *meso*-(alkylthio)carbocyanines by treatment with secondary amines (equation 32).[58,59]



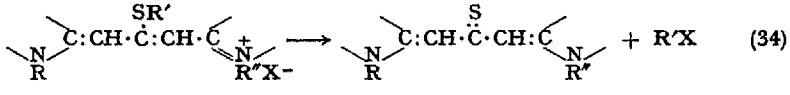
(32)

When a *meso*-alkoxycarbocyanine was treated with a base, another new type of compound arose (cf. VIII-1) (equation 33).[55,58,60,61]



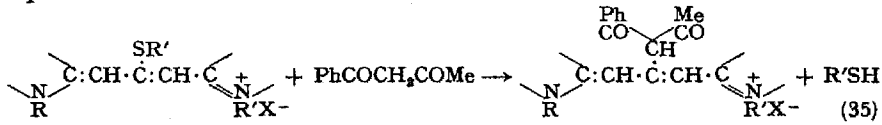
(33)

Their sulphur analogues were obtained by the action of tertiary amines on *meso*-(alkylthio)carbocyanines (equation 34).[55,62]



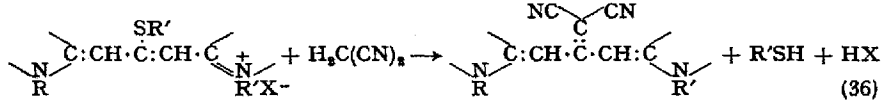
(34)

From a *meso*-(alkylthio)carbocyanine and a diketone, $RCO{\cdot}CH_2{\cdot}COR'$, there were prepared carbocyanines having the group $\cdot CH\langle^{COR}_{COR'}$ in the *meso*-position.[63] Thus with benzoylacetone a reaction occurred as in equation 35.



(35)

By condensation of a *meso*-(alkylthio)carbocyanine with other compounds having a reactive methylene group, there resulted, by removal of acid, non-ionic compounds with groups such as $:C(CN)_2$, $:C(CO_2R)CN$, or $:C(CONH_2)CN$ in the *meso*-position,[64] e.g., equation 36. Carbocyanines having a *meso*- $\cdot CH(COR)_2$ or $\cdot CH(CO_2R')(COR)$ group were converted by strong bases into non-ionic compounds with the group $:C(COR)_2$ or $:C(CO_2R')(COR)$ in the *meso*-position.[65]

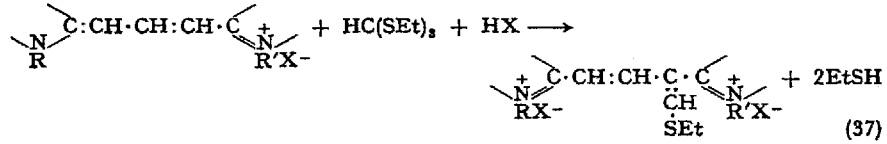


(36)

It was recorded in 1931 that heterocyclic quaternary salts, in which the reactive methyl group was substituted, could take part in

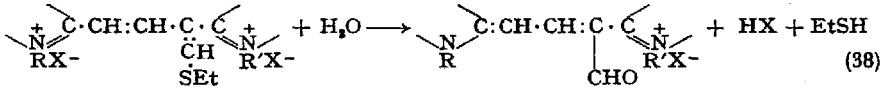
the ortho-ester method (see IV-6), giving rise to αα′-di-substituted symmetrical trimethincyanines. Examples of αα′-dialkyl- or -diaryl-thia- and -selena-carbocyanines were given, and included some which were also substituted in the *meso*-position.[66] Nearly twenty years later, the method was further applied (see Table II).[67,68] By use of quaternary salts having a 2-aryloxymethyl group, trimethincyanines with αα′-diaryloxy-substituents were made.[69] Unsymmetrical trimethincyanines with α-alkyl or αα′-dialkyl groups were photographic sensitisers[70] and were prepared[68,70] by an extension of the method involving the use of diphenylformamidine (V-6) (see Table II). A salt with the group ·CH:CH·SEt (V-10) or a compound with the group :CH·COMe (section 13) could also be condensed with a 2-ethylbenzothiazolium salt (section 17-A), whilst a salt with the group ·CH:CH·SEt could be condensed with a dihydro-base having a 2-:CHCN substituent to give α-cyanotrimethincyanines (sections 17-A, B, and C).

By heating a trimethincyanine with ethyl orthothioformate and an acid, in the presence of a carboxylic anhydride, there resulted a diquaternary salt with an α-:CH·SEt group (equation 37).[71]



(37)

Such salts, derived from 2,2′-, 4,4′-, thia-, and selena-carbocyanines, were described.[71] By their hydrolysis, oxa-, thia-, and selena-carbocyanines with an α-CHO group were made (equation 38).[72] The diquaternary salts were used in the synthesis of trinuclear dyes (XV-3-A



(38)

and C). α-Anilomethyltrimethincyanines were synthesised[73] for the same purpose (XV-3-A and C). It was noted subsequently that *N*-alkyl-α-formylmethylenedihydro-heterocyclic bases underwent, in acetic anhydride, auto-condensation to give α-formyltrimethincyanines. With five of these, belonging to the thiazolino-, thia-, and selena-carbocyanine series, introduction of the α-formyl group led to a batho-

chromic shift of absorption, varying from 310–770 Å. By the condensation of such α-formylcarbocyanines with quaternary salts having a reactive methyl group, trinuclear dyes of the neocyanine type (see XV-3) resulted.[74] Trimethincyanines with an α-CRO group, described as useful sensitisers[75] were usually made by converting the dye bases (see XI-10-B) into their quaternary salts (see also section 17-A).

2. Symmetrical *Meso*-Substituted Carbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, with Benzotrichloride, *etc.*

A. 2,2'- and 4,4'-Carbocyanines

The *meso*-phenyl-2,2'-carbocyanine, I (Y=CH:CH, R=Me, R'=Ph, X=Cl), was prepared by boiling an ethanolic suspension of the dried methylene base prepared from a 1-methylquinaldinium salt, adding benzotrichloride, and boiling for 3–4 minutes; it was recrystallised from methanol. Unlike the unsubstituted parent dye, it was destroyed by alcoholic potassium hydroxide.[2,3] This chloride, and the corresponding iodide, were also prepared from quinaldine methochloride and methiodide respectively, and I (Y=CH:CH, R=Et, R'=Ph, X=I) and its 6,6'-diethoxy-derivative were made similarly.[76]

The corresponding 1,1'-diethyl-*meso*-phenyl-4,4'-carbocyanine and its 6,6'-diethoxy-derivative were prepared by the same method.[76]

B. Indo- and Thia-carbocyanines

The *meso*-cyanoindocarbocyanine, I (Y=CMe_2, R=Me, R'=CN, X=I), was said to result on boiling 2,3,3-trimethylindolenine methiodide, in ten times its weight of pyridine, with trichloroacetonitrile. Alternatively the methylene base was heated with trichloroacetonitrile and pyridine in ethanol and the dye was isolated as perchlorate.[77] The fact that different absorption maxima are given for the iodide and perchlorate indicates that there is something wrong.

The *meso*-cyanothiacarbocyanine, I (Y=S, R=Et, R'=CN, X=I), was made by boiling 2-methylbenzothiazole ethiodide and trichloroacetonitrile in pyridine, whilst the corresponding perchlorate was similarly made from the ethotoluene-*p*-sulphonate, but again the recorded absorption maxima are different. The *meso*-cyanothiacarbo-

cyanines desensitised. In attempts to prepare them from alkiodides and trichloroacetonitrile in acetic anhydride, highly insoluble iodine addition compounds were formed.[77] By boiling a 2-methylbenzothiazolium salt with ethyl trichloroacetate, or with ethyl dichloroethoxyacetate, in acetic anhydride containing sodium acetate, a product which was formulated as a *meso*-carbethoxythiacarbocyanine was obtained.[78]

3. Symmetrical *Meso*-Alkyl- or -Aryl-carbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, with an Ortho-ester in Pyridine

A. Thia-, Oxa-, and Selena-carbocyanines

The *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R'=Me, X=I), was prepared by boiling 2-methylbenzothiazole ethiodide (2 mols.) and ethyl orthoacetate (4 mols.) in pyridine (10 c.c. per g. of salt) for 30 minutes, and recrystallising from methanol; the 45 % yield was halved when the medium was acetic anhydride. The corresponding *NN'*-dimethyl and -diallyl analogues, the latter as bromide, were similarly obtained in yields of 37 % and 53 %.[4] The 6,7,6',7'-dibenzo-derivatives of I (Y=S, R=Me or Et, R'=Me, X=I) were prepared in yields of 43 % and 38%. The *NN'*-dimethyl dye was a weak sensitiser but the *NN'*-diethyl dye was a powerful one, its maximum being shifted 300 Å towards longer wavelengths by the dibenzo-groups.[5] Such 6,7,6',7'-dibenzo-derivatives in which each benzo-group had an alkoxy-substituent were patented.[79] Ethyl orthothiophenate was prepared and used with pyridine to prepare thiacarbocyanines having a *meso*-α-thienyl group: those described were I (Y=S, R=Et, R'=C_4H_3S, X=Br) prepared from 2-methylbenzothiazole ethoethylsulphate, and also its 6,7,6',7'-dibenzo-derivative.[80] By boiling a 2-methylbenzo-thiazolium alkiodide with ethyl orthoacetate in pyridine for 45 minutes, there were prepared *meso*-methylthiacarbocyanines, having *NN'*-di-allyl, -di-n-propyl, or -di-n-butyl groups, in yields varying from 53–64 %. Similarly, by use of an alkiodide and ethyl orthopropionate in pyridine, there resulted *meso*-ethyl analogues, I (Y=S, R=Me, Et, Allyl, Pr^n, or Bu^n, R'=Et, X=I), in yields of 28–56 %. Through toluene-*p*-sulphonates and methyl ortho-n-butyrate in pyridine, the *meso*-n-propyl dye iodides of the *NN'*-dimethyl and -diethyl series were made in yields of 50 % and 55 %. The corresponding pairs of

meso-n-butyl, -n-amyl, and -isoamyl analogues were similarly made by use of methyl ortho-n-valerate, n-caproate, and iso-caproate, respectively, in yields varying from 42–58 %.[6,81] In certain preparations where the particular combination of quaternary salt and alkyl orthopropionate gave a low yield of *meso*-ethylthiacarbocyanine, this compound was accompanied by its *meso*-methyl analogue, the CMe group being doubtless produced by breakdown of part of the 2-methylbenzothiazolium salt (see section 8).[6] Four 6,7,6′,7′-dibenzo-derivatives of the thiacarbocyanines, I (Y=S, R=Me or Et, R′=Me or Et, X=Br), were prepared, in 37–54 % yields, from the appropriate toluene-*p*-sulphonates, with ethyl orthoacetate or methyl orthopropionate, by 1 hour's boiling in pyridine.[6] The corresponding 4,5,4′,5′-dibenzo-derivatives were similarly prepared, in lower yields (19–29 %), by means of ethyl orthoacetate and ethyl orthopropionate.[6,7,82] In preparing the 5,6,5′,6′-dibenzo-derivatives of I (Y=S, R=Et, R′=Me or Et, X=Br), the salt used was 2-methyl-5,6-benzobenzothiazole ethoethylsulphate with ethyl orthoacetate or orthopropionate in pyridine.[83] Substituted *meso*-alkyl groups were also introduced. Thus *meso*-benzylthiacarbocyanines, I (Y=S, R=Me, Et, or Allyl, R′=$PhCH_2$, X=I), were prepared by means of ethyl orthophenylacetate; here metho- and etho-toluene-*p*-sulphonates gave yields of 15 % and 11 %, but the alliodide gave 33 %. The corresponding *meso*-phenoxymethylthiacarbocyanines were made through ethyl orthophenoxyacetate, in yields of 39–48 %.[6,84] By use of ethyl orthobenzoate, a *meso*-phenyl group was introduced into thiacarbocyanines. Thus I (Y=S, R=Me or Et, R′=Ph, X=I) were prepared, both in 56 % yield, from the alkotoluene-*p*-sulphonates; the 6,7,6′,7′- and 4,5,4′,5′-dibenzo-derivatives of the corresponding bromides were similarly made, the yields being 47 % and 38 % for the former pair but only 3 % and 5 % for the latter pair.[6,82,85,86] A thiacarbocyanine having a *meso*-*p*-tolyl group was also described.[85]

The ortho-ester and pyridine method was applied to the preparation of various substituted thiacarbocyanines. Thus improved sensitisers resulted by the presence of 6,6′-di(methylseleno)-groups in I (Y=S, R=Et, R′=Me or Et, X=I).[87] Besides the *meso*-methyl- and *meso*-phenyl-thiacarbocyanines, I (Y=S, R=Et, R′=Me or Ph, X=I), the 6,6′-dimethyl and 6,6′-diethoxy-derivatives of the former were made by this method and their absorption maxima compared.[88] The method was also applied to the preparation of the 4,4′- and 5,5′-dimethyl derivatives[86] and the 6,6′-di(methylthio)-derivative[18] of I (Y=S, R=Et,

R′=Me, X=I). Whilst the dimethyl groups had a greater bathochromic effect in the 5,5′- than in the 6,6′-positions, there was no difference in the sensitising maxima.[89] By use of ethyl ortho(methylthio)acetate and pyridine, there were prepared, in yields of 22 % and 11 %, respectively, two thiacarbocyanines with a *meso*-(methylthio)-methyl group, viz., I (Y=S, R=Et, R′=CH_2SMe, X=I) and its 6,6′-dimethyl derivative: the introduction of such substituents did not increase the sensitising or the stabilising action.[18] The 6,6′-dichloro- and -dibromo-derivatives of I (Y=S, R=Et, R′=Me, Et, or Ph, X=Br or I) were made, the yields varying from 20–50 %.[90] The advantageous sensitising with a gap in the green, claimed for 7,7′-dialkyl- or -dialkoxy-thiacarbocyanines (see IV-6-E), included *meso*-substituted derivatives, e.g., the 7,7′-dimethyl or -dimethoxy-derivatives of I (Y=S, R=Et, R′=Me, X=I).[91] So also, amongst symmetrical thiacarbocyanines having 4,5,6,7-tetrahydrobenzothiazole nuclei (see IV-6-E) there were included the octahydro-derivatives of I (Y=S, R=Et, R′=Me or Et, X=I).[92] The 4,4′-, 5,5′-, 6,6′-, and 7,7′-dimethoxy-derivatives of *meso*-substituted thiacarbocyanines, I (Y=S, R=Me or Et, R′=Me or Et, X=I), were, like those having an unsubstituted chain (see IV-6-E) prepared by heating the appropriate 2-methylbenzothiazole alkotoluene-*p*-sulphonate with an ortho-ester and pyridine, and converting into iodides; the yields of washed products were 26–56 %. The absorption maxima of six 4,4′- or 7,7′-dimethoxy-compounds lay in the range 5440–5480 Å, whilst those of six 5,5′- or 6,6′-isomers lay in the range 5560–5630 Å.[93] By condensation of 2-methyl-4,5-tetramethylenebenzothiazole ethotoluene-*p*-sulphonate in pyridine with ethyl orthoacetate or orthopropionate, instead of orthoformate (see IV-6-E), there were prepared the bis-(4,5-tetramethylene) derivatives of I (Y=S, R=Et, R′=Me or Et, X=I), in yields of 15 % and 10 %, respectively, also the *NN′*-dimethyl analogue of the latter; they were moderate sensitisers.[94] By heating a 2-methylbenzothiazolium salt with an ethyl ortho-ester in pyridine, there were isolated as perchlorates, in 24–38 % yields, the 7,7′-bis(dimethylamino)-derivatives of I (Y=S, R=Me, R′=Me or Et, X=ClO_4), and the *NN′*-diethyl analogue of the first. As with the dyes having an unsubstituted chain (see IV-6-E), entry of the NMe_2 groups caused less bathochromic shift in the 7,7′- than in the 5,5′- or 6,6′-positions.[95] 5,5′-Bis(trifluoromethyl) derivatives of I (Y=S, R=Et, R′=Me or Et, X=I) were prepared through ethyl orthoacetate and orthopropionate. The medium for the former was

acetic anhydride containing a little pyridine (1 drop per c.c.), but, for the latter, pyridine. The 5,5′-difluoro-derivatives were also made, the *meso*-methyl dye in pyridine containing a little acetic anhydride, but the *meso*-ethyl analogue in acetic anhydride containing a little pyridine. The quaternary salts used for the last three dyes were ethoethylsulphates, but the ethiodide was used for the first. The yields of the four products varied from 23–38 %.[9] Amongst symmetrical thiacarbocyanines with 5,5′-dicarboxy-[96] or 5,5′-dicarbalkoxy-groups[97] (see IV-6-E) were such derivatives of I (Y=S, R=Et, R′=Me, X=I or SO_4Et, respectively). The presence of unsaturated substituents could cause a bathochromic shift of absorption, as shown by the 6,6′-distyryl derivative of I (Y=S, R=Et, R′=Me) and by the 6,6′-distyryl, 6,6′-di-*p*-methoxystyryl, and 6,6′-di-β-2-thienylvinyl derivatives of I (Y=S, R=R′=Et).[98] Various hydroxy-2-methylcyclammonium quaternary salts were made by hydrolysing the corresponding alkoxy-salts with hydrobromic acid.[99] By boiling such salts of the benzothiazole series with ethyl ortho-acetate or -propionate in acetic anhydride, there resulted *meso*-methyl- or *meso*-ethyl-thiacarbocyanines having diacetoxy-groups in the 5,5′- or 6,6′-positions.[100]

The first *meso*-substituted oxacarbocyanine was a *meso*-α-thienyl compound, prepared by heating 2-methylbenzoxazole ethiodide (1 part) with ethyl ortho-α-thiophenate (1 part) and pyridine (2 parts) for 1 hour,[80] whereas a negative result had been obtained in an attempt to get the *meso*-methyl compound.[4] In 1933 sensitising by *meso*-substituted oxacarbocyanines having two 4,5- or two 6,7-benzobenzoxazole nuclei was patented. Examples included the 4,5,4′,5′-dibenzo-derivative of I (Y=O, R=Me, R′=Et, X=Br) and the four 6,7,6′,7′-dibenzo-derivatives of I (Y=O, R=Me, R′=Me, Et, Ph, or α-thienyl, X=Br); the quaternary salts used, in conjunction with pyridine and ortho-ester, were all alkoalkylsulphates.[101] Amongst sensitisers prepared from 2-methyl-5,6-benzobenzoxazolium quaternary salts were the 5,6,5′,6′-dibenzo-derivatives of I (Y=O, R=Me, R′=Me or Et, X=Br).[102] The *meso*-methyloxacarbocyanine, I (Y=O, R=Et, R′=Me, X=I), was obtained in 10 % yield by boiling 2-methylbenzoxazole ethiodide (2 mols.) with ethyl orthoacetate (4 mols.), triethylamine (1 mol.), and pyridine (3 c.c. per g. of salt) for 15 minutes, precipitating with ether, washing, and recrystallising from methanol.[7] The corresponding *meso*-ethyl dye was similarly made, and, from 2-methylbenzoxazole metho-toluene-*p*-sulphonate, the *NN*′-dimethyl analogues of both, the yields

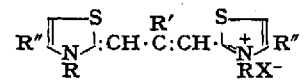
varying from 6–11 %.[6,103] The 5,5′-diphenyl derivative of the *meso*-ethyloxacarbocyanine, I (Y=O, R=R′=Et, X=I), was prepared by heating 2-methyl-5-phenylbenzoxazole ethiodide with ethyl orthopropionate in pyridine for 10 hours.[104] The 5,5′-dicarboxy-derivatives of I (Y=O, R=Et, R′=Me or Et, X=I) were described as good sensitisers leaving no stain;[105] the patents covering oxacarbocyanines with 5,5′-dibenzoyl or -dicarbalkoxy-groups (see IV-6-E) included *meso*-substituted derivatives, such as the 5,5′-dibenzoyl derivatives of I (Y=O, R=Et, R′=Me or Et, X=I),[106] the 5,5′-dicarbomethoxy- or -dicarbethoxy-derivatives of I (Y=O, R=R′=Et, X=I), and the 5,5′-dicarbomethoxy-derivatives of I (Y=O, R=R′=Me, X=I):[107] all these were reached by boiling the appropriate 2-methylbenzoxazolium alkoalkylsulphate with pyridine and ortho-ester. By boiling 5- or 6-hydroxy-2-methylbenzoxazolium salts with ortho-ester in acetic anhydride, there were obtained *meso*-methyl- or *meso*-ethyl-oxacarbocyanines having diacetoxy-groups.[100]

Sensitisation by *meso*-substituted selenacarbocyanines was claimed in a patent of 1931. The four examples were prepared by boiling a 2-methylbenzoselenazole alkoalkylsulphate with an ortho-ester in pyridine for 1 hour, three being isolated as bromides and one as perchlorate. The *meso*-substituents comprised methyl, ethyl, and phenyl groups and, in addition, there were 5,5′-dimethoxy-, or -dipropionylamino-, or 6,6′-diacetylamino-substituents in the nuclei.[108] A selenacarbocyanine having a *meso*-α-thienyl group was also described.[80] The substance, I (Y=Se, R=Et, R′=Me, X=I), was obtained in 23 % yield by boiling 2-methylbenzoselenazole ethotoluene-*p*-sulphonate (2 mols.) and ethyl orthoacetate (2 mols.) in pyridine (2·5 c.c. per g. of salt) for 20 minutes, precipitating with ether, converting to iodide, and recrystallising from methanol.[7] Its *meso*-ethyl and *meso*-phenyl analogues were similarly prepared, also the corresponding three dyes of the *NN*′-dimethyl series: the 3,3′,9-trimethyl compound was isolated as bromide. The yields varied from 13–36 %.[6,109]

B. Thiazolo-, Thiazolino-, and Selenazolino-carbocyanines

Thiazolocarbocyanines having a meso-alkyl substituent were made by this method and were found to be photographic sensitisers. The dyes prepared were VI (R=R′=Et, R″=Me, X=I) and VI (R=Me, R′=Me or Et, R″=Ph, X=I).[110] A 4-aryl-2-methylthiazolium salt was

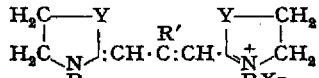
condensed with ethyl orthoacetate, and various 5-aryl-2-methylthiazolium salts were condensed with ethyl ortho-acetate or -propionate, by heating in pyridine containing acetic anhydride. Absorption data were



(VI)

given for the resultant *meso*-methyl-4,4′-di-(5-acenaphthenyl)thiazolocarbocyanine and *meso*-alkyl-5,5′-di-β-(or α-)naphthyl-, -5,5-di-(5-acenaphthenyl)-, and -5,5′-di-*p*-biphenylyl-thiazolocarbocyanines, also for the 4,5,4′,5′-tetra-*p*-biphenylyl derivative of VI (R=R′=Et, R″=H, X=*p*-$SO_3 \cdot C_6H_4Me$).[111]

The *meso*-ethylthiazolinocarbocyanines, VII (Y=S, R=Me or Et, R′=Et, X=I), were prepared in yields of 29 % and 13 % by heating



(VII)

2-methylthiazoline alkotoluene-*p*-sulphonate with ethyl orthopropionate in pyridine for 3–4 hours, converting into iodide, and recrystallising from methanol.[112, 113] The *meso*-substituent caused a bathochromic shift, i.e., the reverse of the effect in the thiacarbocyanine series.[112]

The *meso*-ethylselenazolinocarbocyanine, VII (Y=Se, R=Me, R′=Et, X=I), was prepared by boiling the methiodide with methyl orthopropionate and pyridine for 45 minutes; it was found to sensitise.[114]

4. Symmetrical Meso-Alkylcarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, and an Iminocarboxylic Ester, HN:CR′(OR″) (see equation 1)

A. Thiacarbocyanines

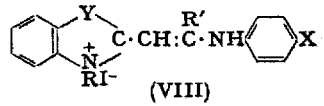
The *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R′=Me, X=I), was prepared by heating 2-methylbenzothiazole ethiodide (1 mol.) with ethyl iminoacetate (2–4 mols.) in ethanol for 30 minutes. Its 6,7,6′,7′-dibenzo-derivative was similarly made. The 4,5,4′,5′-di-

benzo-analogue was prepared by heating the appropriate toluene-*p*-sulphonate with the iminoacetate in pyridine and was converted into bromide.[17] By boiling 2-methylbenzothiazole ethiodide with the methylthio- or ethylthio-derivative of ethyl iminoacetate in ethanol for 1 hour, there were prepared I (Y=S, R=Et, R′=MeS·CH_2 or EtS·CH_2, X=I) in yields of 24 % and 11 %, respectively, the former yield being practically the same as that by the ortho-ester method[18] (see section 3-A).

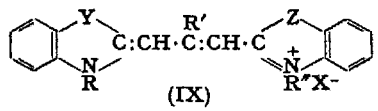
5. Symmetrical and Unsymmetrical *Meso*-Alkylcarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, and an Iminothio-Ester, ArN:CR′(SR″) (see equations 2 and 3)

A. Thia-2′-carbocyanines

By heating 2,6-dimethylbenzothiazole ethiodide with ethyl isothio-(4-chloroacetanilide) at 148–150° for 2 hours, there resulted, in 65 % yield, the 6-methyl derivative of VIII (Y=S, R=Et, R′=Me,



(VIII)



(IX)

X=Cl). By boiling this with quinaldine ethiodide in pyridine for 1·5 hours, it gave a 58 % yield of the 6-methyl derivative of the thia-2′-carbocyanine, IX (Y=S, Z=CH:CH, R=R″=Et, R′=Me, X=I).[20]

B. Thia-, Oxa-, and Selena-carbocyanines

The 5,6,5′,6′-dibenzo-derivatives of the symmetrical thiacarbocyanines, I (Y=S, R=Et, R′=Me or Et, X=I), were prepared by heating 2-methyl-5,6-benzobenzothiazole ethiodide with methyl isothioacetanilide or with ethyl isothiopropionanilide, respectively, in pyridine.[83] On the other hand, the symmetrical thiacarbocyanine, I (Y=S, R=Et, R′=Me, X=I), was prepared by a two-stage process, which consisted firstly in boiling 2-methylbenzothiazole ethiodide with

ethyl isothioacetanilide in acetic anhydride for 4 hours and treating with ether, to isolate the intermediate salt, which was then condensed with 2-methylbenzothiazole ethiodide by heating with piperidine in pyridine for 2 hours.[19] The intermediate salt, VIII (Y=S, R=Et, R′=Me, X=Cl), was prepared in 65 % yield and, by heating with 2-methylbenzothiazole ethiodide in pyridine gave a 40 % yield of the symmetrical thiacarbocyanine, I (Y=S, R=Et, R′=Me, X=I), whereas the unsubstituted salt, VIII (Y=S, R=Et, R′=Me, X=H), gave only a 28 % yield. The 6,6′-dimethyl derivative of the dye was similarly prepared in 39 % yield by use of a *p*-chloro-salt but in only 29 % yield by use of the unsubstituted salt. The 6-methyl derivatives of VIII (Y=S, R=R′=Et, X=Cl, Me, or NO_2) gave, on condensing with 2,6-dimethylbenzothiazole ethiodide, the 6,6′-dimethyl derivative of the symmetrical thiacarbocyanine, I (Y=S, R=R′=Et, X=I), in yields of 52 %, 28 %, and 14 %, respectively.[20] By reaction of the intermediate salt from 2-methylbenzothiazole ethiodide and ethyl isothioacetanilide with 3-ethyl-2-methylbenzothiazolium salts having 4,5- or 6,7-benzo- or 5-diethylamino-substituents, there resulted unsymmetrical *meso*-methylthiacarbocyanines. An intermediate salt was prepared by heating 2-methylbenzothiazole ethiodide with ethyl isothiopropionanilide at 165–170° for 4 hours; it was condensed with 2-methylbenzothiazole ethiodide to give the symmetrical *meso*-ethylthiacarbocyanine, I (Y=S, R=R′=Et, X=I), and both it and its *N*-methyl analogue were used in the preparation of unsymmetrical *meso*-ethylthiacarbocyanines.[19]

The 4,5,4′,5′-dibenzo-derivative of the *meso*-ethyloxacarbocyanine, I (Y=O, R=Me, R′=Et, X=Br), was prepared by heating the metho-methylsulphate of the base with ethyl isothiopropionanilide in pyridine, and converting into bromide.[101]

The symmetrical *meso*-methylselenacarbocyanine, I (Y=Se, R=Et, R′=Me, X=I), was prepared in two stages; by boiling 2- methylbenzoselenazole ethiodide with ethyl isothioacetanilide and acetic anhydride for 5 hours there resulted a salt, which was then boiled with 2-methylbenzoselenazole ethiodide and piperidine in pyridine for another 5 hours.[19] From the *p*-chloro-salt, VIII (Y=Se, R=Et, R′=Me, X=Cl), the yield of this dye was 25 %. The corresponding *meso*-ethyl analogue, I (Y=Se, R=R′=Et, X=I), was obtained in yields of 46 %, 26 %, 25 %, and 22 %, respectively, from VIII (Y=Se, R=R′=Et, X=Br, H, Me, or NO_2).[20] Its 5,5′-dimethoxy-derivative was prepared

in one step by heating 5-methoxy-2-methylbenzoselenazole ethiodide and ethyl isothiopropionanilide in pyridine for 2 hours; the corresponding *meso*-propyl and *meso*-4-methoxyphenyl analogues were similarly made, the former being isolated as perchlorate. An unsymmetrical *meso*-ethylselenacarbocyanine was prepared by heating the salt prepared from 2-methylbenzoselenazole ethiodide and ethyl isothiopropionanilide with 5-methoxy-2-methylbenzoselenazole ethiodide in pyridine.[19]

C. Oxathia- and Selenathia-carbocyanines

The oxathiacarbocyanine, IX (Y=O, Z=S, R=R′=R″=Et, X=I), was prepared by heating the intermediate salt from 2-methylbenzothiazole ethiodide and ethyl isothiopropionanilide with 2-methylbenzoxazole ethiodide in pyridine.[19] The good sensitisation claimed for dyes having a 5-phenylbenzoxazole nucleus (see section 3-A; also II-4-E; and XIII-1-F) included the 5′-methoxy-5-phenyl derivative of the preceding dye: the intermediate salt for this was prepared by heating 2-methyl-5-phenylbenzoxazole ethiodide with methyl isothiopropionanilide at 170° for 30 minutes.[104] The 6-methoxy-derivatives of VIII (Y=O, R=R′=Et, X=Cl or Br) were made and by heating with 2,6-dimethylbenzothiazole ethiodide in pyridine gave the 6-methoxy-6′-methyl derivative of the oxathiacarbocyanine, IX (Y=O, Z=S, R=R′=R″=Et, X=I), in yields of 25 % and 21 %, respectively, whereas the unsubstituted salt gave only 13 %. The *meso*-methyl dye was also made.[20]

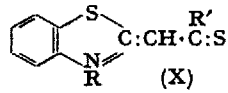
The intermediate salt prepared from 2-methylbenzothiazole ethiodide and ethyl isothiopropionanilide was condensed with 2-methylbenzoselenazole ethiodide, and with its 5-methoxy-derivative, to give the selenathiacarbocyanine, IX (Y=Se, Z=S, R=R′=R″=Et, X=I), and its 5-methoxy-derivative. Another *meso*-ethyl dye was made by condensing an intermediate salt prepared from 2-methylbenzoselenazole ethiodide and ethyl isothiopropionanilide with a 2-methyl-4,5-benzobenzothiazolium salt; two *meso*-methyl analogues were made by condensing the salt prepared from 2-methylbenzoselenazole ethiodide and ethyl isothioacetanilide with 2-methylbenzothiazolium salts having a 5-diethylamino- or 4,5-benzo-substituent.[19] Reaction of 6-methoxy-2-methylbenzoselenazole ethiodide with the three salts, VIII (Y=S, R=R′=Et, X=I, H, or Me), gave the *meso*-ethyl-6-methoxyselenathiacarbocyanine in yields of 35 %, 24 %, and 16 %, respectively; its

reaction with the 6-methyl derivatives of the two salts, VIII (Y=S, R=Et, R'=Me, X=Cl or H), gave 75 % and 45 % yields, respectively.[20]

6. Symmetrical *Meso*-Alkylcarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, and a Dithiocarboxylic Ester, S:CR'(SR") (see equations 4 and 5)

A. Thiacarbocyanines

By boiling together 2-methylbenzothiazole ethiodide, methyl dithioacetate, and triethylamine (2 mols. of each) in pyridine (5 c.c. per g. of salt) for 30 minutes, the *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R'=Me, X=I), separated. More of it was obtained on dilution, together with the thioketone, X (R=Et, R'=Me); the latter was



(X)

extracted with acetone. When the triethylamine was omitted from the preparation, only the thioketone was isolated. The 4,5,4',5'-dibenzo-derivative of the dye, together with the 4,5-benzo-derivative of the thioketone, were prepared by heating the appropriate ethotoluene-*p*-sulphonate with methyl dithioacetate and triethylamine in pyridine, but when triethylamine in ethanol was used again only thioketone was isolated.[21]

B. Thiazolinocarbocyanines

The thiazolinocarbocyanine, VII (Y=S, R=R'=Me, X=I), was prepared by boiling 2-methylthiazoline methiodide with methyl dithioacetate and triethylamine (2 mols. of each) in ethanol (3 c.c. per g. of salt) for 20 minutes, and was accompanied by only a very small amount of the corresponding thioketone.[21]

7. Symmetrical *Meso*-(Alkylthio)carbocyanines from a Heterocyclic Base, Having a Reactive Methyl Group, an Alkyl Toluene-*p*-sulphonate, and an Alkyl Dithiocarbamate, S:C(NRR')(SAlk)

A. Thia- and Oxa-carbocyanines

The *meso*-(methylthio)thiacarbocyanine, I (Y=S, R=Me, R'=SMe, X=I), was prepared by heating 2-methylbenzothiazole (2 mols.) with methyl toluene-*p*-sulphonate (3 mols.) at 150° for 2 hours, then

boiling with methyl phenyldithiocarbamate (not > 1 mol.) in pyridine for 30 minutes, and treating with aqueous potassium iodide; it was made alternatively by use of methyl diethyldithiocarbamate, and with triethylamine in ethanol instead of pyridine. The *meso*-(ethylthio)thiacarbocyanine, I (Y=S, R=Et, R'=SEt, X=I), and its 5,6,5',6'-bis(methylenedioxy)-derivative, were prepared by use of ethyl phenyldithiocarbamate.[24]

The *meso*-(methylthio)oxacarbocyanine, I (Y=O, R=Me, R'=SMe, X=I), and its 5,5'-diphenyl derivative were prepared by use of methyl phenyldithiocarbamate.[24]

8. Symmetrical *Meso*-Alkylcarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, and one or more Bases

A. Thia-, Oxa-, and Selena-carbocyanines

The *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R'=Me, X=I), was prepared in 4 % yield by heating 2-methylbenzothiazole ethiodide in pyridine for several hours, whereas the corresponding ethotoluene-*p*-sulphonate gave a 14 % yield. By boiling the ethiodide with an equimolecular amount of triethylamine in pyridine for only 30 minutes, the yield of washed product was increased to 56 %. The corresponding *NN'*-dimethyl analogue was obtained in 38 % yield. The 6,7,6',7'- and 4,5,4',5'-dibenzo-derivatives of I (Y=S, R=Et, R'=Me, X=I or Br), respectively, were prepared in yields of 8 % and 6 % from the appropriate ethotoluene-*p*-sulphonates.[7]

The *meso*-methyloxacarbocyanine, I (Y=O, R=Et, R'=Me, X=I), was obtained in 6 % yield by boiling 2-methylbenzoxazole ethiodide with an equimolecular quantity of triethylamine in n-propanol (2·5 c.c. per g. of ethiodide) for 1·5 hours, followed by precipitation with ether, washing with water, and treatment with acetone.[7]

The *meso*-methylselenacarbocyanine, I (Y=Se, R=Et, R'=Me, X=I), was prepared in 32 % yield by heating 2-methylbenzoselenazole ethiodide and triethylamine in pyridine for 30 minutes.[7]

9. Symmetrical *Meso*-Methylthiacarbocyanines from a 2-Methylbenzothiazolium Salt, with Potassium Acetate and Acetic Anhydride

A 30 % yield of the *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R'=Me, X=I), was prepared by heating 2-methylbenzothiazole

ethiodide (2 mols.) and potassium acetate (1 mol.) in acetic anhydride (0·5 c.c. per g. of salts) at 165° for 1 hour, and recrystallising from methanol. Its 6,7,6′,7′-dibenzo-derivative was similarly prepared in 7% yield and the 6,6′-dimethyl derivative of I (Y=S, R=R′=Me, X=I) in 20% yield.[27]

10. Symmetrical Carbocyanines, Having a Substituted *Meso*-Vinyl Group, by Reaction of *Meso*-Methylcarbocyanines with Aldehydes or their Anils

A. Thia-, Oxa-, and Selena-carbocyanines

By heating the *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R′=Me, X=I), with benzaldehyde and ethanol containing piperidine (5 drops per c.c.) for 15 minutes at 90°, the *meso*-styryl derivative, I (Y=S, R=Et, R′=CH:CHPh, X=I), was obtained. Its 6,7,6′,7′-dibenzo-derivative was made similarly, also, by use of *p*-dimethylaminobenzaldehyde, there were prepared II and its 6,7,6′,7′-dibenzo-derivative; similar use of furfuraldehyde gave III.[27] Subsequently it was found better to effect condensation by heating the dye and aldehyde in a sealed tube at 80–90° for 0·5–2 hours. The *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R′=Me, X=I), was thus condensed with furfuraldehyde, benzaldehyde, *p*-dimethylamino-, *p*-chloro-, *m*-chloro-, *p*-methyl-, *p*-methoxy-, *p*-hydroxy-, *p*-nitro-, *p*-formyl-, 4-hydroxy-3-methoxy-, and 3,4-dihydroxy-benzaldehyde, also with β-naphthaldehyde. The products derived from *p*-nitrobenzaldehyde and terephthalic aldehyde were desensitisers, whilst sensitising maxima were quoted for the rest. For all of them the absorption maximum in alcohol was at 5600 ± 10 Å.[115] The *meso*-methylthiacarbocyanine, I (Y=S, R=Et, R′=Me, X=Cl), could be condensed with 2-formylbenzothiazole, but not with its anil, by heating them together in pyridine, to give IV (Y=Z=S). It could not, on the other hand, be condensed with 2-formylquinoline, but did condense with its anil to give IV (Y=S, Z=CH:CH), and also with the anil of 4-formylquinoline.[29]

The *meso*-methyloxacarbocyanine, I (Y=O, R=Et, R′=Me, X=I), was heated in a sealed tube at 80–90° with each of the first eleven aldehydes, which had been used with the corresponding thiacarbocyanine, and absorption maxima were given for the products. Nine

of them absorbed with the maximum at 5215 Å in alcohol but the products from *p*-dimethylaminobenzaldehyde and furfuraldehyde had their maximum absorption at 5250 Å. Those derived from *p*-nitrobenzaldehyde and terephthalic aldehyde were desensitisers, but sensitising maxima were quoted for the rest.[115]

The *meso*-methylselenacarbocyanine, I (Y=Se, R=Et, R'=Me, X=Cl), was condensed with the anil of 2-formylquinoline, by heating them in pyridine, to give IV (Y=Se, Z=CH:CH).[29]

11. Symmetrical Carbocyanines, Having a Meso-Substituent, from a Quaternary Salt, Having a Reactive Methyl Group, a 2-Substituted Benzoxazolium Salt, and Alkali in Alcohol (see equations 6 and 7)

A. Thia- and Selena-carbocyanines

The *meso*-ethylthiacarbocyanine, I (Y=S, R=R'=Et, X=I), was prepared by heating 2-ethylbenzoxazole methomethylsulphate with sodium ethoxide in alcohol, to give the acetal of the substituted amide (equation 6; R=Me, R'=Et, X=SO_4Me), then adding 2-methylbenzothiazole ethiodide and boiling for 30–60 minutes (equation 7). Benzoxazoles having a 2-propyl, -pentadecyl, -cyclohexyl, or -furyl group were prepared and converted into quaternary salts by methyl sulphate. Through their fission with alcoholic sodium ethoxide, and reaction of the products with 2-methylbenzothiazole ethiodide, each of these groups from the 2-position of the benzoxazole nucleus was introduced into the *meso*-position of the resultant thiacarbocyanine.[30] The method was also applied to the preparation of a *meso*-ethylthiacarbocyanine having 5,6,5',6'-dibenzo-groups.[83] The *meso*-pentadecylthiacarbocyanine, I (Y=S, R=Et, R'=$C_{15}H_{31}$, X=I), was prepared by treating a mixture of 2-pentadecylbenzoxazole methomethylsulphate (1 mol.) and 2-methylbenzothiazole ethiodide (2 mols.) in boiling ethanol with a solution of sodium (3 atoms) in ethanol, and boiling for 2 minutes. The washed product was converted into iodide, which was recrystallised from ethyl acetate. Its 5,5'-, 6,6'-, and 7,7'-dichloro-derivatives were prepared in yields of 20 %, 17 %, and 8 %, its 5,6,5',6'-tetramethoxy-derivative in 13 % yield, and its 6,7,6',7'-dibenzo-derivative in 18 % yield. The corresponding *meso*-undecylthiacarbocyanine was similarly made, also its 5,5'- and 6,6'-dichloro-, and 6,7,6',7'-dibenzo-derivatives. By heating 2-methylbenzothiazole ethiodide and sodium ethoxide in

alcohol with 2-*p*-dimethylaminostyrylbenzoxazole ethotoluene-*p*-sulphonate, there resulted II, whilst by heating them with V (Z=S or CH:CH) there were obtained IV (Y=S or CH:CH).[29]

The *meso*-ethylselenacarbocyanine, I (Y=Se, R=R'=Et, X=I), was prepared by treating 2-methylbenzoxazole methomethylsulphate with sodium ethoxide in ethanol and boiling the mixture with 2-methylbenzoselenazole ethiodide for 30–60 minutes. Similarly there were introduced a *meso*-propyl, -pentadecyl, -cyclohexyl, or -furyl group.[30]

12. Symmetrical Carbocyanines, Having a *Meso*-*o*-Carboxyphenyl or a *Meso*-*β*-Carboxyethyl Group, from a Quaternary Salt, Having a Reactive Methyl Group, and Phthalic Anhydride or Succinic Anhydride, in Pyridine (see equations 8 and 9)

A. Thia-, Oxa-, and Selena-carbocyanines

The *meso*-*o*-carboxyphenylthiacarbocyanine, I (Y=S, R=Et, R'=*o*-$C_6H_4 \cdot CO_2H$, X=I), was prepared by boiling 2-methylbenzothiazole ethiodide and phthalic anhydride (700 % excess) with pyridine (10 c.c. per g. of salt) for 10 minutes, and was precipitated by ether in 65 % yield. Its 4,5,4',5'-dibenzo-derivative was prepared as toluene-*p*-sulphonate; its 5,5'-dichloro-derivative was made from a toluene-*p*-sulphonate but converted into iodide: their yields were 16 % and 49 %, respectively. The methyl and ethyl esters of the dibenzo-compound were prepared by passing dry hydrogen chloride into its methanolic or ethanolic solution for 3 hours and were isolated as bromides in 72 % and 77 % yields. The *meso*-*β*-carboxyethylthiacarbocyanine, I (Y=S, R=Et, R'=$CH_2CH_2CO_2H$, X=ClO_4), was obtained in 13 % yield by boiling 2-methylbenzothiazole ethiodide with excess of succinic anhydride in pyridine and converting the product into perchlorate.[31]

The *meso*-*o*-carboxyphenyloxacarbocyanine, I (Y=O, R=Me, R'=*o*-$C_6H_4 \cdot CO_2H$, X=I), was prepared by heating 2-methylbenzoxazole methiodide with excess of phthalic anhydride in pyridine; after precipitation by ether and recrystallisation, it resulted in 11 % yield.[31]

The *meso*-*o*-carboxyphenylselenacarbocyanine, I (Y=Se, R=Et, R'=*o*-$C_6H_4 \cdot CO_2H$, X=I), was made similarly, the yield of washed compound being 28 %.[31]

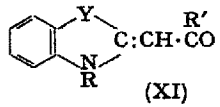
B. Thiazolinocarbocyanines

The *meso-o*-carboxyphenylthiazolinocarbocyanine, VII (Y=S, R=Et, R′=*o*-$C_6H_4 \cdot CO_2H$, X=I), was prepared by heating 2-methylthiazoline ethiodide and excess of phthalic anhydride in pyridine, and precipitating with ether. After recrystallisation from methanol, the yield was 23%. This compound had practically no sensitising action.[31]

13. Symmetrical and Unsymmetrical *Meso*-Alkyl-, -Aryl-, or -CO_2R-carbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, and a Heterocyclic Ketone Comprising the Group: CH·CR′O

A. Indocarbocyanines

1,3,3-Trimethyl-2-methyleneindoline by reaction with benzoyl chloride in benzene gave the ketone, XI (Y=CMe_2, R=Me, R′=Ph), which, on heating with more methylene base and phosphorus oxychloride in toluene, yielded the symmetrical *meso*-phenylindocarbocyanine, I (Y=CMe_2, R=Me, R′=Ph, X=Cl), a blue-violet dye. By



(XI)

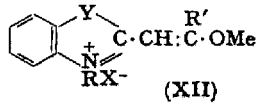
using *p*-chlorobenzoyl chloride and crotonyl chloride, the corresponding ketones were made and thence the corresponding dyes, I (Y=CMe_2, R=Me, R′=*p*-C_6H_4Cl or ·CH:CH·Me, X=Cl), the latter being precipitated as a zinc chloride double salt. The 5-methoxy-derivative of XI (Y=CMe_2, R=Me, R′=·CH:CH·Me) was condensed with the 6,7-benzo-derivative of 1,3,3-trimethyl-2-methyleneindoline to give an unsymmetrical indocarbocyanine.[32]

B. Thiacarbocyanines

The 4,5-benzo-derivative of the ketone, XI (Y=S, R=Et, R′=Me), was prepared by adding acetyl chloride to a suspension of 2-methyl-4,5-benzobenzothiazole ethotoluene-*p*-sulphonate in anhydrous pyridine; the addition was made below 10° but the temperature was later

raised to 100°. After removal of the pyridine and treatment with water, the yield was 74 %.[33] By heating this ketone with 2-methyl-4,5-benzobenzothiazole ethotoluene-*p*-sulphonate (1 mol. of each) in acetic anhydride (5 c.c. per g. of solids) for 15 minutes, precipitating with ether, and converting into bromide, there resulted the 4,5,4′,5′-dibenzo-derivative of the symmetrical thiacarbocyanine, I (Y=S, R=Et, R′=Me, X=Br). The symmetrical dye, I (Y=S, R=Et, R′=Ph, X=I), was reached through the ketone, XI (Y=S, R=Et, R′=Ph). An unsymmetrical thiacarbocyanine, the 4,5-benzo-derivative of I (Y=S, R=Et, R′=Me, X=I) was prepared by alternative methods, involving the ketone, XI (Y=S, R=Et, R′=Me), and its 4,5-benzo-derivative; another, having a 5-chloro-group in one nucleus, was also reached by alternative routes. Three *meso*-ethylthiacarbocyanines with a 5-chloro- or 4,5-benzo-substituent in one nucleus were prepared by the ketone method.[116]

The *meso*-carbethoxythiacarbocyanine, I (Y=S, R=Me, R′=CO_2Et, X=SO_4Me), was prepared by heating XI (Y=S, R=Me, R′=CO_2Et) with 2-methylbenzothiazole methomethylsulphate in acetic anhydride for 30 minutes; the bromide of its 4,5-benzo-derivative was obtained by use of the same ketone. On the other hand, to make the *meso*-carboxythiacarbocyanine, I (Y=S, R=Me, R′=CO_2H, X=I), the salt, XII (Y=S, R=Me, R′=CO_2H), was heated with 2-methyl-



(XII)

benzothiazole methomethylsulphate and triethylamine in acetic anhydride for 15 minutes; its 4,5-benzo-derivative was made from the same salt.[35]

C. Indothia-, Oxaselena-, Oxathia-, and Selenathia-carbocyanines

The methylene base obtained by the action of alkali on 2-methylbenzothiazole methomethylsulphate was converted by benzoyl chloride in benzene into the ketone, XI (Y=S, R=Me, R′=Ph); reaction of this with 1,3,3-trimethyl-2-methyleneindoline gave the *meso*-phenylindothiacarbocyanine, IX (Y=CMe_2, Z=S, R=R″=Me, R′=Ph, X=Cl).[32]

The *meso*-methyloxaselenacarbocyanine, IX (Y=O, Z=Se, R=

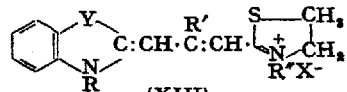
R″=Et, R′=Me, X=I), was prepared by heating the ketone, XI (Y=Se, R=Et, R′=Me), with 2-methylbenzoxazole ethiodide in acetic anhydride;[117] a 6,7-benzo-derivative was similarly prepared by reaction of the ketone with 2-methyl-6,7-benzobenzoxazole ethotoluene-*p*-sulphonate.[118]

Two oxathiacarbocyanines, IX (Y=O, Z=S, R=R′=Et, R″=Me, X=I; and Y=O, Z=S, R=R″=Et, R′=Me, X=I), were prepared by heating 2-methylbenzoxazole alkiodide with the respective ketones, XI (Y=S, R=Me, R′=Et; and Y=S, R=Et, R′=Me).[116, 117] Analogues having a 6,7-benzo-group in the benzoxazole nucleus, or a 4,5-benzo-group in that or in the benzothiazole nucleus, were also described.[116, 118] The *meso*-carbethoxyoxathiacarbocyanine, IX (Y=O, Z=S, R=R″=Me, R′=CO_2Et, X=I), was prepared through the ketone, XI (Y=S, R=Me, R′=CO_2Et), and the corresponding *meso*-carboxy-dye through the salt, XII (Y=S, R=Me, R′=CO_2H), by heating with 2-methylbenzoxazole methiodide in acetic anhydride, in the latter instance in the presence of triethylamine.[35]

4′,5′-Benzo-derivatives of the selenathiacarbocyanines, IX (Y=Se, Z=S, R=R″=Et, R′=Me or Et, X=I), were prepared by heating 2-methylbenzoselenazole ethiodide, in acetic anhydride, with the 4,5-benzo-derivative of the ketone, XI (Y=S, R=Et, R′=Me or Et); analogues were also described.[116]

D. Selenathiazolino- and Thiathiazolino-carbocyanines

The *meso*-methylselenathiazolinocarbocyanine, XIII (Y=Se, R=R″=Et, R′=Me, X=I), was prepared by heating the ketone, XI (Y=Se, R=Et, R′=Me), with 2-methylthiazoline ethotoluene-*p*-sulphonate in propionic anhydride, and converting the product into iodide.[119]



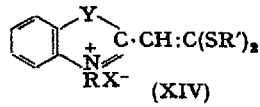
(XIII)

The *meso*-methylthiathiazolinocarbocyanine, XIII (Y=S, R=R″=Et, R′=Me, X=I), and its 4,5-benzo-derivative, were prepared from the ketone, XI (Y=S, R=Et, R′=Me), and its 4,5-benzo-derivative, with the same thiazolinium salt in acetic anhydride.[119]

14. Symmetrical and Unsymmetrical *Meso*-(Alkylthio)-carbocyanines Through a Quaternary Salt Having the Group ·CH:C(SR)$_2$ (see equation 26)

A. Thia-2′-carbocyanines

The 4,5-benzo-derivative of XIV (Y=S, R=Me, R′=Et, X=Br) was condensed with quinaldine methomethylsulphate, by heating with



(XIV)

triethylamine in ethanol, followed by potassium iodide, to give the 4,5-benzo-derivative of the *meso*-(ethylthio)thia-2′-carbocyanine, IX (Y=S, Z=CH:CH, R=R″=Me, R′=SEt, X=I).[23]

B. Thia- and Selena-carbocyanines

The symmetrical *meso*-(methylthio)thiacarbocyanine, I (Y=S, R=Et, R′=SMe, X=Br), was prepared by heating XIV (Y=S, R=R′=Me, X=SO_4Me) with 2-methylbenzothiazole methomethylsulphate in pyridine and methanol for 1 hour, and treating with potassium bromide. The 6,6′-dimethyl derivative of its *meso*-ethylthio-analogue was isolated as iodide. Unsymmetrical analogues of the first dye having a 4,5-benzo- or a 6-methyl group in one nucleus were isolated as iodides. Other unsymmetrical thiacarbocyanines were the 4,5-benzo- and 6-dimethylamino-derivatives of I (Y=S, R=R″=Me, R′=SEt, X=I) and the 4,5,6′,7′-dibenzo-derivative of the bromide.[23]

The unsymmetrical 6-methyl derivative of the *meso*-(ethylthio)-selenacarbocyanine, I (Y=Se, R=Me, R′=SEt, X=I), was prepared by condensing the salt, XIV (Y=Se, R=Me, R′=Et, X=Br), with 2,6-dimethylbenzoselenazole methomethylsulphate.[23]

C. Selenathiacarbocyanines

In preparing *meso*-(alkylthio)selenathiacarbocyanines, salts such as XIV (Y=S or Se, R=Me, R′=Me or Et, X=SO_4Me or Br) were used, in conjunction with a 2-methylbenzoselenazolium, or 2-methylbenzothiazolium, salt; the dyes included IX (Y=Se, Z=S, R=R″=Me, R′=SMe or SEt, X=Br or I), and derivatives having a substituent in one or the other nucleus.[23]

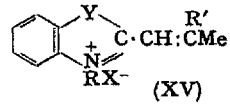
D. Thiathiazolinocarbocyanines

Each of the quaternary salts, XIV (Y=S, R=R′=Me, X=SO_4Me and Y=S; R=Me, R′=Et, X=I), was condensed with 2-methylthiazoline methiodide, by boiling with triethylamine in methanol for 1 hour, and treating with iodide, to give the *meso*-(alkylthio)thiathiazolinocarbocyanines, XIII (Y=S, R=R″=Me, R′=SMe or SEt, X=I).[23]

15. Symmetrical and Unsymmetrical Meso-Alkoxy-, -Alkylthio-, -Methyl-, or -Phenyl-carbocyanines, Through a Salt with the Group ·CH:CMe(OAlk), ·CH:CMe(SAlk), ·CH:CMe_2, or ·CH:CMePh

A. Thia-2′-carbocyanines

By reaction of XV (Y=S, R=Et, R′=SMe, X=SO_4Me) with 2-iodoquinoline ethiodide, the *meso*-(methylthio)thia-2′-carbocyanine, IX (Y=S, Z=CH:CH, R=R″=Et, R′=SMe, X=ClO_4), was reached.[50]



(XV)

The 4,5-benzo-derivative of the *meso*-methoxy-dye, IX (Y=S, Z=CH:CH, R=Me, R″=Et, R′=OMe, X=I), was prepared by condensing the 4,5-benzo-derivative of XV (Y=S, R=Me, R′=OMe, X=SO_4Me) with 2-methylthioquinoline ethiodide.[15] The *meso*-methoxy-dye, IX (Y=S, Z=CH:CH, R=R″=Me, R′=OMe, X=I), was prepared by heating a mixture of XI (Y=S, R=R′=Me), 2-ethylthioquinoline, and methyl toluene-*p*-sulphonate at 100° for 5 hours, boiling the salts with triethylamine in ethanol for 30 minutes, and treating with aqueous potassium iodide.[51]

B. Thiacarbocyanines

A symmetrical *meso*-(benzylthio)thiacarbocyanine, I (Y=S, R=Et, R′=SCH_2Ph, X=ClO_4), was prepared from XV (Y=S, R=Et, R′=SCH_2Ph, X=Br) by heating it with 2-methylthiobenzothiazole ethotoluene-*p*-sulphonate and triethylamine in pyridine, and treating with aqueous sodium perchlorate. Its analogues having a *meso*-methylthio-, -phenylthio-, -(*β*-carboxyethylthio)-, or -methoxy-group were similarly made, and also its unsymmetrical 4,5-benzo-derivative.[50] The

sensitising action of *meso*-alkoxy-dyes was exemplified by such symmetrical substances as I (Y=S, R=Me, R′=OMe, X=Br and Y=S, R=Et, R′=OEt or OCH_2CO_2H, X=I or ClO_4, respectively), and by the unsymmetrical IX (Y=Z=S, R=Et, R″=Ph, R′=OMe, X=ClO_4).[15] In preparing the four symmetrical thiacarbocyanines, I (Y=S, R=Me or Et, R′=MeO or EtO, X=I), the method was to fuse the ketone, XI (Y=S, R=Me or Et, R′=Me), with alkyl toluene-*p*-sulphonate, e.g., for 4 hours at 100°, to give the salt, XV (Y=S, R=Me or Et, R′=MeO or EtO, X=*p*-$SO_3 \cdot C_6H_4Me$), which was then boiled with a 2-alkylthiobenzothiazolium salt and triethylamine in ethanol for 30 minutes. Other symmetrical dyes had a *meso*-n-propoxy-, or -*β*-phenylethoxy-, group and various unsymmetrical ones were also made. Sometimes a mixture of ketone and 2-alkylthiobenzothiazole was fused with alkyl toluene-*p*-sulphonate and used for dye formation.[51]

The *meso*-methylthiacarbocyanine, IX (Y=Z=S, R=Et, R′=R″=Me, X=Br), was prepared by boiling the salts, XV (Y=S, R=R′=Me, X=SO_4Me), and 2-methylthiobenzothiazole methotoluene-*p*-sulphonate in methanol and converting into bromide; its analogue, IX (Y=Z=S, R=R″=Et, R′=Ph, X=I), was prepared similarly, and both dyes were repeatedly recrystallised from ethanol.[53]

C. Indothia-, Indoxa-, Oxathia-, and Selenathia-carbocyanines

The *meso*-methoxyindothiacarbocyanine, IX (Y=CMe_2, Z=S, R=R″=Me, R′=OMe, X=ClO_4), was prepared from the ketone, XI Y=CMe_2, R=R′=Me), by heating it and methyl toluene-*p*-sulphonate, either with 2-methylthiobenzothiazole, or with 3-methylbenzothiazoline-2-thione, at 100° for 4 hours, boiling the resultant mixture of salts with triethylamine in ethanol for 30 minutes, and converting into perchlorate.[51]

The *meso*-methoxyindoxacarbocyanine, IX (Y=CMe_2, Z=O, R=R″=Me, R′=OMe, X=ClO_4), was similarly prepared from the same ketone.[51]

The *meso*-methoxyoxathiacarbocyanine, IX (Y=O, Z=S, R=R″=Et, R′=OMe, X=I), and the bromide of its 4,5-benzo-derivative, were prepared by heating 2-methylthiobenzoxazole ethotoluene-*p*-sulphonate and the salt, XV (Y=S, R=Et, R′=OMe, X=SO_4Me), or its 4,5-benzo-derivative, with triethylamine in acetic anhydride for 15 minutes. The analogous dye, IX (Y=O, Z=S, R=Me, R″=CH_2Ph, R′=OEt, X=SO_4Me), was also made.[15] The *meso*-methyl dye, IX

(Y=O, Z=S, R=R″=Et, R′=Me, X=I), was prepared by boiling XV (Y=O, R=Et, R′=Me, X=I) with 2-methylthiobenzothiazole ethotoluene-*p*-sulphonate in ethanol, with addition of triethylamine, and treating with potassium iodide.[53] A tetrahydro-derivative of the *meso*-methyl dye, IX (Y=O, Z=S, R=R″=Et, R′=Me, X=I), was prepared by interaction of 2-methyl-4,5,6,7-tetrahydrobenzoxazole ethiodide and XV (Y=S, R=Et, R′=SMe, X=*p*-$SO_3 \cdot C_6H_4Me$).[120]

The *meso*-ethoxyselenathiacarbocyanine, IX (Y=Se, Z=S, R=R″=Me, R′=OEt, X=ClO_4), was prepared from the salts, XV (Y=Se, R=Me, R′=OEt, X=SO_4Et), and 2-methylthiobenzothiazole methiodide, by boiling with triethylamine in ethanol for 10 minutes, and converting into perchlorate.[15]

16. Symmetrical and Unsymmetrical Carbocyanines with a Meso-NRR′, or Meso-CH(COR)$_2$ Group, etc., from Meso-(Alkylthio)-carbocyanines: Non-Ionic Dyes with the Chain :CH·C·CH:, where Q = :NR, :O, :S, :Se, :C(COR)$_2$, etc.

A. 2,2′- and 4,4′-Carbocyanines

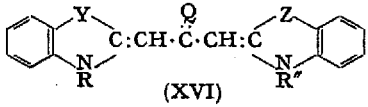
1,1′-Dimethyl-*meso*-piperidino-2,2′-carbocyanine iodide was prepared by heating the corresponding *meso*-methylthio-dye with piperidine and triethylamine in pyridine at 50° for 3 hours.[59]

1,1′-Dimethyl-*meso*-pyrrolidino-4,4′-carbocyanine iodide was made similarly but heating with pyrrolidine and triethylamine in pyridine was at 40° for 8 hours.[59]

B. Thia-2′-carbocyanines

The thia-2′-carbocyanine, IX (Y=S, Z=CH:CH, R=Et, R″=Me, R′=*p*-NHC_6H_4Me, X=ClO_4), was prepared from the corresponding *meso*-ethylthio-compound by heating with *p*-toluidine at 140° for 1·5 hours and precipitating with ether.[54] An analogue with a *meso*-$NHCH_2Ph$ group was also made.[59]

The *meso*-methoxy-dye, IX (Y=S, Z=CH:CH, R=R″=Me, R′=OMe, X=I) (see section 15-A), was converted, by boiling with pyridine for 40 minutes, into XVI (Y=S, Z=CH:CH, R=R″=Me, Q=O). After recrystallising from methanol, the orange crystals had



(XVI)

m.p. 294–296°.[60] Another compound of a related type, the 6′-methoxy-derivative of XVI (Y=S, Z=CH:CH, R=R″=Et, Q=S) was prepared by heating the 6′-methoxy-derivative of the *meso*-(methylthio)-thia-2′-carbocyanine, IX (Y=S, Z=CH:CH, R=R″=Et, R′=SMe, X=I) with sodium sulphide in aqueous alcohol for 10 minutes.[61]

C. Thia- and Oxa-carbocyanines

By heating the symmetrical dye, I (Y=S, R=Et, R′=SEt, X=I), with aniline at 100° for 25 hours, the blue colour of the *meso*-ethylthio- changed to the pinkish orange of the *meso*-anilino-thiacarbocyanine; derivatives with a *p*-ethoxy- or *p*-methoxy-substituent in the anilino-group were similarly made, also the bromide of its *NN′*-dimethyl analogue. Unsymmetrical thiacarbocyanines with a meso-NHR group included IX (Y=Z=S, R=Me, R″=Et, R′=NHMe, NHC_6H_{11}, NHPh, *p*-NHC_6H_4OEt, *p*-NHC_6H_4OMe, *p*-NHC_6H_4Cl, or $NHCH_2Ph$, X=I).[54] 3,3′-Diethylthiacarbocyanines with a *meso*-dimethylamino-, -propylamino-, or -pyrrolidino-group were prepared.[59]

Reaction of a *meso*-(methylthio)thiacarbocyanine with butylamine or piperidine in hot ethanol was complete in 15–20 minutes; reaction with aniline was slower and, after 15–20 hours at 100°, three products were isolated, the *meso*-anilinothiacarbocyanine being accompanied by compounds of type XVI (Q=:NPh and :S, respectively).[55] The conversion of *meso*-NHR-thiacarbocyanines into non-ionic compounds with the chain $RN:C(\cdot CH:)_2$ could be effected by boiling with sodium methoxide in methanol for 30 minutes, or by grinding an acetone suspension of the dye with aqueous sodium hydroxide, or by treating with sodium hydroxide in aqueous methanol. Thereby the red colour of IX (Y=Z=S, R=Me, R″=Et, R′=NHPh, *p*-NHC_6H_4OEt, NHC_6H_{11}, or NHMe, X=I) changed to the yellow of XVI (Y=Z=S, R=Me, R″=Et, Q=:NPh, *p*-$:N\cdot C_6H_4OEt$, $:NC_6H_{11}$, or :NMe). The first of these products could be converted into the *meso*-(methylanilino)thia-carbocyanine, IX (Y=Z=S, R=Me, R″=Et, R′=NMePh, X=I), either by boiling with methyl iodide for 10 hours, or by heating with methyl toluene-*p*-sulphonate at 100° for 5 hours, whilst by boiling with ethyl iodide it gave the corresponding *meso*-NEtPh-dye. The second and third products were converted by methyl iodide into the *meso*-NMe*p*-C_6H_4OEt- and *meso*-$NMeC_6H_{11}$-thiacarbocyanines, the former being isolated as perchlorate. From the fourth product, by the action of

methyl iodide and ethyl iodide, thiacarbocyanines with a *meso*-NMe_2 or -NEtMe group were made, as perchlorates.[56] A *meso*-piperidino-thiacarbocyanine, IX (Y=Z=S, R=Me, R″=Et, R′=NC_5H_{10}, X=I), was prepared by heating the *meso*-ethylthio- or -phenylthio-analogue with piperidine for 30 minutes. Its *meso*-morpholino-analogue was made similarly. Its *meso*-dimethylamino-analogue was prepared from the *meso*-ethylthio-dye by heating with aqueous dimethylamine, and was isolated as perchlorate.[58] The thiacarbocyanines, I (Y=S, R=Et, R′=NHPh, $NHCH_2Ph$, or $NHC_4H_9^n$), were converted by alkali into the substances, XVI (Y=Z=S, R=R″=Et, R′=:NPh, $:NCH_2Ph$ or $:NC_4H_9^n$). Acetyl chloride converted these into the thiacarbocyanines, I (Y=S, R=Et, R=PhNCOMe, $PhCH_2NCOMe$, or $C_4H_9^nNCOMe$).[55] The sensitising properties of symmetrical thiacarbocyanines with a *meso*-NRCOMe group were patented: of these, I (Y=S, R=Me, R′=PhNCOMe, X=*p*-$SO_3 \cdot C_6H_4Me$) was prepared by boiling the *meso*-anilino-dye with acetic anhydride and pyridine for 7 minutes. Analogues in which the *meso*-PhNCOMe carried a *p*-ethoxy- or -methyl, or *m*-chloro- or -methyl substituent in the phenyl group were also described, also the 4,5,4′,5′-dibenzo-derivative of the first. Others had as *meso*-substituent $Me(CH_2)_6N \cdot COMe$, $PhCH_2NCOMe$, or β-$C_{10}H_7NCOMe$. Passage of dry ammonia into a suspension of a *meso*-(methylthio)thiacarbocyanine in pyridine containing triethylamine gave the *meso*-amino-analogue, which, on acetylation, gave the dye with a *meso*-NHCOMe group.[57] The *meso*-ethoxythiacarbocyanines, I (R=Me or Et, R′=OEt, X=I), could be converted into the non-ionic compounds, XVI (Y=Z=S, R=R″=Me or Et, Q=O), by heating with aniline at 150°, by heating with pyridine, or by the action of sodium ethoxide in ethanol. An *N*-ethyl-*N*′-methyl analogue was also made, and its 6,7-benzo-derivative.[60] Alternatively the *meso*-(methylthio)-thiacarbocyanine, I (Y=S, R=Et, R′=SMe, X=I), yielded XVI (Y=Z=S, R=R″=Et, Q=O) by boiling with potassium hydroxide in aqueous ethanol for 15 minutes.[61] Treatment of a *meso*-alkoxythiacarbocyanine with a primary or secondary amine gave a *meso*-NHR-thiacarbocyanine, but use of a tertiary amine gave a compound with the chain $O:C(\cdot CH:)_2$.[55]

By boiling the *meso*-(ethylthio)thiacarbocyanine, IX (Y=Z=S, R=R″=Et, R′=SEt, X=I), with pyridine for 4 hours, its blue colour changed to pink and the compound XVI (Y=Z=S, R=R″=Et, Q=S) was precipitated with water and extracted with ether. Its

5-methyl derivative was made from the 5-methyl-*meso*-(methylthio)-thiacarbocyanine; its *N*-ethyl-*N'*-methyl analogue, and the 4',5'-benzo-derivative of that were also made.[62] Compounds with the chain $S:C(\cdot CH:)_2$ and $Se:C(\cdot CH:)_2$ were also made by the action of a metal sulphide or selenide on a *meso*-(alkylthio)thiacarbocyanine. Thus by heating I (Y=S, R=Et, R'=SMe, X=I) in ethanol with aqueous sodium sulphide or selenide, there resulted XVI (Y=Z=S, R=R''= Et, Q=S or Se) in yields of 68 % and 50 % after purification; a 4,5-benzo- and 6,7,6',7'-dibenzo-derivative of the former were also made.[61]

By heating the *meso*-(ethylthio)thiacarbocyanine, I (Y=S, R=Et, R'=SEt, X=I), with acetylacetone and triethylamine at 100° for 10 hours, and precipitating with ether, an analogue with the group $\cdot CH(COMe)_2$ in the *meso*-position was obtained; the 5-chloro-, 5-methyl, and 5,5'-dimethyl derivatives of this dye were similarly made, also its *NN'*-dimethyl analogue (as bromide), its *N*-ethyl-*N'*-methyl analogue, and the 4',5'-benzo-derivative of the last. The *meso*-R'-thiacarbocyanines, IX (Y=Z=S, R=Me, R''=Et, X=I), were prepared, where R' was $\cdot CH(COEt)_2$, $\cdot CH(COMe)(COPh)$, $\cdot CH(COMe)(CO_2Et)$, $\cdot CH(COPh)(CO_2Et)$, or $\cdot CH(COMe)(CONHPh)$; the *NN'*-diethyl analogue with a $\cdot CH(COMe)(CO_2Me)$ group was also made.[63]

By heating the *meso*-(ethylthio)thiacarbocyanine, I (Y=S, R=Me, R'=SEt, X=I), with ethyl cyanoacetate and triethylamine, the compound XVI (Y=Z=S, R=Me, Q=$:C(CO_2Et)CN$) was prepared. Its *N*-ethyl-*N'*-methyl and *NN'*-diethyl analogues were made, besides substances with substituents such as 4,5-benzo-, 5-chloro-, 5-chloro-5',6'-dimethoxy-, or 6-methyl groups. Instead of triethylamine, the condensing agent might be sodium ethoxide in ethanol, or potassium carbonate. Other substances with a reactive methylene group could take the place of ethyl cyanoacetate giving compounds, XVI, in which Q was $:C(CO_2Me)CN$, $:C(CONH_2)CN$, $:C(CONHEt)CN$, $:C(CONHPh)CN$, $:C(CO_2CH_2Ph)CN$, or $:C(CN)_2$.[64]

The *meso*-*p*-toluidino-oxacarbocyanine, I (Y=O, R=Me, R'= *p*-$NH\cdot C_6H_4Me$, X=I), was prepared by heating the corresponding *meso*-methylthio-dye with *p*-toluidine at 100° for 3 hours, and precipitating with ether.[54]

The 5,5'-diphenyl derivative of the compound, XVI (Y=Z=O, R=R'=Me, Q=$:C(CO_2Et)CN$), was prepared by heating the corresponding *meso*-(methylthio)oxacarbocyanine with chloroform, ethyl cyanoacetate, and triethylamine at 100° for 4 hours.[64]

D. Indothia-, Indoxa-, Oxathia-, and Selenathia-carbocyanines

The indothiacarbocyanine, IX ($Y=CMe_2$, $Z=S$, $R=R''=Me$, $R'=p$-$MeN\cdot C_6H_4OEt$, $X=I$), was prepared from the compound, XVI ($Y=CMe_2$, $Z=S$, $R=R''=Me$, $Q=p$-$:NC_6H_4OEt$), by boiling with methyl iodide for 2·5 hours.[56]

A *meso*-methoxyindothiacarbocyanine was boiled with pyridine for 2 hours, whereby the orange colour changed to the yellow of a compound with the chain $O:C(\cdot CH:)_2$.[60]

A *meso*-methoxyindoxacarbocyanine was converted by boiling with pyridine for 10 hours into a compound with the chain $O:C(\cdot CH:)_2$.[60]

The *meso*-*p*-toluidino-oxathiacarbocyanine, I X($Y=O$, $Z=S$, $R=R''=Me$, $R'=p$-NHC_6H_4Me, $X=I$), was prepared by heating the corresponding *meso*-methylthio-dye with *p*-toluidine at 100°. Its 5'-chloro-derivative was made, also the 5,6-dimethyl derivative of its *N'*-ethyl-*N*-methyl analogue.[52] By heating a *meso*-*p*-toluidino-dye with sodium methoxide in methanol, there was obtained the compound XVI ($Y=O$, $Z=S$, $R=Me$, $R''=Et$, $Q=p$-$:NC_6H_4Me$) which was converted by methyl iodide, followed by perchlorate, into IX ($Y=O$, $Z=S$, $R=Me$, $R''=Et$, $R'=p$-$NMeC_6H_4Me$, $X=ClO_4$).[54] The 5'-chloro-derivative of a compound, XVI ($Y=O$, $Z=S$, $R=R''=Et$, $Q=S$), was prepared from a *meso*-(methylthio)oxathiacarbocyanine by heating with sodium sulphide in aqueous alcohol.[58]

By heating the *meso*-(ethylthio)oxathiacarbocyanine, IX ($Y=O$, $Z=S$, $R=Et$, $R'=SEt$, $R''=Me$, $X=I$), with acetylacetone and triethylamine at 100° for 4·5 hours, the group $\cdot CH(COMe)_2$ was introduced into the *meso*-position.[61] By heating the 5,6-dimethyl derivative of IX ($Y=O$, $Z=S$, $R=R''=Me$, $R'=SEt$, $X=I$) with ethyl cyanoacetate and triethylamine for 4 hours, it was converted into the 5,6-dimethyl derivative of the compound, XVI ($Y=O$, $Z=S$, $R=R''=Me$, $Q=:C(CO_2Et)CN$).[62]

A *meso*-(diacetylmethyl)selenathiacarbocyanine, IX ($Y=Se$, $Z=S$, $R=R''=Et$, $R'=CH(COMe)_2$, $X=I$), was prepared by the action of acetylacetone and triethylamine on the *meso*-ethylthio-dye.[61] By heating the *meso*-(methylthio)selenathiacarbocyanine, IX ($Y=Se$, $Z=S$, $R=R''=Et$, $R'=SMe$, $X=I$), with sodium sulphide in aqueous alcohol for 10 minutes, the compound, XVI ($Y=Se$, $Z=S$, $R=R''=Et$, $Q=S$), was obtained.[58]

E. Thia-(1,3,4-thiadiazolo)carbocyanine

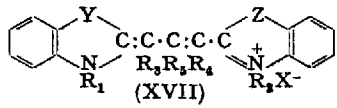
A *meso*-(methylthio)carbocyanine, having one benzothiazole and one 1,3,4-thiadiazole nucleus, was converted into the *meso*-morpholino-analogue.[59]

In Table III the properties of some compounds of formula XVI are given. The more general formula XXII is there used, in order that two similar substances with a five-membered carbon chain (see VII-8-E) may be included.

17. α-Substituted or αα'-Di-substituted Carbocyanines

A. Indo-2'- and Oxa-2'-carbocyanines

The α'-cyano-indo-2'-carbocyanine, XVII (Y=CMe_2, Z=CH:CH, R^1=R^2=Me, R^3=R^5=H, R^4=CN, X=I), was prepared by heating 2-β-ethylthiovinyl-3,3-dimethylindolenine methotoluene-*p*-sulphonate and 2-cyanomethylene-1-methyldihydroquinoline in acetic anhydride, followed by treatment with iodide.[121]



(XVII)

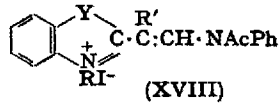
The α'-cyano-oxa-2'-carbocyanine, XVII (Y=O, Z=CH:CH, R^1=R^2=Me, R^3=R^5=H, R^4=CN, X=I), was prepared analogously.[121]

B. Thia-, Oxa-, and Selena-carbocyanines

By an extension of the method of Chapter IV-6, the symmetrical αα'-dimethylthiacarbocyanine, XVII (Y=S, R^1=R^2=Et, R^3=R^4=Me, R^5=H, X=I), was prepared by boiling 2-ethylbenzothiazole ethiodide and ethyl orthoformate in pyridine. Its 6,7,6',7'-dibenzo-derivative was similarly made and also, by use of ethyl orthoacetate, the *meso*-methyl derivative of the latter.[66] Ethyl orthoformate was used in pyridine for preparing XVII (Y=Z=S, R^1=R^2=R^3=R^4=Me, R^5=H, X=I) but in acetic anhydride, with boiling for 1 hour, for preparing the corresponding XVII (Y=S, R^1=R^2=Me, R^3=R^4=Ph, α-$C_{10}H_7$, or β-$C_{10}H_{11}$, R^5=H) from the methiodides of 2-benzyl-, 2-α-naphthylmethyl-, or 2-β-tetrahydronaphthylmethyl-benzothiazole, respectively, and the last dye was isolated as perchlorate; the yields of these last three recrystallised products were 22 %, 29 %, and 25 %. The

narrow absorption curve of the dye with an unsubstituted chain broadened on introduction of $\alpha\alpha'$-dimethyl or $\alpha\alpha'$-diphenyl groups.[68] A series of $\alpha\alpha'$-disubstituted symmetrical thiacarbocyanines with *NN'*-diphenyl groups (see X-4-C) was prepared by use of the appropriate ortho-esters in pyridine: the $\alpha\alpha'$-substituents were dimethyl, diethyl and dibromo, the first two dyes being iodides and the third a bromide; the yields were 72 %, 6 %, and 17 %. The ortho-ester in acetic anhydride was used, and gave a 25 % yield, for the corresponding dye with $\alpha\alpha'$-diphenyl groups, as pyridine failed. The thiacarbocyanine, XVII (Y=Z=S, R^1=R^2=Ph, R^3=R^4=Br, R^5=Me, X=Br), was obtained in 22 % yield.[122] Absorption data for some of the dyes[67,68] are given in Table II. By boiling 2-ethoxymethylbenzothiazole methotoluene-*p*-sulphonate with ethyl orthoformate in pyridine for 35 minutes, there resulted XVII (Y=Z=S, R^1=R^2=Me, R^3=R^4=OEt, R^5=H, X=I). The corresponding dye with $\alpha\alpha'$-di-β-naphthoxy-substituents was made, also the bromide with $\alpha\alpha'$-di-(*m*-methylphenoxy)-substituents, the toluene-*p*-sulphonate with di-(*p*-chlorophenoxy)-groups, and 4,5,4',5'- and 6,7,6',7'-dibenzo-derivatives of the bromide with $\alpha\alpha'$-diphenoxy-groups.[69]

By boiling diphenylformamidine in acetic anhydride (V-6) with 2-ethyl- or with 2-n-propyl-benzothiazole ethiodide, the salts, XVIII (Y=S, R=Et, R'=Me or Pr^n), resulted. The former was condensed



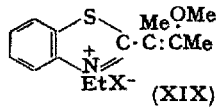
(XVIII)

with 4,5-benzo-, or 5-diethylamino-, 2-methylbenzothiazole ethiodide in pyridine to give the 4,5-benzo- and 5-diethylamino-derivatives of XVII (Y=Z=S, R^1=R^2=Et, R^3=Me, R^4=R^5=H, X=I and ClO_4, respectively), whilst the latter was condensed with 2-methyl-6,7-benzobenzothiazole ethiodide.[70] Absorption data were given for some α-substituted thiacarbocyanines, of which XVII (Y=Z=S, R^1=Ph, R^2=Et, R^3=R^5=H, R^4=Me, X=I) was prepared in 60 % yield by boiling 2-ethylbenzothiazole ethiodide, 2-β-acetanilidovinylbenzothiazole phen-iodide, and pyridine for 1 hour and recrystallising twice; its isomer, XVII (Y=Z=S, R^1=Ph, R^2=Et, R^3=Me, R^4=R^5=H, X=I), was similarly prepared from 2-ethylbenzothiazole phenochloride and 2-β-acetanilidovinylbenzothiazole ethiodide in pyridine; XVII (Y=Z=S, R^1=R^2=Ph, R^3=R^5=H, R^4=Me, X=I) was prepared from two

pheniodides.[66] The dye, XVII (Y=Z=S, R^1=R^2=Et, R^3=COMe, R^4=R^5=H, X=I), was prepared by heating 2-acetonylbenzothiazole ethiodide and 2-β-acetanilidovinylbenzothiazole ethiodide in pyridine.[75] The α-hydroxythiacarbocyanine, XVII (Y=Z=S, R^1=Me, R^2=Et, R^3=OH, R^4=R^5=H, X=ClO_4), was prepared by heating 2-hydroxymethylbenzothiazole methotoluene-*p*-sulphonate and 2-β-acetanilidovinylbenzothiazole ethiodide with triethylamine in ethanol, and treating the product with sodium perchlorate. Its orange-red solution changed with triethylamine to a transient green.[123]

The α-cyanothiacarbocyanine, XVII (Y=Z=S, R^1=R^2=Et, R^3=CN,R^4 =R^5=H, X=I), was prepared by heating 2-cyanomethylene-3-ethylbenzothiazoline with a benzothiazolium salt having the group ·CH:CH·SEt in acetic anhydride. The 5-chloro-derivative of such a salt was used in the preparation of the 5-chloro-derivative of XVII (Y=Z=S, R^1=R^2=Me, R^3=CN, R^4=R^5=H, X=I).[121]

By the method of Chapter V-10,2-β-ethylthiovinylbenzothiazole methiodide was condensed with 2-ethylbenzothiazole methotoluene-*p*-sulphonate, by heating in pyridine, to give XVII (Y=Z=S, R^1=R^2=R^3=Me, R^4=R^5=H, X=I).[124] By the method of section 13, 2-ethylbenzothiazole ethiodide was heated in acetic anhydride with the 4,5-benzo-derivative of XI (Y=S, R=Et, R′=Me) to give the 4,5-benzo-



(XIX)

derivative of XVII (Y=Z=S, R^1=R^2=Et, R^3=H, R^4=R^5=Me, X=I).[116] By the method of section 15, XIX was prepared, condensed with 2-methylthiobenzothiazole ethotoluene-*p*-sulphonate by use of triethylamine in ethanol, and converted into the iodide, XVII (Y=Z=S, R^1=R^2=Et, R^3=Me, R^4=H, R^5=OMe, X=I).[15]

By the ortho-ester method (see IV-6), the 5,5′-diphenyl, and 4,5,4′,5′- and 6,7,6′,7′-dibenzo-derivatives of the oxacarbocyanine, XVII (Y=Z=O, R^1=R^2=Me, R^3=R^4=OPh, R^5=H, X=ClO_4, I, and SO_4Me, respectively), were prepared from the appropriate 2-phenoxymethylbenzoxazolium salts. There were also made XVII (Y=Z=O, R^1=R^2=Me, R^3=R^4=OEt or *p*-OC_6H_4OMe, R^5=H, X=ClO_4).[69]

The 5,5′-diethoxy-derivative of the αα′-dimethylselenacarbocyanine, XVII (Y=Z=Se, R^1=R^2=R^3=R^4=Me, R^5=H, X=Br), was

prepared from 5-ethoxy-2-ethylbenzoselenazole methomethylsulphate and ethyl orthoformate in pyridine. Similarly, by use of ethyl orthoacetate and ethyl orthopropionate, respectively, there were made XVII (Y=Z=Se, $R^1=R^2=R^3=R^4=Me$, $R^5=Me$ or Et, X=Br).[66] By boiling a 2-phenoxymethylbenzoselenazolium salt with ethyl orthoformate in pyridine for 20 minutes, XVII (Y=Z=Se, $R^1=R^2=Me$, $R^3=R^4=OPh$, $R^5=H$, X=Br) was arrived at.[69]

C. Indoselena-, Indothia-, Oxathia-, and Selenathia-carbocyanines

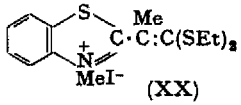
2-Ethylbenzoselenazole ethiodide on heating with diphenylformamidine in acetic anhydride gave XVIII (Y=Se, R=Et, R'=Me) which, by reaction with 2,3,3,6-tetramethylindolenine methiodide in pyridine, gave the 6-methyl derivative of the indoselenacarbocyanine, XVII ($Y=CMe_2$, Z=Se, $R^1=R^4=Me$, $R^2=Et$, $R^3=R^5=H$, X=ClO_4).[70]

A sample of α'-cyanoindothiacarbocyanine, XVII ($Y=CMe_2$, Z=S, $R^1=Me$, $R^2=Et$, $R^3=R^5=H$, $R^4=CN$, X=I), was prepared by heating 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide with 2-cyanomethylene-3-ethylbenzothiazoline in pyridine.[121]

The oxathiacarbocyanine, XVII (Y=O, Z=S, $R^1=R^2=Et$, $R^3=R^5=H$, $R^4=Me$, X=I), was prepared by heating the salt, XVIII (Y=S, R=Et, R'=Me), with 2-methylbenzoxazole ethiodide in pyridine.[70]

The salt, XVIII (Y=S, R=Et, R'=Me), was heated in pyridine with 2-methyl-, or 2-ethyl-, benzoselenazole ethiodide to give the selenathiacarbocyanines, XVII (Y=Se, Z=S, $R^1=R^2=Et$, $R^3=H$ or Me, $R^4=Me$, $R^5=H$, X=I).[70]

The intermediate salt, XX, by an extension of the method of



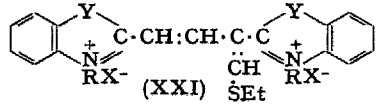
(XX)

section 14, was condensed with 2-methylbenzoselenazole methiodide to give XVII (Y=Se, Z=S, $R^1=R^2=R^4=Me$, $R^3=H$, $R^5=SEt$, X=I).[23]

18. Carbocyanines with an α-CHO Group, Synthesised from Carbocyanines with an Unsubstituted Chain

A. Thia-, Oxa-, and Selena-carbocyanines

By boiling the thiacarbocyanine, I (Y=S, R=Et, R′=H, X=*p*-$SO_3 \cdot C_6H_4Me$), with toluene-*p*-sulphonic acid and ethyl orthothioformate in acetic anhydride, the colour changed to yellow, and ether precipitated an orange oil, XXI (Y=S, R=Et, X=*p*-$SO_3 \cdot C_6H_4Me$).



(XXI)

Methyl or benzyl orthothioformate could likewise be used and gave oily salts with the group :CH·SMe or :CH·SCH_2Ph, respectively. Similar salts were prepared from 5,5′-dichloro- or -dimethyl-, or 4,5,4′,5′-dibenzo-thiacarbocyanines. Where a dye iodide was used as starting point, the resultant salt was called an iodide toluene-*p*-sulphonate: they could be converted into the di-iodides.[71] When the 5,5′-dichloro- or -dimethyl-, or the 4,5,4′,5′-dibenzo-derivatives of XXI (Y=S, R=Et, X=I) were boiled with methanol for 30 minutes, they were converted into the corresponding derivatives of the α-formylthiacarbocyanine, XVII (Y=Z=S, $R^1=R^2$=Et, $R^3=R^5$=H, R^4=CHO, X=I). Alternatively, instead of precipitating XXI from the original reaction mixture by means of ether, removal of the solvent in a vacuum, and treatment of the residue with ethanol and aqueous potassium iodide, gave the α-formylthiacarbocyanine.[72]

The 4,5,4′,5′-dibenzo-derivative of the α-formyloxacarbocyanine, XVII (Y=Z=O, $R^1=R^2$=Et, $R^3=R^5$=H, R^4=CHO, X=I), was prepared by boiling together for 1 hour the 4,5,4′,5′-dibenzo-derivative of I (Y=O, R=Et, R′=H, X=*p*-$SO_3 \cdot C_6H_4Me$), toluene-*p*-sulphonic acid, ethyl orthothioformate, and acetic anhydride, removing the solvent, dissolving the washed residue in ethanol, and treating with potassium iodide.[72]

The salt, XXI (Y=Se, R=Et, X=*p*-$SO_3 \cdot C_6H_4Me$), was prepared from the selenacarbocyanine, I (Y=Se, R=Et, R′=H, X=*p*-$SO_3 \cdot C_6H_4Me$), by heating with toluene-*p*-sulphonic acid, ethyl orthothioformate, and acetic anhydride, being precipitated by ether as a brown oil.[71] Removal of the solvent, however, and treatment of the residue with potassium iodide, gave the α-formylselenacarbocyanine, XVII (Y=Z=Se, $R^1=R^2$=Et, $R^3=R^5$=H, R^4=CHO, X=I).[72]

TABLE I. Some Properties of Some Symmetrical *Meso*-Substituted Thiacarbocyanines (Formula I; Y=S, R=Et, X=I)

R′	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Bathochromic shift on substitution (Å)	Sensitising (Å) Maximum	Extent	Ref.
H	steel-blue prisms	269	5575	—	5900 (and 5330)	6000	6, 125, 126
Me	copper-coloured	280–290	5430	— 145	5900 (and 5200)	6400	4
Et	prisms; blue and green reflex	236–237	5475	— 105	6300	—	6, 15
Pr^n	greenish-bronze prisms	246–248	5475	— 105	—	—	6
cyclo-Pr	green	202–204	—	—	5800	6600	127
$C_{16}H_{31}$	green	124–210	5450	— 125	5800	—	29
$\cdot CH_2Ph$	emerald-green prisms	242–243	5500	— 75	—	—	6
$\cdot CH_2OPh$	reddish-coppery	202–204	5525	— 50	—	—	6
$\cdot CH{:}CHPh$	steel-blue	266	5600	25	6000	—	27
Ph	greenish-bronze	300–301	5600	25	—	—	6
$o\text{-}C_6H_4CO_2H$	green; golden reflex	205–207	5650	75	5900	6450	31[a]
OMe	—	207–209[b]	4950	625	5200	—	15, 55
SMe	—	—	5810 (and 5400)	235 (and — 175)	6600	6900	23, 55[c]
CO_2Et	—	236–237[b]	5640	65	—	—	35[d]
NHC_4H_9	—	177–178[b]	4700	— 875	—	—	55[e]
NC_4H_9COMe	—	—	5670	105	—	—	55
NHPh	dark red	237[b] / 184–186[b]	5010	— 565	5900	6200	54, 55
NPhCOMe	—	—	5640	65	—	—	55

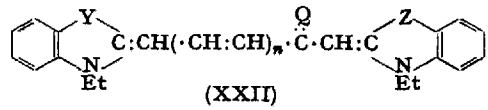
[a] Data for 5,5′-dichloro-derivative.
[b] Decomp. not record.
[c] Sensitising data for 6-Me-derivative.
[d] R=R″=Me, X=SO_4Me.
[e] X=ClO_4

TABLE II. Some Properties of Some αα′-Di-substituted and α-Substituted Thiacarbocyanines (Formula XVII; Y=Z=S, R^5=H, X=I)

R^1	R^2	R^3	R^4	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	$\varepsilon \times 10^{-4}$	Sensitising Maximum	(Å) Extent	Ref.
Me	Me	H	H	—	280	5580	14·0	—	—	64, 66, 128
Me	Me	Me	Me	bronze needles	223	5700	7·0	6000[a]	6600[a]	63, 64, 66
Me	Me	Ph	Ph	violet	152	5800	4·1	—	—	64, 66[b]
Me	Me	α-$C_{10}H_7$	α-$C_{10}H_7$	violet	176	5680	3·7	—	—	66[b]
Me	Me	β-$C_{10}H_{11}$	β-$C_{10}H_{11}$	blue	152	5780	2·1	—	—	66[b]
Me	Me	*m*-OC_6H_4Me	*m*-OC_6H_4Me	brassy green	234–235	5750	—	6400	6700	67[c]
Ph	Ph	H	H	—	—	5650	15·5	—	—	64, 65
Ph	Ph	Me	Me	—	—	6020	8·8	—	—	64, 66
Ph	Ph	Et	Et	—	—	6000	6·6	—	—	64, 66
Ph	Ph	Ph	Ph	—	—	6010	4·0	—	—	64, 66[c]
Ph	Ph	α-$C_{10}H_7$	α-$C_{10}H_7$	bronze	196–197[d]	5920	9·5	—	—	66[b]
Ph	Et	H	H	dark green tablets	243	5600	14·8	—	—	66
Ph	Et	H	Me	bronze lustre	158[d]	5620	11·0	—	—	66
Ph	Et	Me	H	blue-green	252[d]	5700	14·8	—	—	66
Ph	Ph	H	Me	—	275	5720	15·0	—	—	66
Et	Et	H	COMe	—	—	5700	—	6100	6400	71
Et	Me	H	OPh	dark green	212–214	—	—	6250	6400	67
Et	Et	H	CHO	orange; green reflex	253	—	—	5500	5800	70
Et	Et	H	CO_2Et	—	215–216[d]	5040	—	—	—	39

[a] Sensitising data for R^1=R^3=Et.
[b] X=ClO_4.
[c] X=Br.
[d] Decomp. not recorded.

TABLE III. Some Properties of Compounds of Formula XXII



(XXII)

Y	Z	Q	n	Appearance	M.p. (°C) (decomp.)	Sensitising (Å) Maximum	Extent	Ref.
O	S	O	1	dark red	152–155[a]	—	—	60[b]
S	S	O	1	orange	131–137	5300	6200	60
S	S	O	0	canary yellow needles	253–256	4450	5100	60
O	S	S	0	brownish needles	221–222	—	5650	61[c]
S	S	S	0	red; blue reflex	291–292 269[a]	5250 and 5600	6100	61, 62
Se	S	S	0	reddish	274–275	5300 and 5800	6300	61
S	S	Se	0	green	269–271	5400 to 5900	6300	61
S	S	:NPh	0	—	175[a]	—	—	55
S	S	$:C\langle^{CN}_{CO_2Et}$	0	red plates	184–186[a]	5600	6250	64
S	S	$:C\langle^{CN}_{CN}$	0	orange-red	262–263[a]	5200	5900	64
S	S	$:C\langle^{CN}_{CONHPh}$	0	orange-red	134–138	—	—	64

[a] Decomp. not recorded.
[b] Data for *NN'*-dimethyl analogue.
[c] 5-Cl in benzothiazoline nucleus.

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CHAPTER VII

Symmetrical and Unsymmetrical Pentamethincyanines, Including those with Substituents on the Chain

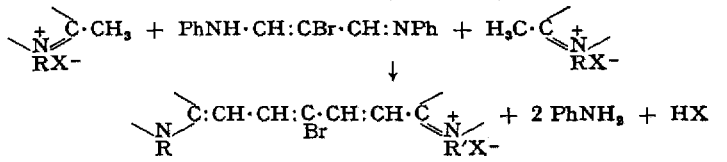
1. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, by Use of a 1-Anilino-3-aniloprop-1-ene, or its Salt

A. General

The first preparations of a pentamethincyanine were patented in 1922 (see section 2-A and 4-A). Patents of the present method appeared in 1930 and dealt with the preparation, firstly, of *meso*-substituted symmetrical pentamethincyanines[1] and, secondly, of intermediate compounds leading to symmetrical and unsymmetrical pentamethincyanines with an unsubstituted chain.[2] Soon after their acceptance, there appeared in the scientific literature a comprehensive account of the *meso*-substituted symmetrical pentamethincyanines.[3] It seems suitable to include in the present chapter dicarbocyanines carrying substituents on the chain as well as those with an unsubstituted chain.

This method is analogous to the diphenylformamidine method for trimethincyanines (see IV-9; V-6). α-Bromo-(or α-chloro-)β-anilinoacraldehyde anil, PhNH·CH:CBr·CH:NPh, i.e., 1-anilino-3-anilo-2-bromoprop-1-ene, was chosen as starting point, because of its ready accessibility by the action of aniline in ethanol on mucobromic acid, OCH·CBr:CBr·CO_2H; β-anilino-α-nitroacraldehyde anil was also used, being prepared by treating mucobromic acid with sodium nitrite, followed by aniline. By condensing a quaternary salt, having a reactive methyl group, with the α-substituted-β-anilinoacraldehyde anil, *meso*-substituted dicarbocyanines of the 2,2′-, 4,4′-, thia-, oxa-, and indo-series were made, as described in the following sections; condensation was induced by heating with an excess of piperidine in pyridine or with

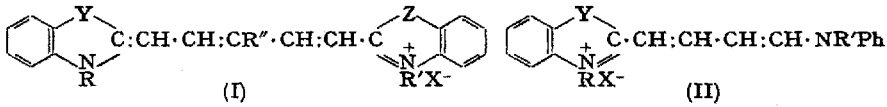
potassium acetate in acetic anhydride. The course of the reaction is indicated in equation 1.



(1)

The absorption maxima of the *meso*-bromo- or -chloro-pentamethincyanines lay at a longer wavelength by 920 Å than those of trimethincyanines possessing the same nuclei; some of the new dyes, but not those with a *meso*-nitro-substituent, possessed photographic sensitising properties, and the maximum sensitisation occurred at a longer wavelength by 1030 Å than that of trimethincyanines with the same nuclei. Whereas a *meso*-chloro- or -bromo-indodicarbocyanine dyed wool a brilliant blue, and a *meso*-chloro- or -bromo-2,2′-dicarbocyanine dyed it a dull greenish blue, the *meso*-nitro-compound of each type gave a dull red dyeing. Moreover the *meso*-nitro-2,2′-dicarbocyanine had two wide absorption bands instead of the normal absorption of a cyanine dye.[1,3] High yields of certain symmetrical *meso*-bromopentamethincyanines were subsequently obtained by the action of piperidine at 0°, during several hours, on an alcoholic suspension of the finely divided reactants.[4]

The unsubstituted 1-anilino-3-aniloprop-1-ene hydrochloride was condensed with two mols. of 1,3,3-trimethyl-2-methyleneindoline, by boiling in acetic anhydride, whence the symmetrical indodicarbocyanine, I (Y=Z=CMe_2, R=R′=Me, R″=H, X=I), was reached. Besides



(I) (II)

this, one mol. of the propene was condensed with one of a quaternary salt having a reactive methyl group, by boiling them in acetic anhydride, to give an intermediate salt, II (R′=Ac). Such salts of the benzothiazole and indolenine series were described and the latter type was also prepared from the corresponding methylene base. By reaction of such a salt, e.g., II (Y=CMe_2, R=Me, R′=Ac, X=I), with one having

a 2-methyl group and a different heterocyclic nucleus, e.g., 2-methylbenzothiazole ethiodide, an unsymmetrical pentamethincyanine, I (Y=CMe_2, Z=S, R=Me, R′=Et, R″=H, X=I), was obtained.[2] Whereas for preparing trimethincyanines, acetanilidovinyl salts gave better yields than anilinovinyl salts (see V-6-A), for pentamethincyanines the non-acetylated salts of type II (R′=H) were the better; these salts were made by heating an alcoholic solution of a quaternary salt, having a reactive methyl group, and a 1-anilino-3-aniloprop-1-ene salt, with a strong base. The propene salt could be more generally formulated as XArRN:CH·CH:CH·NRAr, where R could be hydrogen or alkyl, and there might be an alkyl group on the trimethin chain. Through these intermediate compounds, so wide a variety of unsymmetrical pentamethincyanines was prepared that almost any desired sensitising maximum became attainable.[5] The use of triethylamine at 0° gave good yields of certain unsymmetrical pentamethincyanines with an unsubstituted chain, and it is noteworthy that in these preparations it was the acetylated intermediate salts that were used.[6]

When it came to preparing analytically pure specimens of intermediate salts, having the group ·CH:CH·CH:CHNHPh, three methods were applied. One was to boil an alcoholic solution of a salt, having the group ·CH:CH·CH:CH·NAcPh, with excess of aniline for 20–30 minutes, and recrystallise the product, and this method was used in the 2-quinoline and benzothiazole series.[7] The second was to convert the crude 4-anilino-1,3-butadienyl salt by means of alkali into an *N*-alkyl base, having the group :CH·CH:CH·CH:NPh, whence, by treatment with acid and aqueous sodium perchlorate, pure perchlorates were obtained: these were made in the 2- and 4-quinoline, benzothiazole, benzoselenazole, and indolenine series.[6] The third method of preparing quaternary salts with the group ·CH:CH·CH:CH·NHPh was by the action of aniline on quaternary salts having the group ·CH:CH·CH:CH·OEt[8] (see section 2-A) and it was applied to the preparation of pure salts of the 2- and 4-quinoline, benzothiazole, benzoselenazole, benzoxazole, and thiazoline series.[6]

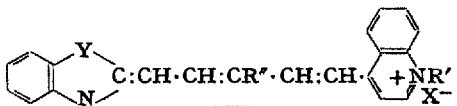
B. 2,2′-, 2,4′-, and 4,4′-Dicarbocyanines

The symmetrical *meso*-chloro-2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Et, R″=Cl, X=I), was prepared by boiling together for an hour quinaldine ethiodide, 1-anilino-3-anilo-2-chloroprop-1-ene, and

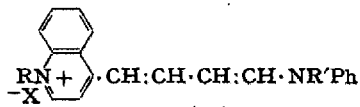
piperidine in pyridine, and was recrystallised from alcohol, in which it gave a deep-blue solution. The corresponding *meso*-nitro- and *meso*-bromo-compounds were similarly made, also the 4,4′-diphenyl derivative of the last; the 4,4′-diphenyl derivative of the *meso*-chloro-compound was prepared by boiling 4-phenylquinaldine ethiodide, 1-anilino-3-anilo-2-chloroprop-1-ene, and anhydrous potassium acetate in acetic anhydride for 1·5 hours. Both diphenyl dyes were sparingly soluble in ethanol and their green solutions had their absorption maxima at longer wavelengths than those of the corresponding unsubstituted dyes, whilst the sensitising action was weaker.[3] When the *meso*-bromo-dye, I (Y=Z=CH:CH, R=R′=Et, R″=X=Br), was prepared at 0° with piperidine in ethanol, starting from quinaldine ethotoluene-*p*-sulphonate, the yield of washed dye was 87 %.[4] 1-Anilino-3-anilo-2-methylprop-1-ene hydrochloride was synthesised and, by boiling for 5 minutes with quinaldine ethotoluene-*p*-sulphonate, sodium acetate, and acetic anhydride, and pouring into aqueous potassium iodide, gave the *meso*-methyl-2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Et, R″=Me, X=I), in 38 % yield after washing, and recrystallisation from methanol.[9]

The unsubstituted symmetrical 2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Et, R″=H, X=I), was prepared in 55 % yield by heating quinaldine ethiodide and 1-anilino-3-aniloprop-1-ene with acetic anhydride and anhydrous potassium acetate, and was recrystallised from methanol. Its melting point, sensitising maximum, and the colour of its alcoholic solution were compared with those of its trimethin- and heptamethin-analogues,[10,11] whilst its absorption maximum was compared with those of the methin-, trimethin-, and heptamethin-analogues.[12] With piperidine as condensing agent, the yield was only 13 %.[13]

The 2,4′-dicarbocyanine, III (Y=CH:CH, R=R′=Et, R″=H, X=I), was obtained in 21 % yield by the reaction at 0° of an alcoholic



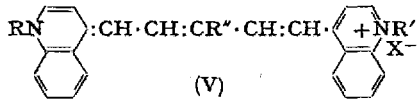
(III)



(IV)

suspension of IV (R=Et, R′=Ac, X=I) and quinaldine ethiodide (1 mol. of each) with triethylamine (2 mols.), followed by thorough washing and by two recrystallisations from methanol.[6]

The symmetrical *meso*-chloro-4,4′-dicarbocyanine iodide, V (R=R′=Et, R″=Cl, X=I), was prepared by 5 minutes' boiling of lepidine ethiodide, 1-anilino-3-anilo-2-chloroprop-1-ene, and anhydrous potassium acetate in acetic anhydride. The corresponding *meso*-bromo-compound could not be made similarly but was prepared by boiling



(V)

lepidine ethiodide and 1-anilino-3-anilo-2-bromoprop-1-ene hydrobromide in pyridine, which contained piperidine; both dyes gave green solutions and had their absorption and sensitising maxima in the infra-red. The *meso*-chloro- or -bromo-dicarbocyanines with quinoline nuclei were better sensitisers than those with other heterocyclic nuclei.[3] By preparing the *meso*-bromo-dye, V (R″=Br), at 0°, from the propene hydrobromide and lepidine ethotoluene-*p*-sulphonate, with piperidine as condensing agent, the yield, after washing the product with acetone until the filtrate was clear and green, was 70 %.[4] The symmetrical *meso*-methyl-4,4′-dicarbocyanine, V (R=R′=Et, R″=Me, X=I), was prepared in 3 % yield by one minute's boiling of lepidine ethotoluene-*p*-sulphonate, 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride, and sodium acetate in acetic anhydride, followed by treatment with aqueous potassium iodide and ammonia, washing, and recrystallisation.[9]

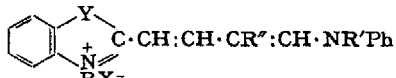
The unsubstituted symmetrical 4,4′-dicarbocyanine, V (R=R′=Et, R″=H, X=I), was prepared in 24 % yield from the appropriate dianil, with potassium acetate in acetic anhydride as condensing agent[10,11] and in 16 % yield when piperidine was used.[13] Its melting point and sensitising maximum, and the colour of its solution were compared with those of the trimethin- and heptamethin-analogues[10,11] and the absorption maximum was compared with those of the methin-, trimethin-, and heptamethin-analogues.[12]

C. Thia-2′- and Selena-2′-dicarbocyanines

Condensation of quinaldine ethiodide with 1-anilino-3-aniloprop-1-ene hydrochloride gave the intermediate salt, II (Y=CH:CH, R=Et, R′=H, X=I); this was condensed with 6-acetylamino-2-methylbenzothiazole ethoethylsulphate to give a thia-2′-dicarbocyanine, I (Y=S, Z=CH:CH, R=R′=Et, R″=H, X=I), with a 6-acetylamino-group in

the benzothiazole nucleus: both stages were effected by heating with triethanolamine in ethanol.[5] The absorption maximum of a thia-2'-dicarbocyanine with unsubstituted nuclei was compared with those of the corresponding symmetrical thia- and 2,2'-carbocyanines; a similar comparison was made with derivatives having a benzo-group in the 4,5- or 6,7-positions of the benzothiazole nucleus or in the 5,6-positions of the quinoline nucleus; also with dibenzo-derivatives having one such group in the 4,5- or 6,7-positions of the benzothiazole and the other in the 5,6-positions of the quinoline nucleus.[14]

By condensing a chain-substituted salt, namely 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride, with 2,5,6-trimethylbenzothiazole ethiodide, there resulted the 5,6-dimethyl-derivative of the intermediate salt, VI (Y=S, R=Et, R'=H, R''=Me, X=I). By heating it



(VI)

with *p*-toluquinaldine ethiodide and diethylamine in alcohol, followed by sodium perchlorate, it gave a trimethyl-derivative of the *meso*-methylthia-2'-dicarbocyanine, I (Y=S, Z=CH:CH, R=R'=Et, R''=Me, X=ClO_4.)[5]

A disubstituted derivative of the selena-2'-dicarbocyanine, I (Y=Se, Z=CH:CH, R=R'=Et, R''=H, X=I), was prepared by reaction of 5-methoxy-2-methylbenzoselenazole ethiodide with 1-anilino-3-aniloprop-1-ene hydrochloride, and condensation of the product with *p*-toluquinaldine ethiodide.[5] The absorption maxima of the unsubstituted dye, and of its derivative having a 5,6-benzo-group in the quinoline nucleus, were compared with those of the corresponding selena- and 2,2'-dicarbocyanines.[14]

D. Thia-4'- and Selena-4'-dicarbocyanines

The thia-4'-dicarbocyanine, III (Y=S, R=Et, R'=Me, R''=H, X=I), was prepared by heating 2-methylbenzothiazole ethiodide and IV (R=Me, R'=H, X=I) with diethylamine in alcohol.[5] The absorption maxima of the corresponding diethyl dye, and of its derivatives having a 4,5- or 6,7-benzo-group in the benzothiazole nucleus, were compared with those of the related thia- and 4,4'-dicarbocyanines.[14]

The *meso*-methyl derivative, III (Y=S, R=R'=Et, R"=Me, X=I), was prepared by heating VI (Y=S, R=Et, R'=H, R"=Me, X=I) and lepidine ethiodide with diethylamine in alcohol.[5]

A selena-4'-dicarbocyanine, the 5-methoxy-6'-methyl-derivative of III (Y=Se, R=Et, R'=Me, R"=H, X=I), was prepared by heating 5-methoxy-2-methylbenzoselenazole ethiodide with pyridine and condensing the resultant salt with 4,6-dimethylquinoline methiodide by use of diethylamine in ethanol.[5] The absorption maximum of the unsubstituted diethyl dye was compared with those of the related symmetrical dyes.[14]

E. Indo-, Thia-, Oxa-, and Selena-dicarbocyanines

The symmetrical *meso*-bromoindodicarbocyanine, I (Y=Z=CMe_2, R=R'=Me, R"=Br, X=I), was readily formed under various conditions; for instance 2,3,3-trimethylindolenine methiodide might be heated, either with 1-anilino-3-anilo-2-bromoprop-1-ene or with mucobromic acid, with sufficient potassium acetate to absorb the liberated acid; alternatively the dye could be prepared by heating together equimolecular quantities of the indoleninium salt, the methylene base derived from it, and the propene. In preparing the corresponding *meso*-chloro-dye, acetic anhydride was the solvent; it was also made by boiling 2,3,3-trimethylindolenine methiodide and 1-anilino-3-anilo-2-chloroprop-1-ene hydrochloride with anhydrous potassium acetate in ethanol. Its diethyl analogue, I (Y=Z=CMe_2, R=R'=Et, R"=Cl, X=I), was prepared by heating the indoleninium salt, the propene hydrochloride, and potassium acetate in acetic anhydride for one hour; the corresponding dye chloride, prepared by heating the methylene base with the propene hydrochloride, was more soluble in water.[1,3] The *meso*-nitroindodicarbocyanine, I (Y=Z=CMe_2, R=R'=Me, R"=NO_2, X=I), was prepared by boiling 2,3,3,-trimethylindolenine methodide and 1-anilino-3-anilo-2-nitroprop-1-ene in ethanol for 40 minutes. Although its concentrated alcoholic solution was blue, dilution caused the colour to change to deep red.[3] The *meso*-methylindodicarbocyanine, I (Y=Z=CMe_2, R=R'=R"=Me, X=I), was prepared by 2 minutes' boiling of 2,3,3-trimethylindolenine methiodide, 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride, and anhydrous sodium acetate in acetic anhydride, followed by treatment with potassium iodide. After washing, and crystallisation from aqueous methanol, the yield was 68 %: this dye did not sensitise.[9]

The unsubstituted symmetrical indodicarbocyanine, I (Y=Z=CMe_2, R=R′=Me, R″=H, X=Cl), was prepared by heating 1,3,3-trimethyl-2-methyleneindoline with 1-anilino-3-aniloprop-1-ene hydrochloride in acetic anhydride at 100° for 1·5 hours, removing the solvent, washing with water, and acidifying with hydrochloric acid.[2] The corresponding iodide was made in two stages, by heating equimolecular amounts of 2,3,3-trimethylindolenine methiodide and 1-anilino-3-aniloprop-1-ene at 100° for 5 minutes, then adding another mol. of the indoleninium salt, 4 mols. of anhydrous potassium acetate, and 4 mols. of acetic anhydride, and heating for 30 minutes; after washing the product with acetone and ether, the yield was 24 %.[10] It was not obtained when the condensing agent was piperidine.[13] The colour of the dye, its melting point, and sensitising maximum were compared with those of the corresponding tri- and hepta-methincyanines: the sensitising maximum moved regularly towards the infrared as the polymethin chain was lengthened.[10,11] This dye chloride has been called Indolenine Violet.[15]

The symmetrical *meso*-chlorothiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=Cl, X=I), was prepared by adding 2-methylbenzothiazole ethiodide to a boiling solution of 1-anilino-3-anilo-2-chloroprop-1-ene and potassium acetate in acetic anhydride, and allowing to cool as soon as it had dissolved;[1,3] the corresponding *meso*-bromo-dye was also made.[1,3,16] both gave brilliant blue shades on wool and silk.[1,3] By reaction of small crystals of 2-methylbenzothiazole ethiodide with 1-anilino-3-anilo-2-bromoprop-1-ene hydrobromide and piperidine in ethanol at 0° for 12 hours, the yield of washed *meso*-bromo-dye was 94 %. Its 6,7,6′,7′-dibenzo-derivative was similarly prepared in 95 % yield from 2-methyl-6,7-benzobenzothiazole ethotoluene-*p*-sulphonate.[4] The 6,6′-dichloro-derivative of the *meso*-chloro-dye, I (Y=Z=S, R=R′=Et, R″=Cl, X=I), and the 6,6′-dibromo-derivative of the *meso*-bromo-dye, I (Y=Z=S, R=R′=Et, R″=X=Br), were prepared, by heating the reactants with sodium ethoxide in ethanol for 3 minutes, in yields of 51 % and 42 %, respectively, after recrystallisation; their absorption and sensitising maxima were compared with those of the 6,6′-dihalogeno-dyes having an unsubstituted chain.[17] The symmetrical *meso*-methylthiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=Me, X=I), was prepared in 45 % yield by boiling an ethanolic solution of 2-methylbenzothiazole ethiodide and 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride with sodium ethoxide for 3 minutes. Its 5,6,5′,6′-

tetramethoxy- and 6,7,6′,7′-dibenzo-derivatives were similarly prepared, in 34 % and 45 % yields, respectively, also the 5,5′-dichloro-derivative of the corresponding chloride, in 34 % yield.[9] In preparations of the *meso*-methyl dye, I (Y=Z=S, R=R′=Et, R″=Me, X=I), and of its 6,6′-dimethyl- and 4,5,4′,5′-dibenzo-derivatives, with piperidine in pyridine or alcohol, it had been reported that the central three carbon atoms of the five-carbon chain were provided by 1-anilino-3,3-dimethoxy-2-methylprop-1-ene hydrobromide, obtained by the action of aniline hydrobromide on 1-bromo-3,3-dimethoxy-2-methyl-prop-1-ene[16] but this was surprising in that such a reaction with 1-bromo-3,3-diethoxy-2-methylprop-1-ene gave a 1-anilino-3-anilo-2-methylprop-1-ene salt.[9]

The symmetrical thiadicarbocyanine with an unsubstituted chain, I (Y=Z=S, R=R′=Et, R″=H, X=I), was prepared by heating together 2-methylbenzothiazole ethiodide and 1-anilino-3-aniloprop-1-ene: with piperidine as condensing agent, the yield was 19 %, and with sodium acetate or potassium acetate in acetic anhydride, 61 %. The melting point and sensitising maximum of the dye were compared with those of the tri- and hepta-methincyanines.[18, 19] Its absorption maximum, and those of its 4,5,4′,5′- and 6,7,6′7′-dibenzo-derivatives, were compared with those of analogues of the methin-, trimethin-, and heptamethin-series.[12] Its 6,6′-dichloro- and -dibromo-derivatives, the former as iodide, the latter as toluene-*p*-sulphonate, were both obtained in 52 % yield through the propene hydrochloride in ethanol, with sodium ethoxide as condensing agent.[17]

Unsymmetrical thiadicarbocyanines with an unsubstituted chain were prepared by reaction of 1-anilino-3-aniloprop-1-ene hydrochloride with a 2-methylbenzothiazolium iodide, followed by reaction with a different salt; the condensing agents used were diethylamine, triethanolamine, or piperidine in ethanol; sometimes the dye was isolated as perchlorate. Examples included compounds with a 6,7-benzo-substituent in one nucleus, the other being unsubstituted or with a 5-diethylamino-group; also one with 6-ethoxy in one nucleus and 6,7-tetramethylene in the other.[5] The absorption maxima of derivatives of I (Y=Z=S, R=R′=Et, R″=H, X=I) having a 4,5- or 6,7-benzo-group in one nucleus were compared with those of their methin- and trimethin-analogues; the absorption of a derivative with a 4,5-benzo-group in one nucleus and a 6,7-benzo-group in the other was compared with that of its trimethin-analogue.[14]

An unsymmetrical *meso*-methylthiadicarbocyanine, the 6,7-benzo-derivative of I (Y = Z = S, R = R′ = Et, R″ = Me, X = I), was prepared by condensing 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride with 2-methylbenzothiazole ethiodide, by heating with piperidine in ethanol, followed by reaction of the product with 2-methyl-6,7-benzobenzothiazole ethiodide by 30 minutes' heating in pyridine.[5]

The symmetrical *meso*-chloro-oxadicarbocyanine, I (Y=Z=O, R=R′=Et, R″=Cl, X=I), was prepared with difficulty: the successful method consisted in adding 2-methylbenzoxazole ethiodide, during 5 minutes, to a boiling, stirred solution of 1-anilino-3-anilo-2-chloroprop-1-ene and anhydrous potassium acetate in acetic anhydride (10 c.c. per g. of ethiodide), and recrystallising from acetone. In preparing the *meso*-bromo-dye, more acetic anhydride was used.[3] A similar method gave excellent yields, namely 85% and 89%, of the 5,5′- and 7,7′-diphenyl-derivatives of the *meso*-bromo-dye. The phenyl groups caused a weak bathochromic shift of the absorption maximum.[20]

The absorption maxima of the unsubstituted oxadicarbocyanine, I (Y=Z=O, R=R′=Et, R″=H, X=I), and of its 4,5,4′,5′- and 6,7,6′,7′-dibenzo-derivatives, were compared with those of the corresponding methin- and trimethin-analogues. Alcoholic solutions of the three oxadicarbocyanines were strikingly fluorescent.[12] The unsubstituted oxadicarbocyanine was prepared by putting a mixture of 2-methylbenzoxazole ethotoluene-*p*-sulphonate (2 mols.), 1-anilino-3-aniloprop-1-ene hydrochloride (1 mol.), anhydrous potassium acetate (4 mols.), and acetic anhydride into a bath at 60°, and stirring whilst raising the temperature to 130° during 10 minutes, then holding it there for 0·5 minute; the tar precipitated by aqueous potassium iodide was washed with water, then with ether, then with ethyl acetate containing a little methanol, and finally with ethyl acetate: after recrystallisation from methanol, the product resulted in 3% yield.[9,21] For oxadicarbocyanines, specifically, the method of section 5 was better,[9] but that of section 2-E was better still.

An unsymmetrical *meso*-methylselenadicarbocyanine was prepared by heating 2-methylbenzoselenazole ethiodide and 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride with diethylamine in ethanol, to give VI (Y=Se, R=Et, R′=H, R″=Me, X=I); this product, by heating with 2-methyl-5,6-ethylenedioxybenzoselenazole ethiodide in

the same condensing agent, gave the 5,6-ethylenedioxy-derivative of I (Y=Z=Se, R=R′=Et, R″=Me, X=I).[5]

A symmetrical *meso*-methylselenadicarbocyanine, I (Y=Z=Se, R=R′=Et, R″=Me, X=Cl), was prepared by adding 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride to a solution of 2-methylbenzoselenazole ethoethylsulphate in hot ethanol, boiling with sodium ethoxide, and pouring into hot aqueous ammonium chloride solution: the yield of washed, recrystallised dye was 43 %.[9]

The absorption maximum of the unsubstituted selenadicarbocyanine, I (Y = Z = Se, R = R′ = Et, R″ = H, X = I), was compared with those of its methin-, trimethin-, and heptamethin-analogues.[12]

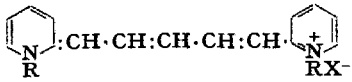
F. Indothia- and Selenathia-dicarbocyanines

In the original patent, the indothiadicarbocyanine, I (Y=CMe_2, Z=S, R=Me, R′=Et, R″=H, X=I), was prepared, firstly, by heating together II (Y=CMe_2, R=Me, R′=Ac, X=I), 2-methylbenzothiazole ethiodide, anhydrous potassium acetate, and acetic anhydride; it was also prepared from II (Y=S, R=Et, R′=Ac, X=I) and 1,3,3-trimethyl-2-methyleneindoline.[2]

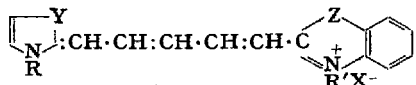
Three selenathiadicarbocyanines, derivatives of I (Y=Se, Z=S, R=R′=Et, R″=H, X=I), were prepared by use of 1-anilino-3-anilo-prop-1-ene hydrochloride. For the first, the intermediate prepared from it and 2-methylbenzothiazole ethiodide was condensed with 2,5,6-trimethylbenzoselenazole ethiodide; for the second, the intermediate made from it and 2,5,6-trimethylbenzothiazole ethiodide was condensed with 5-chloro-2-methylbenzoselenazole ethiodide; for the third, the intermediate from it and 5-ethoxy-2-methylbenzoselenazole ethiodide was condensed with 5-chloro-2-6-dimethylbenzothiazole ethiodide: the condensations were effected by heating with diethylamine in ethanol, with pyridine, and with sodium ethoxide in ethanol, respectively.[5]

G. 2,2′-Pyridodicarbocyanines

The 2,2′-pyridodicarbocyanine, VII (R=R′=Me, X=I), was prepared by heating together 2-picoline methiodide, 1-anilino-3-anilo-prop-1-ene, and piperidine,[19] and the corresponding *NN*′-diethyl dye



(VII)

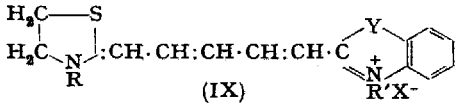


(VIII)

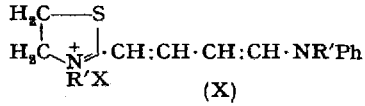
similarly, in 10% yield.[13] The melting point of the former dye was lower than that of the analogous trimethincyanine but higher than that of the heptamethincyanine; its sensitising maximum was compared with that of the trimethincyanine.[19]

H. Thiazolo-2'- and Thiazolino-2'-dicarbocyanines

A carbethoxy-derivative of the thiazolo-2'-dicarbocyanine, VIII (Y=S, Z=CH:CH, R=Me, R'=Et, X=I), was prepared by heating VI (Y=CH:CH, R=Et, R'=R"=H, X=I) and 5-carbethoxy-2,4-dimethylthiazole methiodide with diethylamine in ethanol.[5]



(IX)

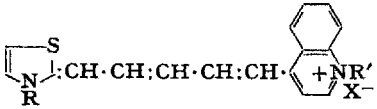


(X)

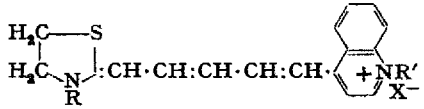
The thiazolino-2'-dicarbocyanine, IX (Z=CH:CH, R=R'=Et, X=I), was prepared in 39 % yield by the reaction at 0°, during 2 days, of triethylamine on an ethanolic suspension of X (R=Et, R'=Ac, X=I) and quinaldine ethiodide, followed by washing, and by two recrystallisations from ethanol.[6]

I. Thiazolo-4'- and Thiazolino-4'-dicarbocyanines

A dimethyl derivative of the thiazolo-4'-dicarbocyanine, XI (R=R'=Me, X=I), was prepared by heating the salt, IV (R=Et, R'=H, X=I), with 2,4,5-trimethylthiazole methiodide and diethylamine in alcohol.[5]



(XI)



(XII)

A thiazolino-4'-dicarbocyanine, XII (R=R'=Et, X=I), was obtained in 51 % yield by reaction at 0°, over 2 days, of equimolecular quantities of X (R=Et, R'=Ac, X=I) and lepidine ethiodide with

triethylamine (4 mols.) in ethanol, followed by washing, and by recrystallisation from methanol.[6]

J. Selenathiazolo-, Thiathiazolo-, Oxathiazolino-, and Thiathiazolinodicarbocyanines

A methyl derivative of the selenathiazolodicarbocyanine, VIII (Y=S, Z=Se, R=R′=Et, X=I), was prepared by heating an alcoholic solution of VI (Y=Se, R=Et, R′=R″=H, X=I) and 2,4-dimethylthiazole ethiodide with sodium ethoxide in ethanol. An intermediate salt, having a 5-ethoxy-group in the benzoselenazole nucleus, was condensed with 2,4-dimethylthiazole methiodide, and one, having a 5-methoxy-group, was condensed with 2-methyl-4-phenylthiazole ethiodide.[5]

A *meso*-methyl derivative of VIII (Y=S, Z=Se, R=Me, R′=Et, X=I), having a 5-ethoxy-group in the benzoselenazole nucleus and a 4-methyl group in the thiazole nucleus, was prepared in two stages; the first consisted in condensation of 5-ethoxy-2-methylbenzoselenazole ethiodide and 1-anilino-3-anilo-2-methylprop-1-ene hydrochloride, by heating them in pyridine, to give the 5-ethoxy-dervative of VI (Y=Se, R=Et, R′=H, R″=Me); this was condensed with 2,4-dimethylthiazole methiodide by means of diethylamine in boiling ethanol.[5]

5,6-Dimethoxy- and -diethoxy-derivatives of the thiathiazolodicarbocyanine, VIII (Y=Z=S, R=R′=Et, X=I), were prepared from the appropriate disubstituted VI (Y=S, R=Et, R′=R″=H, X=I) by heating it with 2,4-dimethylthiazole ethiodide and diethylamine in ethanol. An intermediate salt having a 6,7-benzo-group was also made and was condensed with 5-carbethoxy-2,4-dimethylthiazole ethiodide.[5]

A trisubstituted *meso*-methyl derivative of VIII (Y=Z=S, R=Me, R′=Et, X=I) was made by condensing 2,5,6-trimethylbenzothiazole ethiodide with 1-anilino-3-anilo-2-methyl-prop-1-ene hydrochloride, and the product with 2-methyl-4-phenylthiazole methiodide.[5]

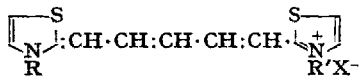
The oxathiazolinodicarbocyanine, IX (Y=O, R=R′=Et, X=I), was prepared in 4% yield by reaction at 0°, over 4 days, of VI (Y=O, R=Et, R′=Ac, R″=H, X=I), 2-methylthiazoline ethiodide, and triethylamine in ethanol, followed by two recrystallisations from ethanol of the washed dye. It was not obtained when the acetanilido-salt was replaced by the anilino-salt, nor by the alternative route from X (R=Et, R′=Ac, X=I).[6]

The *meso*-bromo-derivative of the thiathiazolinodicarbocyanine, IX (Y=S, R=Me, R′=Et, X=I), was arrived at through the intermediate salt, VI (Y=S, R=Et, R′=Ac, R″=Br, X=I); this was prepared by heating equimolecular quantities of 2-methylbenzothiazole ethotoluene-*p*-sulphonate and 1-anilino-3-anilo-2-bromoprop-1-ene hydrobromide in acetic anhydride for 30 minutes, precipitating with ether, and treating with potassium iodide in methanol; the salt was allowed to react at 0° with equimolecular quantities of 2-methylthiazoline methiodide and triethylamine in ethanol.[4]

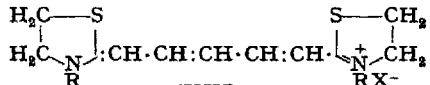
The unsubstituted thiathiazolinodicarbocyanine, IX (Y=S, R=R′=Et, X=I), was prepared by reaction of X (R=Et, R′=Ac, X=I), 2-methylbenzothiazole ethiodide, and triethylamine in ethanol at 0° over 3·5 hours: even at this low temperature and in so short a time, it was accompanied by thiadicarbocyanine. To remove this, the washed product was twice fractionally recrystallised from methanol, and then recrystallised from it with charcoal treatment, after which the yield was 24 %.[6]

K. Thiazolo- and Thiazolino-dicarbocyanines

The symmetrical thiazolodicarbocyanine, XIII (R=Me, X=I), was prepared in 5 % yield by heating 2-methylthiazole methiodide and 1-anilino-3-aniloprop-1-ene with piperidine at 45° for 30 minutes and recrystallising from methanol; its 4,4′-dimethyl derivative was made



(XIII)



(XIV)

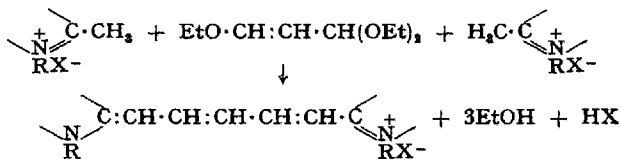
in 24 % yield by heating at 65°: neither was obtained when the condensing agent was sodium acetate or potassium acetate in acetic anhydride. The melting point and sensitising maximum of each were compared with those of the trimethin- and heptamethin-analogues.[18, 19]

The symmetrical thiazolinodicarbocyanine, XIV (R=Me, X=I), was prepared in 30 % yield from 2-methylthiazoline methiodide and 1-anilino-3-aniloprop-1-ene by use of acetic anhydride and sodium acetate or potassium acetate, but with piperidine the dye was not formed. Its melting point and sensitising maximum were intermediate between those of its trimethin- and heptamethin-analogues.[13]

2. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of a 1,3,3-Trialkoxyprop-1-ene

A. General

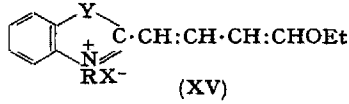
The first dicarbocyanine, I (Y=Z=CH:CH, R=R'=Me, R''=H, X=I), was announced in 1922[22] and was, presumably, prepared by one or both of two methods patented in that year.[23] One of these methods (see also section 4) consisted in the condensation of a quaternary salt, having a reactive methyl group, with β-ethoxyacraldehyde diethyl acetal, i.e. with 1,3,3-triethoxyprop-1-ene. Condensing agents suggested were acetic anhydride, zinc chloride, nitrobenzene, and tetrachloroethane, acting at a raised temperature. Although the method was claimed as being applicable to quaternary salts of the quinaldine, lepidine, 2-methylbenzothiazole, 2-methylbenzoxazole, and 2-methylindolenine series, the only example was an indodicarbocyanine, which was a greenish-blue dye.[23] The course of the reaction is indicated in equation 2.



(2)

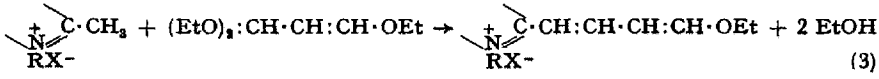
In a patent on the sensitising action to red and infrared light by 2,2'-, 4,4'-, oxa-, thia-, and selena-dicarbocyanines having substituents, these dyes were described as sensitising from 6000–8000 Å, and as being better than kryptocyanine or neocyanine.[24]

By use of substituted 1,3,3-triethoxyprop-1-enes, dicarbocyanines having one or more alkyl groups on the chain were prepared.[25]



(XV)

Reaction of a quaternary salt, having a 2-methyl group, with excess of 1,3,3-triethoxyprop-1-ene in acetic acid gave intermediate salts, XV, having a 4-ethoxy-1,3-butadienyl group (equation 3).



(3)

Such intermediate salts were prepared in the benzoxazole, benzothiazole, benzoselenazole, 2-linked quinoline, and thiazoline series. They often condensed more readily with quaternary salts having a reactive methyl group than did salts of type II (R=Ac), so that they led to good yields, after recrystallisation, of various types of dicarbocyanines; the condensing agent was pyridine, or else triethylamine in acetic anhydride.[8]

B. 2,2'-Dicarbocyanines

The intermediate salt, XV (Y=CH:CH, R=Et, X=I), was made by heating quinaldine ethiodide (1 mol.) with 1,3,3-triethoxyprop-1-ene (2 mols.) in acetic acid for 5 minutes and precipitating with ether. By boiling it with quinaldine ethiodide in pyridine, there resulted a 55 % yield of the symmetrical 2,2'-dicarbocyanine, I (Y=Z=CH:CH, R=R'=Et, R''=H, X=I).[8]

C. Thia-2'- and Oxa-2'-dicarbocyanines

The thia-2'-dicarbocyanine, I (Y=S, Z=CH:CH, R=R'=Et, R''=H, X=I), was prepared in 78% yield by heating the intermediate salt, XV (Y=S, R=Et, X=I), and quinaldine ethiodide with triethylamine in acetic anhydride.[8]

The oxa-2'-dicarbocyanine, I (Y=O, Z=CH:CH, R=R'=Et, R''=H, X=I) was prepared in 44 % yield by heating the intermediate salt, XV (Y=O, R=Et, X=I), quinaldine ethiodide, and triethylamine in acetic anhydride for 1 minute. The intermediate compound itself was made by heating 2-methylbenzoxazole ethiodide with 1,3,3-triethoxyprop-1-ene in acetic acid at 100° for 10 minutes, and precipitating with ether; its 4,5- and 6,7-benzo-derivatives were also prepared.[8]

D. Thia-4'- and Oxa-4'-dicarbocyanines

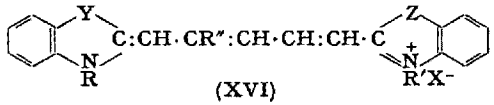
This method, with triethylamine in acetic anhydride as condensing agent, gave, from lepidine ethiodide and XV (Y=S, R=Et, X=I), a 51 % yield of the thia-4'-dicarbocyanine, III (Y=S, R=R'=Et, R''=H, X=I).[8]

The same process was used for making the oxa-4'-dicarbocyanine, III (Y=O, R=R'=Et, R''=H, X=I), from lepidine ethiodide and XV (Y=O, R=Et, X=I) and the yield was 24 %.[8]

E. Indo-, Thia-, Oxa-, and Selena-dicarbocyanines

In the first preparation of the symmetrical indodicarbocyanine, I (Y=Z=CMe_2, R=R′=Me, R″=H, X=I), 2,3,3-trimethylindolenine methiodide, dissolved in acetic anhydride, was boiled with 1,3,3-triethoxyprop-1-ene for 30 minutes.[23]

Its β-methyl derivative, XVI (Y=Z=CMe_2, R=R′=R″=Me, X=I), was prepared in 14% yield by boiling equimolecular quantities



(XVI)

of 2,3,3,-trimethylindolenine methiodide and 1,3,3-triethoxy-1-methylprop-1-ene with pyridine for 15 minutes, precipitating with ether, and recrystallising from aqueous ethanol.[9]

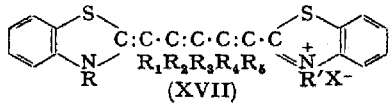
Sensitisation with symmetrical thiadicarbocyanines having substituted nuclei was patented; the spectrograms published included those of the 6,6′-dimethyl- and 5,5′-bisdiethylamino-derivatives of I (Y=Z=S, R=R′=Et, R″=H, X=I). In the only preparation described, the 2-methylbenzothiazolium salt was heated with 1,3,3-triethoxyprop-1-ene in pyridine at 130° for 30 minutes.[24] Symmetrical thiadicarbocyanines with an unsubstituted chain, but having substituents in the 5,6,5′,6′-positions, were said to be particularly good sensitisers. As examples there were mentioned the 5,6,5′,6′-tetramethoxy-, 5,5′-diethoxy-6,6′-dimethyl-, 5,5′-dimethoxy-6,6′-di(methylthio)-, and 5,6,5′,6′-bismethylenedioxy-derivatives of I (Y=Z=S, R=R′=Et, R″=H, X=I),[26] also its 5,6,5′,6′-dibenzo-derivative.[27] Each was prepared by heating the appropriate 2-methylbenzothiazolium salt with 1,3,3-triethoxyprop-1-ene in pyridine.[26,27] The unsubstituted thiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=H, X=I), was obtained in 58% yield by boiling equimolecular quantities of 2-methylbenzothiazole ethiodide and 1,3,3-triethoxy-prop-1-ene in pyridine (15 c.c. per g. of salt) for 30 minutes, and recrystallising from ethanol. Its 4,5,4′,5′-dibenzo-derivative was similarly made.[16]

The intermediate salt, XV (Y=S, R=Et, X=I), was prepared in 49% yield by heating 2-methylbenzothiazole ethiodide (1 mol.) and 1,3,3-triethoxyprop-1-ene (2 mols.) in acetic acid at 100° for 10 minutes, and recrystallising from ethanol. Its 4,5-benzo-derivative was similarly made and was recrystallised from methanol (48% yield). By heating

the former salt with 2-methylbenzothiazole ethiodide in pyridine for 5 minutes, the symmetrical thiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=H, X=I), was obtained, in 75 % yield after recrystallisation from methanol; its unsymmetrical 4,5-benzo-derivative was prepared in 39 % yield by use of the same 4-ethoxy-1,3-butadienyl salt.[8]

The *meso*-methylthiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=Me, X=I), was prepared by heating 2-methylbenzothiazole ethiodide with 1,3,3-triethoxy-2-methylprop-1-ene in pyridine at 130° for 30 minutes, adding water, and recrystallising from ethanol. Its 5,6-5′,6′-tetramethoxy- and 5,5′-bisdiacetylamino-derivatives were prepared similarly.[25]

A thiadicarbocyanine with $\beta\gamma$-dimethyl groups on the chain, XVII (R=R′=Et, R_2=R_3=Me, R_1=R_4=R_5=H, X=I), was prepared by heating 2-methylbenzothiazole ethiodide with 1,3,3-triethoxy-1,2-dimethylprop-1-ene in pyridine.[25]



(XVII)

Thiadicarbocyanines with $\alpha\alpha'$-dimethyl groups on the chain, XVII (R=R′=Me or Et, R_1=R_5=Me, R_2=R_3=R_4=H, X=I), were prepared by reaction of 1,3,3-triethoxyprop-1-ene in pyridine with 2-ethylbenzothiazole ethiodide:[9,16,25] the yield was 38 %.[9] Whereas the dye with a *meso*-methyl group was a good sensitiser, that with $\alpha\alpha'$-dimethyl groups was less good, though better than that with a *meso*-bromo-group (section 1-E).[16]

Thiadicarbocyanines with a β-methyl substituent on the chain were prepared by means of 1,3,3-triethoxy-1-methylprop-1-ene, under various conditions and the yields were variable. Thus XVI (Y=Z=S, R=R′=Et, R″=Me, X=I) was obtained in 32 % yield by boiling the propene and 2-methylbenzothiazole ethiodide (2 mols. of each) in ethanol with triethylamine (1 mol.) for 4 minutes, whilst the yield of its dimethyl analogue was only 12 %; when the diethyl dye was prepared from the propene and 2-methylbenzothiazole ethotoluene-*p*-sulphonate with anhydrous sodium acetate in acetic anhydride at 0° during 10 days, the yield of recrystallised dye iodide was 27 %. This method gave a 58 % yield of its 5,5′-dichloro-derivative, as toluene-*p*-sulphonate, whilst boiling in pyridine gave only a 15 % yield. The 5,6,5′,6′-tetra-

methoxy-, and 4,5,4′,5′-dibenzo-derivatives of XVI (Y=Z=S, R=R′=Et, R″=Me, X=I), and the 6,7,6′,7′-dibenzo-derivatives of the bromide, were prepared by boiling the 2-methylbenzothiazolium salt, the propene, and triethylamine in ethanol, but the yields of recrystallised dyes were only 4 %, 3 %, and 7 %, respectively.[9]

The symmetrical oxadicarbocyanine with an unsubstituted chain, I (Y=Z=O, R=R′=Et, R″=H, X=I), was prepared in 54% yield through the intermediate salt, XV (Y=O, R=Et, X=I), and 2-methylbenzoxazole ethiodide, by heating them in pyridine.[8]

The symmetrical selenadicarbocyanine, I (Y=Z=Se, R=R′=Et, R″=H, X=I), was similarly prepared in 69 % yield, through XV (Y=Se, R=Et, X=I).[8] Substituents in the 5,6,5′,6′-positions improved sensitising; the 5,6,5′,6′-bisethylenedioxy-derivative was prepared by heating 2-methyl-5,6-ethylenedioxybenzoselenazole ethiodide with 1,3,3-triethoxyprop-1-ene in pyridine.[26]

The *meso*-methylselenadicarbocyanine, I (Y=Z=Se, R=R′=Et, R″=Me, X=I), was prepared by heating 2-methylbenzoselenazole ethiodide and 1,3,3-triethoxy-2-methylprop-1-ene in pyridine at 130° for 30 minutes.[25] The yield of washed dye obtained by interaction of 2-methylbenzoselenazole ethoethylsulphate, the propene, sodium acetate, and acetic anhydride at 0° for 4 days, followed by treatment with potassium iodide, was 20 %, but it was unstable, so that the yield after recrystallisation from methanol was only 4 %.[9]

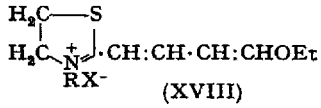
F. Oxaselena-, Oxathia-, and Selenathia-dicarbocyanines

By means of a 4-ethoxy-1,3-butadienyl salt, there were prepared the oxaselenadicarbocyanine, I (Y=O, Z=Se, R=R′=Et, R″=H, X=I), the oxathiadicarbocyanine, I (Y=O, Z=S, R=R′=Et, R″=H, X=I), and the selenathiadicarbocyanine, I (Y=Se, Z=S, R=R′=Et, R″=H, X=I), in yields of 43 %, 58 % and 74 %, respectively, each condensation being effected by heating with a 2-methyl salt in pyridine; the first and third dyes were made by use of XV (Y=Se, R=Et, X=I), and the second by use of XV (Y=O, R=Et, X=I).[8]

G. Thiathiazolinodicarbocyanines

The intermediate salt of the thiazoline series, XVIII (R=Me, X=I), was prepared by heating 2-methylthiazoline methiodide (1 mol.)

and 1,3,3-triethoxyprop-1-ene (2 mols.) in acetic acid at 100° for 10 minutes, and precipitating with ether; washing with acetone gave a 24% yield. By heating it with 2-methylbenzothiazole ethiodide in



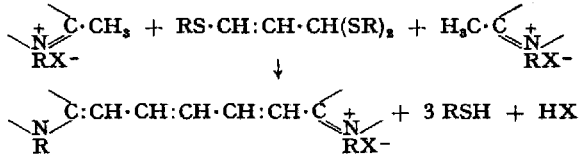
(XVIII)

pyridine, it gave a 26% yield of the thiathiazolinodicarbocyanine, IX (Y=S, R=Me, R'=Et, X=I).[8]

3. From a Quaternary Salt, Having a Reactive Methyl Group, by Use of a 3,3-Dialkoxy-1-alkylthioprop-1-ene or of a 1,3,3-Tri-(alkylthio)prop-1-ene

A. General

As noted in an earlier chapter (IV-11), ethyl orthothioformate, $HC(SEt)_3$, found only a limited use in the preparation of symmetrical trimethincyanines from quaternary salts having a reactive methyl group. For preparing symmetrical pentamethincyanines from such salts, the analogous 1,3,3-tri(alkylthio)-prop-1-ene, $RS\cdot CH:CH\cdot CH(SR)_2$, was recommended, as was also 3,3-dialkoxy-1-(alkylthio)prop-1-ene, $RS\cdot CH:CH\cdot CH(OR)_2$. As the reaction medium for the former, acetic anhydride was used first to combine with the mercaptan which was eliminated, and was followed by a base, but for the latter pyridine was better.[28] With the former, the reaction proceeds according to equation 4.



(4)

1,3,3-Tri(alkylthio)prop-1-ene could be prepared by the action of alkyl mercaptan and an acid condensing agent on 1,3,3-trialkoxyprop-1-ene, on 3,3-dialkoxy-1-(alkylthio)prop-1-ene, on 3,3-dialkoxyprop-1-yne, or on 3,3-di(alkylthio)prop-1-yne, or from the last with alkyl mercaptan and a basic condensing agent under pressure.[29]

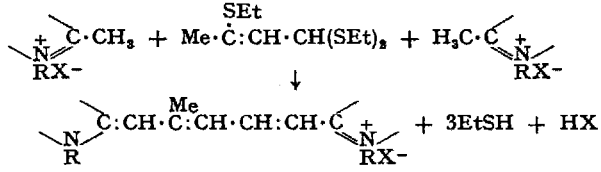
Subsequently a methyl derivative was made from sodioformyl-

acetone in ether, by the action of ethyl mercaptan and dry hydrochloric acid, but whether this product was 1,3,3-tri(ethylthio)-1-methylprop-1-ene (equation 5) or 1,3,3-tri(ethylthio)-3-methylprop-1-ene (equation 6) was not determined.

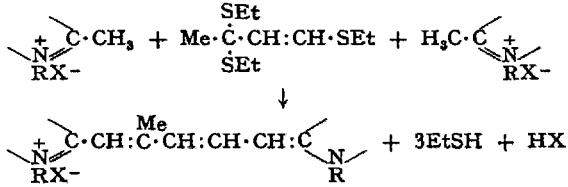
$$Me\cdot CO\cdot CH{:}CH\cdot ONa + 3EtSH + HCl \longrightarrow Me\cdot \overset{SEt}{\overset{|}{C}}{:}CH\cdot CH(SEt)_2 + NaCl + 2H_2O \quad (5)$$

$$Me\cdot CO\cdot CH{:}CH\cdot ONa + 3EtSH + HCl \longrightarrow Me\cdot \overset{SEt}{\overset{|}{\underset{SEt}{\overset{|}{C}}}}\cdot CH{:}CH\cdot SEt + NaCl + 2H_2O \quad (6)$$

A phenyl derivative was made from sodioformylacetophenone, with the same doubt as to its exact structure.[30] By heating such a propene with a 2-methyl-benzothiazole, or -benzoselenazole, quaternary salt, in the presence of acetic anhydride and a strong base, a β-methylthia- or β-methylselena-dicarbocyanine was produced,[31] according to equations 7 or 8.



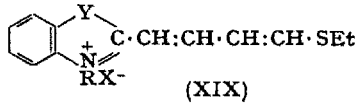
(7)



(8)

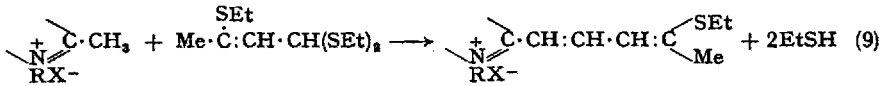
Just as alkyl orthothioformate could be condensed with salts having a reactive methyl group, by heating in acetic anhydride, to give salts having the 2-alkylthiovinyl group, $\cdot CH{:}CH\cdot SR$ (V-10-A), so, similarly, could its analogue, 1,3,3-tri(alkylthio)prop-1-ene, be condensed to yield salts having the 4-alkylthio-1,3-butadienyl group, $\cdot CH{:}CH\cdot CH{:}CH\cdot SR$; toluene-*p*-sulphonates gave the best yields. Such intermediate salts were described in the benzothiazole, benzoxazole, benzoselenazole, 2- and 4-linked quinoline, and indolenine series.[32] From them, by interaction with another heterocyclic salt, having a reactive methyl group, and a basic condensing agent, various types of unsymmetrical pentamethincyanines were made.[33]

By heating the methyl or phenyl derivative of 1,3,3-tri(alkylthio)-prop-1-ene with a quaternary salt, having a reactive methyl group, in acetic anhydride, there resulted a salt of type XIX but with a methyl

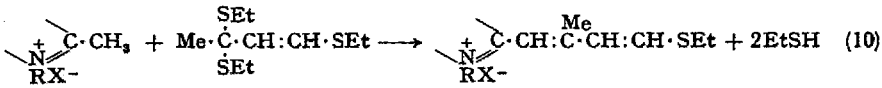


(XIX)

or phenyl substituent on the chain. This might have the substituent in the δ- or the β-position, depending on the structure of the propene (equations 9 and 10).



(9)



(10)

Salts of this type belonging to the benzothiazole, indolenine, and 2- and 4-quinoline series, were described.[34] When one of these intermediate salts was condensed with another having a reactive methyl group, a pentamethincyanine with a β-methyl group on the chain resulted. The dye could only be exactly formulated in instances where the two nuclei were identical.[35]

B. 2,2′-Dicarbocyanines

The symmetrical 2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Et, R″=H, X=I), was prepared by boiling quinaldine ethiodide with 1,3,3-tri(alkylthio)prop-1-ene in acetic anhydride, adding triethylamine, boiling for 10 minutes, and precipitating the dye with ether.[28]

The β-phenyl derivative of an unsymmetrical 2,2′-dicarbocyanine, i.e., XVI (Y=Z=CH:CH, R=CH_2CH_2OH, R′=CH_2CH_2OAc, R″=Ph, X=I), was prepared by heating quinaldine 2-dihydroxyethiodide with 2-(4-ethylthio-2-, or 4-, phenyl-1,3-butadienyl)quinoline 2-acetoxyethiodide, pyridine, and triethylamine.[35]

C. Thia-2′- and Oxa-2′-dicarbocyanines

The intermediate salt, XIX (Y=S, R=Me, X=I), was prepared by heating 2-methylbenzothiazole methotoluene-p-sulphonate with

1,3,3-tri(ethylthio)prop-1-ene, or with 3,3-diethoxy-1-(ethylthio)prop-1-ene, in acetic anhydride for 10 minutes, and treating with aqueous potassium iodide.[32] It was condensed with quinaldine ethiodide, by boiling for 12 minutes with triethylamine in ethanol, to give the thia-2'-dicarbocyanine, I (Y=S, Z=CH:CH, R=Me, R'=Et, R''=H, X=I).[33]

The β- or δ-phenyl derivative of a thia-2'-dicarbocyanine was prepared by reaction of quinaldine ethiodide and 2-(4-alkylthio-2-, or 4-, phenyl-1,3-butadienyl)benzothiazole ethiodide.[35]

The intermediate salt, XIX (Y=O, R=Et, X=$O_3S\cdot C_6H_4Me$), was prepared by boiling 2-methylbenzoxazole ethotoluene-*p*-sulphonate and 1,3,3-tri(ethylthio)prop-1-ene in acetic anhydride for 12 minutes; the solvent was taken off under a vacuum and the residue washed with ether.[32] It was dissolved in ethanol, treated with quinaldine methiodide and triethylamine, and heated for 12 minutes, giving the oxa-2'-dicarbocyanine, I (Y=O, Z=CH:CH, R=Et, R'=Me, R''=H, X=I).[33]

D. Thia-4'-dicarbocyanines

The thia-4'-dicarbocyanine, III (Y=S, R=Me, R'=Et, R''=H, X=I), was prepared by heating XIX (Y=S, R=Me, X=I) and lepidine ethiodide with triethylamine in ethanol; another was prepared analogously.[33]

E. Indo-, Thia-, and Selena-dicarbocyanines

The symmetrical indodicarbocyanine, I (Y=Z=CMe_2, R=R'=Me, R''=H, X=I), was prepared by heating 2,3,3-trimethylindolenine methiodide with 1,3,3-tri(ethylthio)prop-1-ene and acetic anhydride until partly dissolved, adding triethylamine, and heating for 5 minutes; the dye was precipitated with ether and recrystallised from methanol.[28]

In preparing the symmetrical thiadicarbocyanine, I (Y=Z=S, R=R'=Et, R''=H, X=I), 2-methylbenzothiazole ethiodide and 3,3-diethoxy-1-(ethylthio)prop-1-ene were heated in pyridine for 15 minutes, and the reaction mixture treated with aqueous potassium iodide; the dye was recrystallised from methanol.[29]

Its β-methyl derivative was prepared by heating 2-methylbenzothiazole ethiodide and 1,3,3-tri(ethylthio)-1(or 3)-methylprop-1-ene with acetic anhydride, adding triethylamine, and further heating; the 5,5'-dimethyl derivative of this dye was similarly made. The β-phenyl

derivatives of I (Y=Z=S, R=R'=Et or CH_2CH_2OAc, R''=H, X=I) were similarly prepared by condensation of 1,3,3-tri(ethylthio)-1(or 3)-phenylprop-1-ene with 2-methylbenzothiazole ethiodide, or β-acetoxyethiodide, respectively.[31]

An unsymmetrical thiadicarbocyanine, I (Y=Z=S, R=Me, R'=$CH_2 \cdot CH_2OH$, R''=H, X=I), was prepared by condensing XIX (Y=S, R=Me, X=I) with 2-methylbenzothiazole β-hydroxyethiodide by heating for 12 minutes with triethylamine in ethanol. Another, I (Y=Z=S, R=$CH_2 \cdot CH_2OAc$, R'=$CH_2 \cdot CH_2OH$, R''=H, X=I), was prepared from the intermediate salt, XIX (Y=S, R=$CH_2 \cdot CH_2OAc$, X=I), and 2-methylbenzothiazole β-hydroxyethiodide; the intermediate salt was made by dissolving 2-methylbenzothiazole β-hydroxyethiodide in acetic anhydride, adding 3,3-diethoxy-1-(ethylthio)prop-1-ene, and boiling for 10 minutes, then removing the solvent under reduced pressure.[33]

The β-phenyl derivative of the symmetrical thiadicarbocyanine, i.e., XVI (Y=Z=S, R=R'=Et, R''=Ph, X=I), was obtained by the two-stage process, which involved the preparation of 2-(4-ethylthio-2-, or 4-, phenyl-1,3-butadienyl)benzothiazole ethiodide, followed by its condensation with 2-methylbenzothiazole ethiodide, by heating with pyridine and triethylamine. The β-phenyl derivatives of three unsymmetrical thiadicarbocyanines, and the β-methyl derivative of one, were similarly prepared but in those instances the substituent might alternatively occupy the β'-position on the chain.[35]

The β-phenylselenadicarbocyanine, XVI (Y=Z=Se, R=R'=Et, R''=Ph, X=I), was prepared by heating 2-methylbenzoselenazole ethotoluene-*p*-sulphonate with acetic anhydride and 1,3,3-tri(ethylthio)-1 (or 3)-phenylprop-1-ene for 10 minutes; the dye salt precipitated by ether was dissolved in pyridine and treated with aqueous potassium iodide. The corresponding β-methyl dye was prepared similarly from 2-methylbenzoselenazole ethiodide and 1,3,3-tri(ethylthio)-1(or 3)-methylprop-1-ene, but the reaction mixture was treated with triethylamine after boiling.[31]

F. Indoselena-, Indothia-, Indoxa-, Oxathia-, and Selenathiadicarbocyanines

The indoselenadicarbocyanine, I (Y=CMe_2, Z=Se, R=Me, R'=Et, R''=H, X=ClO_4), was prepared by heating XIX (Y=Se, R=Et, X=I) and 2,3,3-trimethylindolenine methiodide with triethylamine in

ethanol for 10 minutes, pouring into aqueous potassium perchlorate solution, treating with acetone, and recrystallising from methanol.[33]

The indothiadicarbocyanine, I (Y=CMe_2, Z=S, R=Me, R′=Et, R″=H, X=I), was prepared by boiling XIX (Y=S, R=Et, X=I) and 2,3,3-trimethylindolenine methiodide with ethanol, adding an alcoholic solution of anhydrous sodium acetate, boiling for 12 minutes, and recrystallising from methanol.[33]

The β-, or β'-, methyl derivative of the indothiadicarbocyanine, I (Y=CMe_2, Z=S, R=Me, R′=Et, R″=H, X=I), was prepared by heating 2,3,3-trimethylindolenine methiodide with 2-(4-ethylthio-2-, or 4-, methyl-1,3-butadienyl)benzothiazole ethiodide in pyridine, adding triethylamine after cooling, and precipitating with ether.[35]

The indoxadicarbocyanine, I (Y=CMe_2, Z=O, R=Me, R′=Et, R″=H, X=ClO_4), was prepared by heating an alcoholic solution of XIX (Y=O, R=Et, X=$O_3S \cdot C_6H_4 \cdot Me$) with 2,3,3-trimethylindolenine methiodide, adding triethylamine, and boiling for 12 minutes; the dye, precipitated by water, alcohol, and ether, was dissolved in hot methanol and treated with aqueous potassium perchlorate.[33]

The oxathiadicarbocyanine, I (Y=O, Z=S, R=R′=Me, R″=H, X=I), was prepared by dissolving XIX (Y=S, R=Me, X=I), and 2-methylbenzoxazole methiodide in ethanol, adding triethylamine, and boiling for 10 minutes, then adding more triethylamine in ethanol; the crystalline dye was washed.[33]

The selenathiadicarbocyanine, I (Y=Se, Z=S, R=Et, R′=Me, R″=H, X=I), was prepared by heating XIX (Y=Se, R=Et, X=I) and 2-methylbenzothiazole methiodide with ethanol, adding triethylamine, and boiling for 10 minutes.[33]

G. Indothiazolinodicarbocyanines

2-Methylthiazoline methotoluene-*p*-sulphonate was warmed with XIX (Y=CMe_2, R=Me, X=ClO_4) and ethanol, treated with triethylamine, and boiled for 10 minutes, during which process the indothiazolinodicarbocyanine, IX (Y=CMe_2, R=R′=Me, X=ClO_4), separated.[33]

H. Thiazolinodicarbocyanines

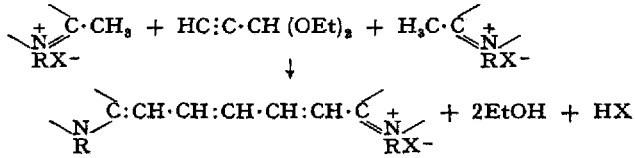
The symmetrical thiazolinodicarbocyanine, XIV (R=Me, X=I), was prepared by boiling 2-methylthiazoline methiodide, 1,3,3-tri-

(ethylthio)prop-1-ene and acetic anhydride, adding triethylamine, and boiling for 6 minutes. The cooled mixture was washed with light petroleum, then diluted with ether to precipitate the dye.[28]

4. From a Quaternary Salt, Having a Reactive Methyl Group, by use of 3,3-Diethoxyprop-1-yne

A. General

The first pentamethincyanines were described in a patent of 1922, where two methods were noted.[23] One involved the condensation of 1,3,3-triethoxyprop-1-ene (see section 2), the other that of propargyl aldehyde acetal, i.e. 3,3-diethoxyprop-1-yne, with quaternary salts having a reactive methyl group. In the only example given, an indodicarbocyanine was thus prepared, in boiling acetic anhydride.[23] Nine years later, the preparation was again patented, with pyridine as medium. The examples included four types of dyes.[36] Only symmetrical dicarbocyanines are thus obtainable; the net result of such a condensation is as indicated in equation 11.



(11)

It is remarkable that, when pure, the propyne gave only one-fifth the yield given when crude, whilst the reaction took considerably longer. The crude product, as prepared by the action of alcoholic potassium hydroxide on acraldehyde dibromide diethyl acetal, extraction with ether, and distillation, had b.p. 138–180°; to purify it, it was left over potassium hydroxide, then twice fractionated, and had b.p. 138–140°.[36]

B. 2,2′-Dicarbocyanines

To prepare the 2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Et, R″=H, X=I), quinaldine ethiodide (1 mol.) and pure 3,3-diethoxyprop-1-yne (3 mols.) were boiled with 4-hydroxy-4-methyl-2-pentanone; on adding anhydrous sodium acetate (1 mol.), a deep green colour developed; after 15 minutes' boiling, water was added.[36]

C. Indo-, Thia-, Oxa-, and Selena-dicarbocyanines

The indodicarbocyanine, I (Y=Z=CMe_2, R=R'=Me, R''=H, X=I), was prepared by boiling 2,3,3-trimethylindolenine methiodide and 3,3-diethoxyprop-1-yne in acetic anhydride.[23]

To prepare the thiadicarbocyanine, I (Y=Z=S, R=R'=Et, R''=H, X=I), 2-methylbenzothiazole ethiodide (1 mol.) and crude 3,3-diethoxyprop-1-yne (2 mols.) were boiled in pyridine for 30 minutes; with the pure propyne (3 mols.), 2·5 hours' boiling was necessary and water had to be added to precipitate the dye. Its 6,7,6',7'-dibenzo-derivative was prepared through the crude propyne.[36]

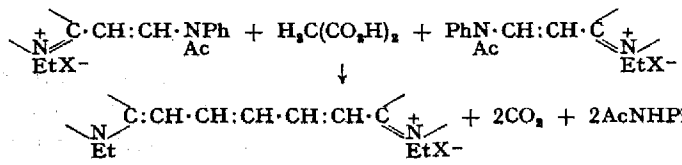
The oxadicarbocyanine, I (Y=Z=O, R=R'=Et, R''=H, X=I), was prepared by boiling 2-methylbenzoxazole ethiodide, 3,3-diethoxyprop-1-yne, and pyridine for 15 minutes, and treating the reaction mixture with water.[38]

The selenadicarbocyanine, I (Y=Z=Se, R=R'=Et, R''=H, X=I), was prepared by boiling 2-methylbenzoselenazole ethiodide and pure 3,3-diethoxyprop-1-yne with 4-hydroxy-4-methyl-2-pentanone, adding anhydrous sodium acetate, boiling for 12 minutes, and treating with water.[36]

5. Symmetrical Pentamethincyanines from a Quaternary Salt, Having a β-Acetanilidovinyl Group, or a β-Ethylthiovinyl Group, with Malonic Acid or with Alkylmalonic Acid

A. General

The condensation of a quaternary, heterocyclic, ammonium salt, having a 2-β-acetanilidovinyl group, with malonic acid was described in 1937 as a general method of preparing pentamethincyanines, and was successfully applied to the preparation of oxadicarbocyanines. The reaction proceeds as in equation 12.[37,38]



(12)

The recorded yields of recrystallised dye were 17%[37] and 15%[9]. The

method was a better one for oxadicarbocyanines than that involving the use of 1-anilino-3-aniloprop-1-ene (section 1-E).[9] The two-stage process with 1,3,3-triethoxyprop-1-ene, however, gave a considerably greater yield (section 2-E). The present method was applied to the preparation of *meso*-alkyl dyes.[38] Subsequently a salt having a 2-ethylthiovinyl group was condensed with malonic acid.[39]

B. 2,2′-Dicarbocyanine

The symmetrical 2,2′-dicarbocyanine, I (Y=Z=CH:CH, R=R′=Me, R″=H, X=I), was prepared by heating 2-ethylthiovinylquinoline methotoluene-*p*-sulphonate with malonic acid in pyridine and converting the product into iodide.[39]

C. Oxadicarbocyanines

The symmetrical oxadicarbocyanine, I (Y=Z=O, R=R′=Et, R″=H, X=I), was prepared by heating a mixture of 2-*β*-acetanilidovinylbenzoxazole ethiodide, malonic acid, and triethylamine at 80° for 10 minutes, washing the product with ether, and recrystallising from alcohol; its absorption and sensitising maxima were recorded. The dimethyl analogue was also made.[37] Similar preparations carried out but with methylmalonic acid, or ethylmalonic acid, led to the *meso*-alkyloxadicarbocyanines, I (Y=Z=O, R=R′=Et, R″=Me or Et, X=I), in 36 % and 6 % yields, respectively;[38] repetition of the preparations gave a 3 % yield of the former dye and a negative result with the latter one.[9]

6. Symmetrical Pentamethincyanines from a Quaternary Salt, Having an Alkylthio- Group, and Sorbic Anhydride

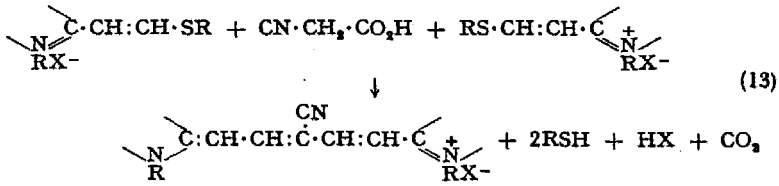
The whole chain of a symmetrical pentamethincyanine might be provided by sorbic anhydride, $(Me{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO)_2O$, analogously to the provision by crotonic anhydride of the chain of a symmetrical trimethincyanine (see IV-14), by its reaction with a quaternary heterocyclic ammonium salt, having an alkythio-group, in the presence of an acid-binding agent. In the one example given, the thiadicarbocyanine, I (Y=Z=S, R=R′=Me, R″=H, X=I), was prepared by

heating 2-methylbenzothiazole methotoluene-*p*-sulphonate with sorbic anhydride in pyridine for 1·5 hours, then pouring the solution into one of potassium iodide.[40]

7. Symmetrical Pentamethincyanines, Having a *Meso*-Cyano- or a *Meso*-Carbalkoxy-Group, by Two Routes

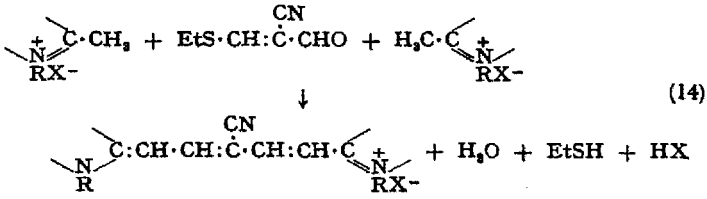
A. General

Two mols. of a heterocyclic salt, having a 2-*β*-alkylthiovinyl, or a 2-*β*-anilinovinyl group, such as had been used in the preparation of trimethincyanines (see V-6 and 10), proved capable of reacting with one mol. of cyanoacetic acid, in the presence of pyridine, to give symmetrical *meso*-cyanopentamethincyanines (equation 13).[41]



(13)

Alternatively, such dyes could be prepared by condensing two mols. of a salt, having a 2-methyl group, with one mol. of 2-cyano-3-ethylthio-1-oxo-prop-2-ene, or of 3-anilino-2-cyano-1-oxoprop-2-ene (equation 14).[42]



(14)

Similarly, by this second route, a *meso*-carbalkoxy-group could be introduced by use of 2-carbalkoxy-3-ethylthio-1-oxoprop-2-ene, or of 3-anilino-2-carbalkoxy-1-oxoprop-2-ene.[42]

The four propene derivatives for the second method were prepared from ethyl sodioformylacetate (or the corresponding nitrile) by treatment with ethyl mercaptan and dry hydrochloric acid in ether (or with aniline and aqueous acetic acid), followed by heating each of the four

products with ethyl formate and sodium in ether, and pouring into water under carbon dioxide.[42] For example:

$$NaO\cdot CH{:}CH\cdot CO_2Et \longrightarrow EtS\cdot CH{:}CH\cdot CO_2Et \longrightarrow EtS\cdot CH{:}\overset{\overset{CHO}{|}}{C}\cdot CO_2Et.$$

B. 2,2'-Dicarbocyanines

According to the first method, the *meso*-cyano-2,2'-dicarbocyanine, I (Y=Z=CH:CH, R=R'=Et, R''=CN, X=I), was prepared by heating 2-β-ethylthiovinylquinoline ethotoluene-*p*-sulphonate with cyanoacetic acid in pyridine for 30 minutes, and treating with aqueous potassium iodide solution.[41]

By the second method, the *meso*-carbethoxy-2,2'-dicarbocyanine, I (Y=Z=CH:CH, R=R'=Et, R''=CO_2Et, X=I), was prepared by heating quinaldine ethiodide with 3-anilino-2-carbethoxy-1-oxoprop-2-ene in pyridine for 3 minutes; a reddish-green colour developed and, on adding triethylamine and further boiling for 20 minutes, slowly changed to green; the reaction mixture was poured into water. Another dye of this type, I (Y=Z=CH:CH, R=R'=CH_2CH_2OAc, R''=CO_2Pr^n, X=I), was prepared from quinaldine β-hydroxyethiodide and the appropriate propene, by heating with triethylamine in acetic anhydride.[42]

C. Indo-, Thia-, and Selena-dicarbocyanines

By the first route, the *meso*-cyanoindodicarbocyanine, I (Y=Z=CMe_2, R=R'=Me, R''=CN, X=I), was prepared from 2-β-ethylthiovinyl-3,3-dimethylindolenine methiodide, cyanoacetic acid, and pyridine, followed by potassium iodide.[41]

By the second route, the *meso*-carbethoxy-analogue, I (Y=Z=CMe_2, R=R'=Me, R''=CO_2Et, X=I), was prepared by heating 2,3,3-trimethylindolenine methiodide with 3-anilino-2-carbethoxy-1-oxoprop-2-ene in pyridine.[42]

By the first method, the *meso*-cyanothiadicarbocyanine, I (Y=Z=S, R=R'=Me, R''=CN, X=$O_3S\cdot C_6H_4\cdot$Me), was prepared by heating 2-β-ethylthiovinylbenzothiazole methotoluene-*p*-sulphonate with cyanoacetic acid and pyridine at 100° for 30 minutes. An analogue, I (Y=Z=S, R=R'=Et, R''=CN, X=I), was prepared by boiling 2-β-anilinovinylbenzothiazole ethiodide and cyanoacetic acid in pyridine for one hour.[41]

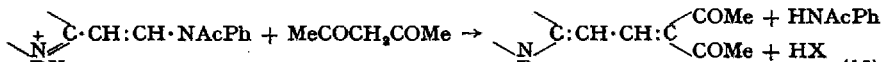
By the second method, the *meso*-carbethoxythiadicarbocyanine, I (Y=Z=S, R=R′=Et, R″=CO_2Et, X=I), was prepared by heating 2-methylbenzothiazole ethiodide and 3-anilino-2-carbethoxy-1-oxoprop-2-ene in pyridine for 3 minutes, adding triethylamine and, when cold, pouring into water. In preparing the corresponding *meso*-cyano-dye, heating with acetic acid was applied, then addition of triethylamine and further heating. Another *meso*-carbethoxy-dye, I (Y=Z=S, R=R′=CH_2CH_2OAc, R″=CO_2Et, X=I), was made by boiling 2-methylbenzothiazole β-hydroxyethiodide and 3-anilino-2-carbethoxy-1-oxoprop-2-ene in acetic anhydride for 2 minutes and cooling to 100°: on adding triethylamine, the deep red solution became blue; the dye was precipitated by ether. Its 5,5′-dichloro-derivative was similarly prepared, as well as its *meso*-carbo-n-propoxy- and *meso*-cyano-analogues.[42]

By the second method, the *meso*-carbethoxyselenadicarbocyanine, I (Y=Z=Se, R=R′=Et, R″=CO_2Et, X=I), was prepared by boiling 2-methylbenzoselenazole ethotoluene-*p*-sulphonate and 3-anilino-2-carbethoxy-1-oxoprop-2-ene in acetic anhydride for 30 minutes, cooling, and adding excess of triethylamine.[42]

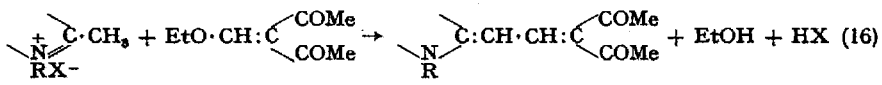
8. Preparation of β-Substituted Pentamethincyanines through Quaternary Salts, Having One of the Groups ·CH:CH·CH:CMe(SR), ·CH:CH·CH:CMe(OR), ·CH:CMe(SR), or ·CH:CMe(OR); Dyes Derived from Them

A. General

Quaternary heterocyclic ammonium salts having in the 2-position a 4-alkylthio-4-methyl-1,3-butadienyl group, ·CH:CH·CH:CMe(SR), were synthesised in 1941 through *N*-alkyl heterocyclic bases, which carried in the 2-position the group: CH·CH:C$(COMe)_2$. Such bases were reached by one of two routes (equations 15 and 16).

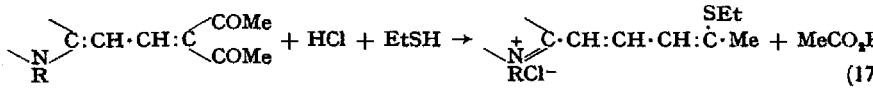


(15)



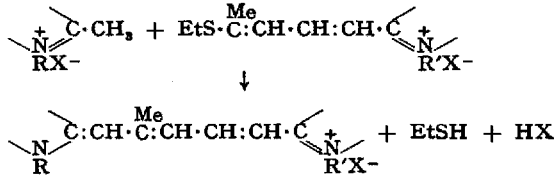
(16)

When a base of this kind was treated with ethyl mercaptan in the presence of dry hydrochloric acid, it underwent conversion to the butadienyl salt, the net result being as in equation 17.



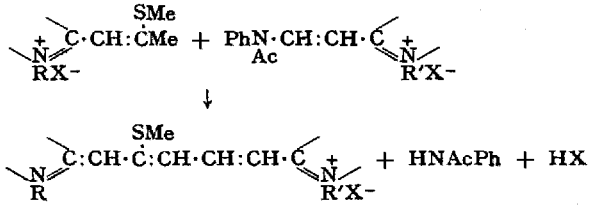
(17)

Salts of this type belonging to the 2-quinoline, benzothiazole, benzoselenazole, and indolenine series were described.[43] By condensing such a salt with a quaternary, heterocyclic ammonium salt, having a reactive methyl group, various types of pentamethincyanines with a β-methyl substituent on the chain were prepared (equation 18).[44]



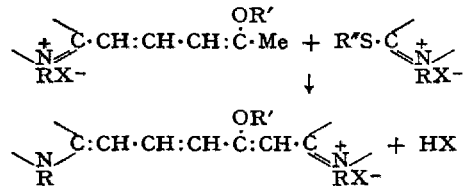
(18)

On the other hand, a quaternary salt, having in the 2-position a 2-alkylthio-2-methylvinyl group, ·CH:CMe(SR) (see VI, 1 and 15), was condensed with one having a 2-β-acetanilidovinyl group to give a pentamethincyanine with an alkylthio-group in the β-position of the chain (equation 19).[45]



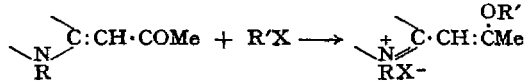
(19)

Quaternary heterocyclic ammonium salts, having in the 2-position a 4-alkoxypenta-1,3-dienyl group, ·CH:CH·CH:CMe(OR), were prepared in 1950 through *N*-alkyl heterocyclic bases, substituted in the 2-position by :CH·CH:CH·COMe or :CH·CH:C(COMe)$_2$, by treatment with anhydrous alcohol and acid below 25°. Representatives of the quinoline, benzothiazole, benzoxazole, and indolenine series were made.[46] Their condensation with quaternary salts having an alkylthio-group gave β-alkoxydicarbocyanines (equation 20).[47]



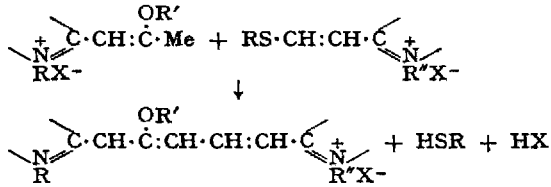
(20)

Other quaternary heterocyclic ammonium salts, having in the 2-position a 2-alkoxy-2-methylvinyl group, ·CH:CMe(OR), were perpared by heating an *N*-alkyl heterocyclic base, having in the 2-position the group: CH·COMe (see VI-1 and 13) with an alkyl toluene-*p*-sulphonate below 160° (equation 21).



(21)

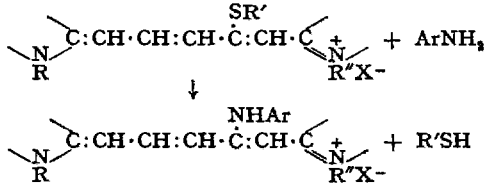
The toluene-*p*-sulphonates could be converted into halides. Examples included eight such salts of the benzothiazole series and one of the indolenine series.[48] They were also prepared by the action of anhydrous alcohol and acid below 25° on *N*-alkyl heterocyclic bases with one of the groups :CH·COMe or :C(COMe)$_2$ in the 2-position.[46] They could be condensed with other salts having a 2-*β*-alkylthiovinyl group, or a 2-*β*-acetanilidovinyl group, to give pentamethincyanines with a *β*-alkoxy-substituent on the chain (e.g., equation 22).[49]



(22)

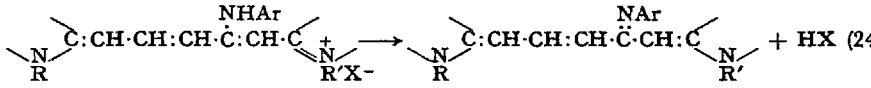
These *β*-substituted pentamethincyanines comprised photographic sensitisers.

By heating a pentamethincyanine having a *β*-alkylthio-group with a primary aromatic amine, a *β*-arylamino-group was introduced (equation 23).[50]



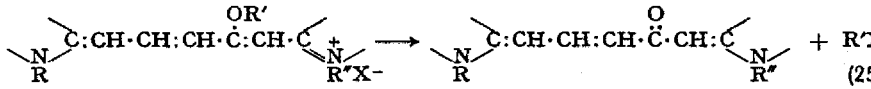
(23)

Just as in the trimethincyanine series (see VI-1 and 16), so also here, the β-substituted dyes gave rise to new types of compounds in which two heterocyclic nuclei were linked by a carbon chain. Thus when an indothiadicarbocyanine having a β′-arylamino-group was treated with a basic substance, acid was eliminated and there arose a new type of coloured substance, which was not a cyanine (equation 24).[51]



(24)

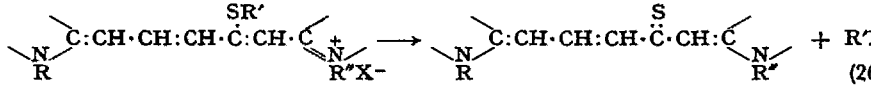
When a β-alkoxypentamethincyanine was treated with a basic substance, there resulted another new type of compound (equation 25).



(25)

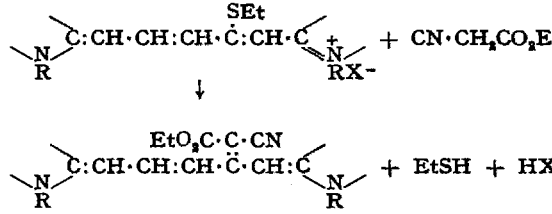
Such compounds derived from thia-, indothia-, and oxathia-dicarbocyanines were described (cf. VIII, 1).[52]

An indothiadicarbocyanine, having a β′-ethylthio-group passed, by treatment with alkali, into a new type of compound with a β-substituted chain (equation 26).[53]



(26)

The same β′-ethylthioindothiadicarbocyanine was converted, by condensation with ethyl cyanoacetate, into a substance of another new type (equation 27).[54]

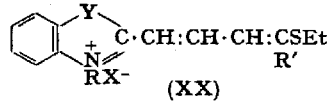


(27)

The substances comprised photographic sensitisers.[51–54] As they dye silver halide, it is correct to refer to them as dyes.

B. Indo-2'- and Thia-2'-dicarbocyanines

To the 4-ethylthio-4-methyl-1,3-butadienyl-salt, XX (Y=CMe_2, R=R'=Me, X=Cl), and *p*-toluquinaldine ethiodide, dissolved in ethanol, was added triethylamine and heat was applied: this led to the 6'-methyl derivative of the β'-methylindo-2'-dicarbocyanine, XVI (Y=CH:CH, Z=CMe_2, R=Et, R=R"=Me, X=I).[44]



(XX)

The β-methylthia-2'-dicarbocyanine, XVI (Y=S, Z=CH:CH, R=Et, R'=R"=Me, X=I), having also a 6-methyl substituent in the quinoline nucleus, was prepared by boiling the 6-methyl derivative of XX (Y=CH:CH, R=R'=Me, X=Cl) with 2-methylbenzothiazole ethiodide and anhydrous sodium acetate in ethanol for 40 minutes.[44] The β-methoxythia-2'-dicarbocyanine, XVI (Y=S, Z=CH:CH, R=R'=Me, R"=OMe, X=I) was prepared by heating 2-(4-methoxypenta-1,3-dienyl)quinoline methochloride and 2-methylthiobenzothiazole methotoluene-*p*-sulphonate with triethylamine in ethanol for 30 minutes, and treating with aqueous potassium iodide.[47]

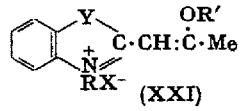
C. Thiadicarbocyanines

The β-methyl derivatives of three symmetrical thiadicarbocyanines were prepared through intermediate salts of type XX. In the first of these, the dye XVI (Y=Z=S, R=R'=Et, R"=Me, X=I) was prepared by heating XX (Y=S, R=Et, R'=Me, X=Cl) and 2-methylbenzothiazole ethiodide with triethylamine in alcohol; its analogue having *NN'*-di-β-hydroxyethyl groups was similarly made; for making its *NN'*-dimethyl analogue, the condensing agent was sodium acetate in ethanol.[44]

The β-methyl derivative of an unsymmetrical thiadicarbocyanine, i.e., the dye, XVI (Y=Z=S, R=Et, R'=R"=Me, X=I), was prepared by heating together 2-(β-methyl-β-methylthio)vinylbenzothiazole ethomethylsulphate, 2-β-acetanilidovinylbenzothiazole methomethylsulphate, anhydrous sodium acetate, and acetic anhydride, and conversion into iodide.[45]

Four β-alkoxythiadicarbocyanines were prepared. To obtain XVI

(Y=Z=S, R=R'=Me, R''=OMe, X=Br) the salt, XXI (Y=S, R=R'=Me, X=*p*-$SO_3 \cdot C_6H_4 \cdot Me$), and 2-*β*-ethylthiovinylbenzothiazole methotoluene-*p*-sulphonate, were heated with triethylamine in ethanol for 10 minutes, then treated with aqueous potassium bromide. To make the second, XVI (Y=Z=S, R=Et, R'=Me, R''=OMe, X=I), the salt of type XXI was first prepared by heating 2-acetylmethylene-3-ethylbenzothiazoline with methyl toluene-*p*-sulphonate at 100° for 4 hours, by then adding the second salt, and proceeding as before. The other two dyes were XVI (Y=Z=S, R=R'=Et, R''=OMe or OEt, X=I).[49] The



(XXI)

alternative method, which involved boiling 2-(4-alkoxypenta-1,3-dienyl)benzothiazole methochloride with 2-methylthiobenzothiazole methotoluene-*p*-sulphonate or methiodide, was applied to the preparation of XVI (Y=Z=S, R=R'=Me, R''=OMe or OEt, X=I).[47]

D. Indoselena-, Indothia-, Oxathia-, and Selenathia-dicarbocyanines

The *β'*-methyl- and *β'*-ethyl-indoselenadicarbocyanines, XVI (Y=Se, Z=CMe_2, R=Me, R'=Et, R''=Me or Et, X=I), were prepared by interaction of 2-methylbenzoselenazole ethiodide and triethylamine in ethanol with the intermediate salts, XX (Y=CMe_2, R=R'=Me, X=Cl and Y=CMe_2, R=Me, R'=Et, X=I), respectively.[44]

The *β'*-methyl- and *β'*-ethyl-indothiadicarbocyanines, XVI (Y=S, Z=CMe_2, R=R'=Me, R''=Me or Et, X=I), were similarly prepared by interaction of 2-methylbenzothiazole methiodide and triethylamine in ethanol with the intermediate salts, XX (Y=CMe_2, R=R'=Me, X=Cl and Y=CMe_2, R=Me, R'=Et, X=I), respectively. Three other *β'*-methylindothiadicarbocyanines were prepared by condensation of the former intermediate salt with 2-methylbenzothiazole ethiodide, by heating with sodium acetate in ethanol, with 2-methylbenzothiazole *β*-hydroxyethiodide, and with 2-methyl-6,7-benzobenzothiazole ethiodide, respectively.[44]

Two *β'*-methoxy-indothiadicarbocyanines were prepared. The first, XVI (Y=S, Z=CMe_2, R=R'=Me, R''=OMe, X=I), was prepared from XXI (Y=S, R=R'=Me, X=*p*-$SO_3 \cdot C_6H_4 \cdot Me$) and 2-*β*-

ethylthiovinyl-3,3-dimethylindolenine methiodide by heating with triethylamine in ethanol for 15 minutes.[49] It was also made by the alternative method from 2-(4-methoxypenta-1,3-dienyl)3,3-dimethylindolenine methochloride and 2-methylthiobenzothiazole methotoluene-*p*-sulphonate with sodium ethylate in ethanol.[47] For making the second, XVI (Y=S, Z=CMe_2, R=Et, R′=Me, R″=OMe, X=I), the intermediate salt, XXI (Y=S, R=Et, R′=Me, X=*p*-$SO_3C_6H_4$·Me), was first prepared by 4 hours' fusion of 2-acetylmethylene-3-ethylbenzothiazoline with methyl toluene-*p*-sulphonate, followed by addition of 2-*β*-ethylthiovinyl-3,3-dimethylindolenine methiodide, ethanol, and triethylamine, boiling for 30 minutes, and conversion of the dye into iodide. For making a *β*-methoxyindothiadicarbocyanine, XVI (Y=CMe_2, Z=S, R=R′=Me, R″=OMe, X=I), 2-acetylmethylene-1,3,3-trimethylindoline was fused with methyl toluene-*p*-sulphonate, and the resultant intermediate salt boiled with 2-*β*-ethylthiobenzothiazole methotoluene-*p*-sulphonate and triethylamine in ethanol for 30 minutes, the reaction mixture being treated with hot aqueous potassium iodide.[49]

When the *β*′-(ethylthio)indothiadicarbocyanine, XVI (Y=S, Z=CMe_2, R=R′=Me, R″=SEt, X=I), was heated with *p*-toluidine at 100° for 30 minutes, the product which was precipitated by ether, redissolved in acetone, and reprecipitated by ether, was the corresponding indothiadicarbocyanine having a *β*′-*p*-NH·C_6H_4Me group. Use of *p*-phenetidine instead of *p*-toluidine led to replacement of the *β*′-ethylthio-group by the *β*′-*p*-NH·C_6H_4·OEt group.[50]

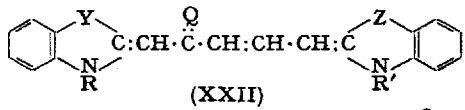
The *β*′-methoxyoxathiadicarbocyanine, XVI (Y=S, Z=O, R=R′=Me, R″=OMe, X=I), was prepared by heating an ethanolic solution of XXI (Y=S, R=R′=Me, X=$O_3S\cdot C_6H_4Me$), 2-*β*-ethylthiovinylbenzoxazole methotoluene-*p*-sulphonate, and triethylamine, followed by treatment with potassium iodide.[49] Alternatively it was prepared from 2-(4-methoxypenta-1,3-dienyl)benzoxazole methochloride and 2-methylthiobenzothiazole methotoluene-*p*-sulphonate by boiling with triethylamine in ethanol for 30 minutes, then treating with potassium iodide.[47]

Two isomeric *β*-methyl- and *β*′-methyl-selenathiadicarbocyanines were prepared. The former, XVI (Y=Se, Z=S, R=Et, R′=R″=Me, X=I), was prepared by boiling XX (Y=S, R=R′=Me, X=Cl) and 2-methylbenzoselenazole ethiodide with sodium acetate in ethanol. The latter, XVI (Y=S, Z=Se, R=Et, R′=R″=Me, X=I), was prepared by

reaction of XX (Y=Se, R=R′=Me, X=Cl), 2-methylbenzothiazole ethiodide, and triethylamine in ethanol.[44]

E. Dyes with the Chain :CH·C(Q):CH:CH·CH: where Q is :NAr, :O, :S, or :C(CO$_2$Et)CN

A base, having the chain :CH·C(NAr)·CH:CH·CH:, was prepared from the β′-substituted indothiadicarbocyanine, XVI (Y=S, Z=CMe$_2$, R=R′=Me, R″=*p*-NH·C$_6$H$_4$OEt, X=I), by dissolving it in ethanol and adding a solution of sodium ethoxide; the product precipitated by water was extracted with ether and formed yellow needles, m.p. 199–201°. This compound, XXII (Y=S, Z=CMe$_2$, R=R′=Me, Q=:N-*p*-C$_6$H$_4$·OEt), sensitised to 6600 Å with the maximum at 6200 Å.[51]



(XXII)

Another type of base with the chain :CH·C(O)·CH:CH·CH: was prepared from the β-ethoxythiadicarbocyanine, XVI (Y=Z=S, R=R′=Et, R″=OEt, X=I), by boiling it with pyridine for 30 minutes. The blue colour became orange-yellow. The product, XXII (Y=Z=S, R=R′=Et, Q=O), was precipitated by water and extracted with light petroleum (see VI–Table III). A β′-methoxyindothiadicarbocyanine was similarly converted into a compound with the chain :CH·CH:CH·C(O)·CH:. The β′-methoxyoxathiadicarbocyanine, XVI (Y=S, Z=O, R=R′=Me, R″=OMe, X=I), was similarly converted into XXII (Y=S, Z=O, R=R′=Me, Q=O) (see VI–Table III).[52]

A compound with two heterocyclic nuclei linked by the chain :CH·C(S)·CH:CH·CH: was made by boiling the β′-(ethylthio)indothiadicarbocyanine, XVI (Y=S, Z=CMe$_2$, R=R′=Me, R″=SEt, X=I), with pyridine for 15 hours, whereupon the deep blue colour changed to purple; after precipitation with water, the product was extracted with ether. The grey-blue crystals of XXII (Y=S, Z=CMe$_2$, R=R′=Me, Q=S) had m.p. 230° and sensitised from 6000–7200 Å with the maximum at 6900 Å.[53]

By reaction of the same β′-(ethylthio)indothiadicarbocyanine with ethyl cyanoacetate and triethylamine at room temperature for 10

TABLE I. Some Properties of Some Symmetrical Pentamethincyanines

Nature of dicarbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising maximum (Å)	Ref.
2,2′-	I (Y=Z=CH:CH, R=R′=Et, R″=H, X=I)	green needles	270	7080	7500	8, 10, 12
5,6,5′,6′-dibenzo-derivative	—	—	—	7380	—	12
4,4′-	V (R=R′=Et, R″=H, X=I)	green	158	8100	8500	10, 11, 12
indo-	I (Y=Z=CMe_2, R=R′=Me, R″=H, X=I)	blue crystals, bronze reflex	205, 238	—	6700	10, 11, 28
thia-	I (Y=Z=S, R=R′=Et, R″=H, X=I)	green needles	253	6500	7000	12, 18, 19
4,5,4′,5′-dibenzo-derivative	—	green	225–227	6910	—	8, 12
6,7,6′-7′-dibenzo-derivative	—	—	—	6870	—	12
oxa-	I (Y=Z=O, R=R′=Et, R″=H, X=I)	steely	232	5800	6200	9, 12, 36
4,5,4′,5′-dibenzo-derivative	—	—	—	6060	—	12
6,7,6′,7′-dibenzo-derivative	—	—	—	6080	—	12
selena-	I (Y=Z=Se, R=R′=Et, R″=H, X=I)	green needles	235–236	6600	—	8,12
2,2′-pyrido-	VII (R=R′=Me, X=I)	—	217	—	6900	19
thiazolo-	XIII (R=R′=Me, X=I)	—	215	—	6900	18, 19
thiazolino-	XIV (R=R′=Me, X=I)	—	225	—	5800	13

TABLE II. Some Properties of Some Unsymmetrical Pentamethincyanines

Nature of dicarbocyanine	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
2,4′-	III (Y=CH:CH, R=R′=Et, X=I)	greenish gold	240	7605	7600 and 8200	8500	6
oxa-2′-	I (Y=O, Z=CH:CH, R=R′=Et, X=I)	green	149–150	—	6900[a]	7000[a]	8, 33
selena-2′-	I (Y=Se, Z=CH:CH, R=R′=Et, X=I)	—	—	6750	—	—	14
thia-2′-	I (Y=S, Z=CH:CH, R=R′=Et, X=I)	green; gold reflex	234–236	6760	7150[b]	7700[b]	8, 14, 33
oxa-4′-	III (Y=O, R=R′=Et, X=I)	green; gold reflex	132–134	—	—	—	8
selena-4′-	III(Y=Se, R=R′=Et, X=I)	—	—	7220	—	—	14
thia-4′-	III (Y=S, R=R′=Et, X=I)	green	175–176	7250	—	—	8, 14
indoselena-	I (Y=CMe_2, Z=Se, R=Me, R′=Et, X=ClO_4)	dark blue	197–204	—	6875	7000	33
indothia-	I (Y=CMe_2, Z=S, R=R′=Me, X=I)	light green	256	—	6850	7400	33
indoxa-	I (Y=CMe_2, Z=O, R=Me, R′=Et, X=ClO_4)	violet	140	—	6400	—	33
oxaselena-	I (Y=O, Z=Se, R=R′=Et, X=I)	green	220–222	—	—	—	8
oxathia-	I (Y=O, Z=S, R=R′=Et, X=I)	green needles	242–244	—	6900[c]	—	8, 33
selenathia-	I (Y=Se, Z=S, R=R′=Et, X=I)	green	236–237	6590	7150[d]	8000[d]	5, 8, 14

[a] Sensitising data for *NN′*-diMe analogue.
[b] Sensitising data for I (Y=S, Z=CH:CH, R=Me, R′=Et, X=I).
[c] Sensitising maximum for I (Y=O, Z=S, R=R′=Me, X=I).
[d] Sensitising data for derivative having 5,6-diMe in benzoselenazole nucleus.

TABLE III. Some Properties of Some Chain-Substituted Symmetrical Pentamethincyanines

Nature of dicarbocyanine	Formula and substituent	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising, (Å) Maximum	Extent	Ref.
2,2′-Series	I (Y=Z=CH:CH, X=I) Unsubstituted: R″=H	—	270	7080	7500	—	10,12
	γ-Me (R″=Me)	green	260–261	7050 (and 6500)	7500 (and 6850)	—	9
	γ-Cl (R″=Cl)	green; bronze reflex	228–230	—	—	—	3
	γ-Br(R″=Br)	brassy green prisms	—	7000	7550	—	3,4
	γ-NO_2(R″=NO_2)	dark brown	—	4900 and 5800	no sensitising		3
	γ-CN(R″=CN)	green matted needles	276	—	—	—	41
	γ-CO_2Et(R″=CO_2Et)	blue green	253	—	6900	7200	42
Thia-Series	I (Y=Z=S, R=R′=Et, X=I). Unsubstituted: R″=H	—	253	6500	7000	—	12, 19
	αα′-diMe, R″=H	dark green	241	6650	7100	7700	9
	β-Me, R″=H	green	206–207	6610	7000	7500	9
	β-Ph, R″H	light green	166	—	7100	7500	31
	β-OMe, R″=H[a]	green; gold reflex	154–157	—	6600	6900	49
	β-OEt, R″=H	green	179–182	—	6600	7000	49
	γ-Me(R″=Me)	dark green; gold reflex	261–263	6400	—	6950	9,25
	γ-Cl(R″=Cl)	bluish green; bronze reflex	233–234	—	—	—	3
	γ-Br(R″=Br)	bluish green; bronze reflex	171–172	6450	6900	—	3, 16
	γ-CN(R″=CN)	green	282	—	—	—	41
	γ-CO_2Et(R″=CO_2Et)	dark green	230	—	6400	6800	42

[a] Data for γ-OMe-derivative of I (Y=Z=S, R=R′=Me, R″=H, X=Br).

minutes, followed by heating for 2 minutes, there was obtained the substance XXII (Y=S, Z=CMe_2, R=R′=Me, Q=:C(CO_2Et)CN). It was isolated by treatment with ether; concentration of the ethereal filtrate gave an oil, which was dissolved in ethanol and precipitated with ether, and had m.p. 138–140°. Its sensitising maxima lay at 5100 Å and 5600 Å.[54]

9. Thiadicarbocyanine from a 2-Methylbenzothiazolium Salt with 2-Chloro-3,3-dimethylindolenine in Pyridine

Reaction of 2-chloro-3,3-dimethylindolenine with a 2-methylbenzothiazolium salt in pyridine gave the thiadicarbocyanine, I (Y=Z=S, R=R′=Me, R″=H, X=I), in 79% yield, whereas, from analogy with the behaviour of 2-chlorobenzoxazole (cf. VIII-1 and 3), the corresponding thiatricarbocyanine was expected. When 3,5-lutidine took the place of pyridine, the product was the *meso*-methylthiadicarbocyanine. Hence it was inferred that cleavage of the pyridine ring had occurred in an unprecedented manner, carbon atoms 2, 3 and 4 providing the three central atoms of the pentamethin chain.[55]

Some properties of typical pentamethincyanines are presented in three Tables. Table I deals with some symmetrical and Table II with some unsymmetrical dyes. In Table III the properties of chain-substituted symmetrical pentamethincyanines of the thia- and 2,2′-series have been summarised. The former series has been far more thoroughly worked on than the latter, probably because the dyes of that series are more useful in photography. Dyes of the indo-series have little photographic value and the data about chain-substituted pentamethincyanines of that series were too sketchy to be worth including in the Table.

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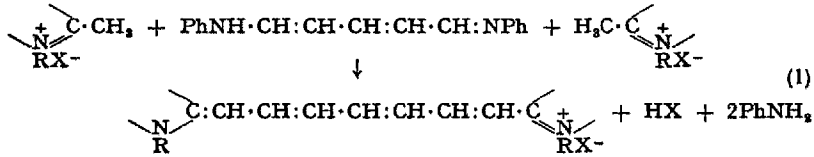
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CHAPTER VIII

Symmetrical and Unsymmetrical Heptamethincyanines, Including those with Substituents on the Chain; Polymethincyanines

1. General Survey

About 1930 there were three independent publications of the discovery of heptamethincyanines. Just as trimethincyanines were prepared by use of diphenylformamidine, PhNH·CH:NPh (IV-9 and V-6), and pentamethincyanines by use of 1-anilino-3-aniloprop-1-ene, PhNH·CH:CH·CH:NPh (VII-1), so symmetrical heptamethincyanines were synthesised through the hydrochloride of glutaconic aldehyde dianilide, PhNH·CH:CH·CH:CH·CH:NPh, i.e., of 1-anilino-5-anilopenta-1,3-diene, by condensation with a heterocyclic quaternary salt having a reactive methyl group (equation 1).

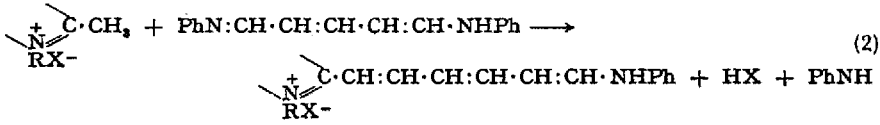


(1)

The dyes described had two 2-linked quinoline, benzothiazole, benzoselenazole, indolenine, or thiazoline nuclei; whilst condensation was usually effected by heating with sodium ethoxide in ethanol, to make the indotricarbocyanines there was used sodium acetate in acetic anhydride. The dyes were unstable to heat and light and their melting points were always lower than those of the corresponding carbocyanines. The bathochromic shift of absorption maximum on passing from carbocyanine to tricarbocyanine was 1900 to 5200 Å.[1] The tricarbocyanines sensitised to infrared light.[1,2] The other two sets of

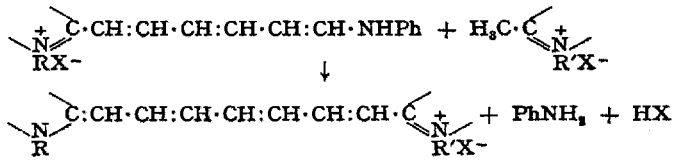
workers applied this method to the preparation of indotricarbocyanines.[3,4] It was recorded in 1933 that both penta- and heptamethincyanines had already been put into commercial use as photographic sensitisers in Germany.[5] From Japan came comparisons of the melting points and sensitising action of tricarbocyanines, of the 2,2'-, 4,4'-, indo-, thia-, and thiazolo-series, with those of their trimethin- and pentamethin-analogues.[6–9] When, in 1940, caustic alkali as a condensing agent had been superseded by a strong base, such as piperidine or triethylamine, improved yields resulted:[10] by use of such reagents at a low temperature, the preparation of symmetrical heptamethincyanines with two 4-linked quinoline nuclei was achieved.[10,11] The sensitising maximum of the 4,4'-tricarbocyanines was at 9800 Å[11,12] and made possible the furthest photographic explorations into the infrared region.[12]

By condensing equimolecular quantities of quaternary salt and anilinoanilo-compound, an intermediate salt resulted (equation 2).



(2)

The first intermediate salt of this type, recorded in 1928, was prepared in acetic anhydride,[3] whence its anilino-group would be acetylated. Subsequently, as for the next lower vinylene homologues (see VII-1-A), an alkaline medium was recommended for the preparation of such intermediate salts of the benzothiazole and benzoselenazole series,[13] whence various unsymmetrical tricarbocyanines could be synthesised (equation 3).[14]



(3

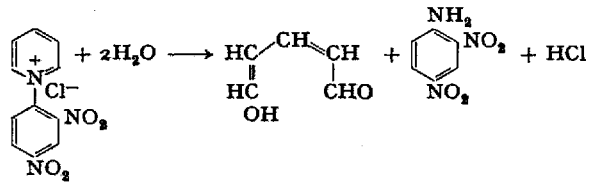
However when a strong base as condensing agent was first successfully applied to the preparation of oxatricarbocyanines, it was acylarylamino-salts that were used (see section 2-D).[15]

The use of the tri- and tetra-acetals, $(MeO)_2CH{\cdot}CH{:}CH{\cdot}CH{:}CH(OMe)$ and $(MeO)_2CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH(OMe)_2$ in place of the anilinoanilo-

compounds, was suggested; they were applied to the preparation of a thiatricarbocyanine[16] but do not seem to have proved further useful.

The sensitising action to infrared light of heptamethincyanines, in which at least one carbon atom of the chain carried an alkyl group, was patented at an early date. The pentadienes which were used were derived from alkylpyridinium cyanogen bromides.[17] Subsequently the 1,5-dimethyl derivative of 1-anilino-5-anilopenta-1,3-diene hydrochloride was thus synthesised, also (as an oil) the 1,3-dimethyl derivative of the corresponding hydrobromide and the 1-, 2-, and 3-methyl derivatives of the hydrobromide. By condensing these with 2-methylbenzothiazolium salts, by means of piperidine in ethanol at a low temperature, there were obtained thiatricarbocyanines with $\beta\beta'$- or $\beta\delta$-dimethyl, or with a β-, γ-, or δ-methyl group on the chain. Absorption maxima were recorded. As sensitisers, the dyes were not in general superior to those with an unsubstituted chain.[18] 1-Anilino-5-anilo-2-halogenopenta-1,3-diene hydrohalides[19] were described in 1935 as making available γ-halogenotricarbocyanines.[20]

1-Anilino-5-anilopenta-1,3-diene hydrochloride (section 2) was originally prepared, either direct from 2,4-dinitrophenylpyridinium chloride, or by its fission and by treatment of the resultant open-chain product, which could not itself be isolated, with aniline and hydrochloric acid[21] (equations 4 and 5). Some of the earliest tricarbocyanines were prepared by a method which consisted in treating such a pyridinium salt with

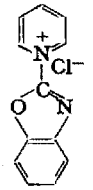


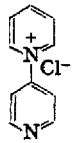
(4)

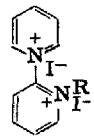
$$OH\cdot CH{:}CH\cdot CH{:}CH\cdot CHO + 2PhNH_2 + HCl \downarrow PhNH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}NPh,\ HCl + 2H_2O \qquad (5)$$

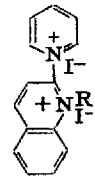
alcoholic alkali, adding a salt having a reactive methyl group, and heating.[1,22] An indotricarbocyanine was obtained by reaction of 1,3,3-trimethyl-2-methyleneindoline with the pyridinium salt or, by a different procedure, an intermediate salt was produced.[3] According to modifi-

cations of the method, the pyridinium salts I, II, III, and IV, prepared by reaction of pyridine with 2-chlorobenzoxazole,[23] 4-chloropyridine,[24]


(I)

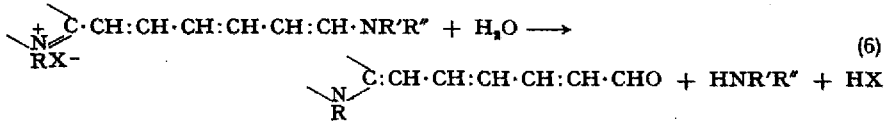

(II)


(III)

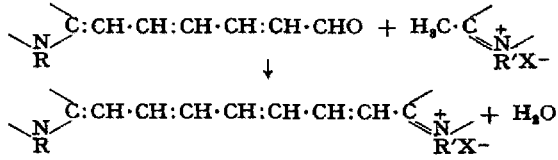

(IV)

2-iodopyridine alkiodide,[25,26] or 2-iodoquinoline alkiodide,[25,26] respectively, were suitable. Use of cyanogen chloride and cyanogen bromide for preparing pyridinium salts[27,28] is important in that the latter combined with 2-, 3-, and 4-methyl-, and 2,4-dimethyl-pyridine, and these substituted pyridinium bromides gave with aniline the substituted 1-anilino-5-anilopenta-1,3-diene salts which were used (section 2-C) for preparing chain-substituted thia- and selena-tricarbocyanines. Although the method involving the direct use of a pyridinium salt (section 3) is particularly interesting, it is not so widely applicable and does not give such good yields, as the preceding method (section 2).

A third method (section 4), patented in 1936, of synthesising tricarbocyanines, was through heterocyclic pentamethin aldehydes.[29] It gave rise to unsymmetrical, as well as symmetrical, dyes. The aldehydes were prepared by the action of alkali on intermediate salts (section 2) having a substituted amino-group (equation 6).[30]

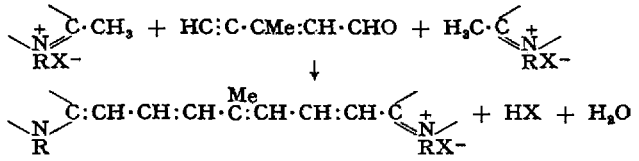

(6)

By condensation with quaternary salts, having a reactive methyl group, they gave heptamethincyanines (equation 7).


(7)

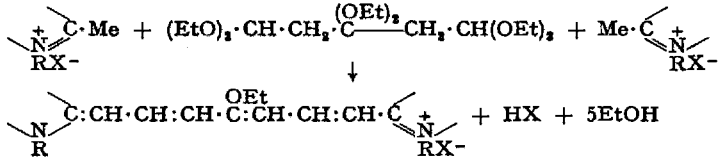
An aldehyde, of the general formula $HC{:}C{\cdot}CR{:}CH{\cdot}CHO$, was condensed with a couple of quaternary salts having a reactive methyl

group, to give two symmetrical *meso*-methyltricarbocyanines (section 5) (equation 8).[31]



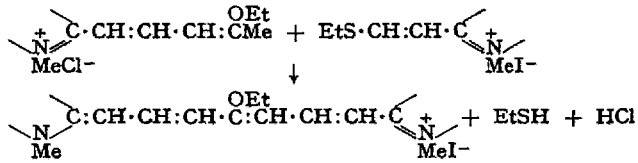
(8)

δ-Ethoxythiatricarbocyanines were obtained by condensation, in the presence of a solvent and acid-binding agent, of a 2-methylbenzothiazolium salt with the reaction product from γ-pyrone and ethyl orthoformate.[32] Probably this product was diformylacetone hexa-ethyl acetal[33] and condensation took place as indicated in equation 9.[32]



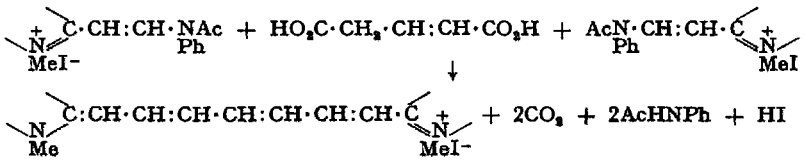
(9)

Just as quaternary heterocyclic salts having the group ·CH:CH·CH:CMe(OR)[34] were condensed with salts having an alkylthio-group, to give β-alkoxy-dicarbocyanines (VII-8-A) so, similarly, a salt of this type was condensed with one having a β-alkylthiovinyl group, to give a *meso*-alkoxyindothiatricarbocyanine (section 6) (equation 10).[35]



(10)

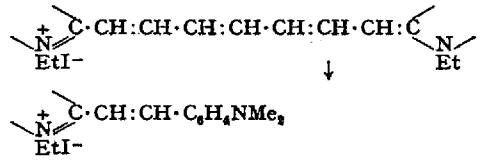
It was noted that the method of preparing pentamethincyanines by reaction of a quaternary salt, having a 2-β-acetanilidovinyl group, with malonic acid (see VII-5) could be extended to heptamethincyanines, by use of glutaconic acid (equation 11).



(11)

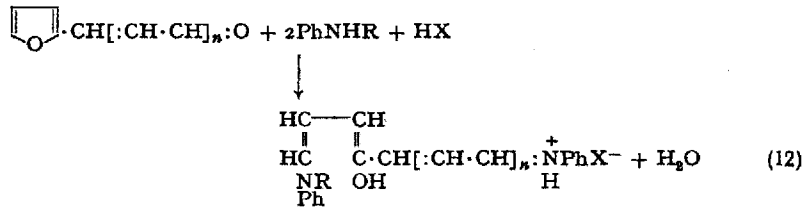
2-β-Acetanilidovinylthiazoline methiodide was thus condensed with glutaconic acid by means of trialkylamine[36] but no further particulars were published.

By heating a thiatricarbocyanine with *p*-dimethylaminobenzaldehyde and acetic anhydride, its chain was ruptured, leading to a styryl compound, thus:



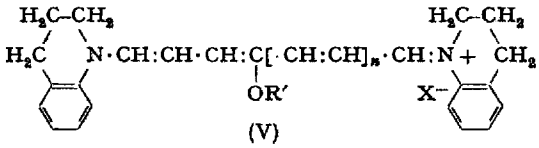
Hence it was concluded that the αβ-linking of the chain is more unstable than the α to nuclear linking.[37]

Much as the pyridinium nucleus was split to give 1-anilino-5-anilopenta-1,3-diene hydrochloride (equations 4 and 5), so, in 1905, rupture of the furfuraldehyde nucleus gave the 4-hydroxy-derivative of the corresponding hydrobromide (equation 12; n=0, R=H, X=



(12)

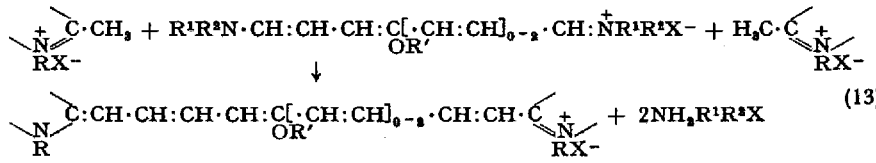
Br),[38] and, in 1913, rupture of 2-β-furylacraldehyde gave the hydrobromide of 1-anilino-7-anilo-4-hydroxyhepta-1,3,5-triene (equation 12; n=1, R=H, X=Br).[39] In 1934, polymethin analogues of these pentamethin and heptamethin salts were made. Thus rupture of the molecules of 5-furylpenta-2,4-dien-1-al and 7-furylhepta-2,4,6-trien-1-al, respectively, by acid and an amine—suitably 1,2,3,4-tetrahydroquinoline—gave V (R′=H, n=2 or 3), but their instability increased



(V)

with lengthening of the chain. By means of acyl chlorides or anhydrides, in the presence of pyridine, all these hydroxy-compounds could be

acylated, giving more stable derivatives.[40] Such derivatives could be condensed with various quaternary salts, having a reactive methyl group, to give cyanines in which the nuclei were joined by a seven-, nine-, or eleven-membered carbon chain, with an ε-acyloxy-substituent (see section 7) (equation 13).



(13)

From examples in a patent,[41] it would seem that the eleven-membered chain is the longest reached in a cyanine, as none prepared from V ($n=3$) has been recorded. These polymethincyanines are sensitisers to infrared light.[41] It was noted, however, that a heptamethincyanine with an unsubstituted chain sensitised four times as powerfully as its ε-acetoxy-derivative.[42] Although it was said that polymethincyanines were obtained pure as bromides or iodides,[42] other workers found that, with the exception of the thiatetracarbocyanine, the polymethincyanine perchlorates were difficult to purify, often decomposing on attempted recrystallisation; it was suggested that the broadness of their sensitising bands might be due to the presence of other dyes.[43] A nonamethincyanine sensitised to 12,000 Å, but the plates kept badly and could only be used with special precautions. The attainable sensitivity decreased with increasing wavelength.[44] Thus for plates sensitised for 8500 Å, 9500 Å, and 10,500 Å, respectively, the attainable sensitivities are as 1: $^1/_{16}$:$^1/_{160}$. Hypersensitising increased the sensitivity 4 to 6 times.[42, 45]

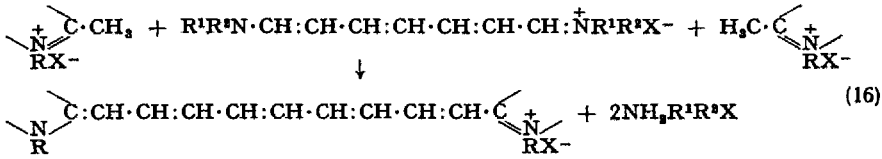
In 1936, the synthesis of nonamethincyanines, belonging to the benzothiazole and benzoselenazole series, and having an unsubstituted chain, was described (see section 8).[46] The starting point was a trimethin salt,[47] which gave on hydrolysis a substituted propenal (equation 14).[48]

$$R^1R^2N\cdot CH:CH\cdot CH:\overset{+}{N}R^1R^2X^- + H_2O \longrightarrow R^1R^2N\cdot CH:CH\cdot CHO + NH_2R^1R^2X \quad (14)$$

The second stage consisted in its reaction with malonic acid, by heating with an acid condensing agent, such as acetic acid, to give a heptamethin salt (equation 15).

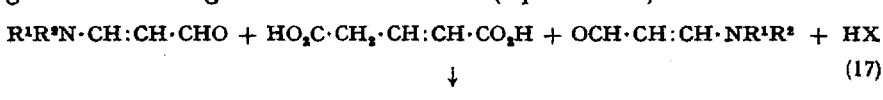
$$\begin{aligned} &R^1R^2N\cdot CH:CH\cdot CHO + H_2C(CO_2H)_2 + OCH\cdot CH:CH\cdot NR^1R^2 + HX \\ &\qquad\qquad\qquad

The salt could be converted into halide. As examples of suitable amines, whence the substituent $\cdot NR^1R^2$ was derived, there were mentioned methylaniline, 1,2,3,4-tetrahydroquinoline, 1,2-dihydroindole, and 3-methyl-2,3-dihydrobenzoxazine.[49] At the final stage, the heptamethin salt was condensed with a quaternary salt, having a reactive methyl group (equation 16).[46]



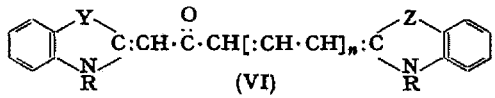
(16)

Reaction of a substituted propenal $R^1R^2N\cdot CH:CH\cdot CHO$ with glutaconic acid gave nonamethin salts (equation 17).



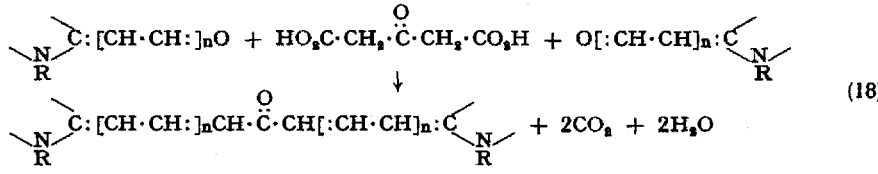
(17)

They were described as useful for making undecamethincyanines with an unsubstituted chain.[50] Such pentacarbocyanines sensitised three or four times as strongly as those with an *s*-acetoxy-substituent.[50,51] An unsubstituted thiapentacarbocyanine had its absorption maximum at 9900 Å (and 5100 Å) and its sensitising maximum at 10,200 Å. The synthesis with glutaconic acid, however, proceeded less smoothly than that with malonic acid.[51]



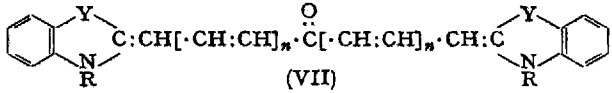
(VI)

The preparation of compounds, VI ($n=0$), from β-alkoxycarbocyanines (see VI-16) and of their analogues, VI ($n=1$), from β-alkoxydicarbocyanines (see VII-8-E) was patented in 1950. It is interesting that, according to a patent of 1937, somewhat similar substances had been produced by reaction of acetone dicarboxylic acid with a heterocyclic aldehyde in the presence of acetic anhydride (equation 18).



(18)

Photographic properties were claimed for them. One example with a seven-membered chain was the 5,5′-dimethoxy-derivative of VII (Y=CMe_2, n=1, R=Me); another, with a fifteen-membered chain, was VII (Y=S, n=3, R=Et).[52]

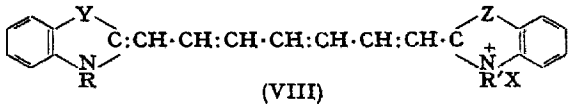


(VII)

2. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, by Use of a 1-Anilino-5-anilopenta-1,3-diene, or its Salt

A. 2,2′- and 4,4′-Tricarbocyanines

The 2,2′-tricarbocyanine, VIII (Y=Z=CH:CH, R=R′=Et, X=I), was prepared by dissolving quinaldine ethiodide (2 mols.) in ethanol (10 c.c. per g.), adding 1-anilino-5-anilopenta-1,3-diene hydrochloride (1 mol.), followed by a solution of sodium (2 atoms) in ethanol,

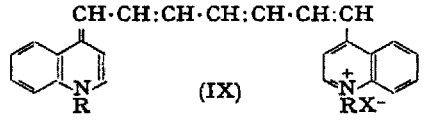


(VIII)

and boiling for 30 seconds. The dye which crystallised was washed, successively, with water, ether, and acetone, then boiled out with methanol, and recrystallised from it, but the final yield was only 2 %. The 6,6′-dimethyl derivative was similarly prepared in 13 % yield.[1] The former dye was subsequently obtained in 50 % yield by heating quinaldine ethiodide (2 mols.) and 1-anilino-5-anilopenta-1,3-diene (1 mol.) with piperidine at 60° for 15 minutes, and recrystallising from methanol;[6] with acetic anhydride, instead of piperidine, the yield was only 26 %.[53] Reaction of piperidine (2 mols.) on an alcoholic suspension of quinaldine ethotoluene-*p*-sulphonate (2 mols.) and 1-anilino-5-anilopenta-1,3-diene hydrochloride (1 mol.), at 0° for a day, gave dye, which was converted into iodide; this was washed with acetone and then with hot methanol until the filtrate was green; on recrystallisation from methanol, the yield was reduced from 49 % to 43 %.[10] The melting point, colour, and sensitising maximum of the dye were compared with those of its tri- and penta-methin analogues,[7] and the absorption maxi-

mum of its methanolic solution was compared with those of its methin, trimethin, and pentamethin analogues.[54] Treatment of glutaconic aldehyde with chlorine in methanol, followed by aniline and hydrochloric acid, gave 1-anilino-5-anilo-2-chloropenta-1,3-diene hydrochloride; the corresponding 2-bromo-hydrobromide and 2-iodo-hydriodide were also described.[19] Use of these salts gave the γ-chloro-, γ-bromo-, and γ-iodo-derivatives of the parent 2,2′-tricarbocyanine which, with its 5,6,5′,6′-dibenzo-derivative, was also made. The presence of halogen in the chain did not affect sensitising power.[20]

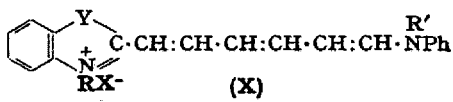
The 4,4′-tricarbocyanine, IX (R=Et, X=I), was prepared in 32 % yield by heating lepidine ethiodide and 1-anilino-5-anilopenta-1,3-diene with piperidine at 60°:[6] with acetic anhydride, instead of piperidine, the yield was only 5 %.[53] The dye was best prepared from lepidine ethiodide,



1-anilino-5-anilopenta-1,3-diene hydrochloride and piperidine in ethanol at a low temperature, the product being washed first with acetone and then with hot methanol until the filtrate was a clear green; it could be recrystallised from methanol. Its *NN′*-dimethyl and -diallyl analogues were similarly made, and their sensitising action to infrared light was patented.[10,11] The melting point, colour, and sensitising maximum of the *NN′*-diethyl dye were compared with those of the corresponding tri- and penta-methin analogues,[6,7] and its absorption maximum was compared with theirs and with that of the methin analogue.[54] The δ-methyl derivative of IX (R=Me, X=ClO_4) resulted on boiling lepidine methiodide with 1-anilino-5-anilo-3-methylpenta-1,3-diene hydrobromide and dimethylamine in ethanol, and treating with sodium perchlorate.[17] The infrared sensitiser xenocyanine is a 4,4′-tricarbocyanine.

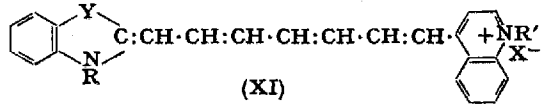
B. Thia-2′-, Thia-4′-, and Selena-4′-tricarbocyanines

The 6′-methyl derivative of the intermediate salt, X (Y=CH:CH·, R=Et, R′=Me, X=I), was prepared by heating *p*-toluquinaldine



ethiodide with the *NN'*-dimethyl derivative of 1-anilino-5-anilopenta-1,3-diene hydrobromide and sodium acetate in acetic anhydride; it was condensed with 2-methylbenzothiazole ethiodide by boiling with sodium ethoxide in ethanol to give the 6'-methyl derivative of the thia-2'-tricarbocyanine, VIII (Y=S, Z=CH:CH, R=R'=Et, X=I).[14]

The hydrobromide of 1-anilino-5-anilopenta-1,3-diene was condensed with 2-methylbenzothiazole ethiodide, by heating with piperidine in ethanol, to give the intermediate salt, X (Y=S, R=Et, R'=H, X=I);[13,14] its reaction with lepidine ethiodide and diethylamine in ethanol gave the thia-4'-tricarbocyanine, XI (Y=S, R=R'=Et, X=ClO_4).[14]



(XI)

An intermediate salt, X (Y=Se, R=Et, R'=Me, X=I), prepared by use of triethanolamine in ethanol[13,14] was condensed with lepidine ethiodide, by heating with triethylamine in ethanol, to give the selena-4'-tricarbocyanine, XI (Y=Se, R=R'=Et, X=I).[14]

C. Indotricarbocyanines

The indotricarbocyanine, VIII (Y=Z=CMe_2, R=R'=Me, X=I), was prepared in 24% yield by boiling 2,3,3-trimethylindolenine methiodide (2 mols.), 1-anilino-5-anilopenta-1,3-diene hydrochloride (1 mol.), and anhydrous sodium acetate (2 mols.) in acetic anhydride (30 c.c. per g. of methiodide) for 10 minutes, pouring the deep blue liquid into hot aqueous potassium iodide solution, and recrystallising the product (70% yield) twice from methanol.[1] In the earliest preparation of an indotricarbocyanine, 1,3,3-trimethyl-2-methyleneindoline (3·5 parts by weight), 5-anilo-1-methylanilinopenta-1,3-diene methochloride (1 part) and anhydrous sodium acetate (0·6 part) were warmed together at 60° for several hours, and the reaction mixture was poured into water. On the other hand, by heating equimolecular quantities of the base and methochloride in acetic anhydride, then pouring into water, the intermediate salt, X (Y=CMe_2, R=R'=Me, X=Cl), resulted.[3] In the third early independent discovery of an indotricarbocyanine, 1,3,3-trimethyl-2-methyleneindoline, 1-anilino-5-anilopenta-1,3-diene hydrochloride, and acetic anhydride were first heated at 100°

for 45 minutes, then boiled, and the reaction mixture was poured into water and treated with hydrochloric acid and potassium iodide; the photographic sensitising properties of the dye were noted.[4] A two-stage process, recorded as giving a 47 % yield of indotricarbocyanine, consisted first in heating together equimolecular amounts of 2,3,3-trimethylindolenine methiodide and 1-anilino-5-anilopenta-1,3-diene, then adding more methiodide (1 mol.), potassium acetate (4 mols.), and acetic anhydride (4 mols.) heating at 60° for 10 minutes, and crystallising the washed dye from butanol.[6,53] The melting point, colour, and sensitising maximum of the dye were compared with those of its tri- and penta-methin analogues.[7] The dye chloride has been called Indolenine Blue.[55]

D. Thia-, Oxa-, and Selena-tricarbocyanines

The first thiatricarbocyanine, VIII (Y=Z=S, R=R'=Et, X=I), was prepared in 41 % yield by boiling 2-methylbenzothiazole ethiodide (2 mols.) and 1-anilino-5-anilopenta-1,3-diene hydrochloride (1 mol.) in ethanol (10 c.c. per g. of ethiodide), adding a solution of sodium (2 atoms) in ethanol, and boiling and stirring for 2 minutes; the crystalline dye was washed with water and ether (49 % yield) and recrystallised from methanol (500 c.c. per g.). The *NN'*-dimethyl analogue of its chloride was similarly prepared in 34 % yield, and the 6,7,6',7'- and 4,5,4',5'-dibenzo-derivatives of both dyes were also made. In preparations of VIII (Y=Z=S, R=R'=Et, X=I), the hydrochloride of ArNH·CH:CH·CH:CH·CH:NAr, where Ar=Ph, was replaced by those where Ar=*p*-C_6H_4Me or 2-$C_{10}H_7$, and these gave yields of 44 % and 55 %, respectively.[1] As with pentamethincyanines (see VII-2-E), so also here, derivatives having 5,6,5',6'-substituents were claimed to be good sensitisers: 5,6,5',6'-tetramethoxy-, or -tetraethoxy-, 5,5'-dimethoxy-6,6'-di(methylthio)-, and 5,6,5',6'-bismethylenedioxy-derivatives of VIII (Y=Z=S, R=R'=Et, X=I) were described,[56] also its 5,6,5',6'-dibenzo-derivative;[57] condensing agents were pyridine, or else diethylamine or piperidine in ethanol; besides 1-anilino-5-anilopenta-1,3-diene hydrobromide, its *NN'*-dimethyl derivative was also used.[56,57] By heating 2-methylbenzothiazole ethiodide and 1-anilino-5-anilopenta-1,3-diene in acetic anhydride, a 40 % yield of thiatricarbocyanine resulted, but in piperidine the yield was only 14 %.[3,53] The 6,6'-dichloro-derivative of VIII (Y=Z=S, R=R'=Et, X=I) was prepared

in 36 % yield and the 6,6′-dibromo-derivative of the corresponding toluene-*p*-sulphonate in 42 % yield.[58] By application of the strong base method, a suspension of 2-methylbenzothiazole ethiodide in ethanol reacted with 1-anilino-5-anilopenta-1,3-diene hydrochloride and triethylamine in ethanol at 0° for 2 days; after washing with acetone and hot water, the yield of residual dye was 70 %.[10] A substance with 6,6′-difluoro-substituents showed similar absorption to that of the parent dye.[59] The melting point and sensitising maximum of VIII (Y=Z=S, R=R′=Et, X=I) were compared with those of its tri- and pentamethin analogues.[9] Its absorption maximum, and those of its 4,5,4′,5′- and 6,7,6′,7′-dibenzo-derivatives were compared with those of the corresponding methin-, trimethin-, and pentamethin compounds.[54]

Unsymmetrical thiatricarbocyanines with a 4,5-benzo- or 6,7-tetrahydrobenzo-substituent were made by condensing the intermediate salts, X (Y=S, R=Et, R′=H or Me, respectively, X=I), with the appropriately substituted 2-methylbenzothiazolium salts. The *δ*-methyl-5,6-benzo-derivative of VIII (Y=Z=S, R=R′=Et, X=I) was also described.[14] The sensitising power of VIII (Y=Z=S, R=R′=Et, X=I) was unaffected by introduction of a *γ*-chloro-, *γ*-bromo-, or *γ*-iodo-substituent, and similarly with a dibenzo-series (but whether 4,5,4′,5′- or 6,7,6′,7′-dibenzo- is not clear).[20] The *β*-methyl derivative of VIII (Y=Z=S, R=R′=Et, X=I), also the *δ*-methyl derivative of its 6,7,6′,7′-dibenzo-derivative, were patented in 1931.[17] The former was prepared by interaction at 0° during 3 days of a suspension of 2-methylbenzothiazole ethiodide (2 mols.), 1-anilino-5-anilo-1-methylpenta-1,3-diene hydrobromide (1 mol.) and piperidine (2·2 mols.) in ethanol (12 c.c. per g. of ethiodide). The washed dye (65 % yield) gave after two recrystallisations from methanol a 10 % yield. The *γ*- and *δ*-methyl analogues, also the 6,7,6′,7′-dibenzo-derivative of the latter, were prepared in yields of 16 %, 43 %, and 18 %, respectively, by use of the 2- and 3-methyl derivatives of 1-anilino-5-anilopenta-1,3-diene hydrobromide. By means of 1-anilino-5-anilo-1,5-dimethylpenta-1,3-diene hydrochloride, the *ββ*′-dimethyl derivative of VIII (Y=Z=S, R=R′=Et, X=I) was prepared in 10 % yield; its 5,6,5′,6′-tetramethoxy- and 6,7,6′,7′-dibenzo-derivatives were also made. Through crude 1-anilino-5-anilo-1,3-dimethylpenta-1,3-diene hydrobromide, a minute yield of the *ββ*′-dimethyl derivative of VIII (Y=Z=S, R=R′=Et, X=I) was isolated.[18]

To obtain the oxatricarbocyanine, VIII (Y=Z=O, R=R′=Et,

X=I), the first stage was reaction of equimolecular quantities of 2-methylbenzoxazole ethiodide and 1-anilino-5-anilopenta-1,3-diene hydrochloride, by heating them in acetic anhydride for 5 minutes. In the second stage, reaction of the washed intermediate salt, X (Y=O, R=Et, R'=Ac, X=I), and 2-methylbenzoxazole ethiodide was effected by heating with excess of triethylamine in ethanol for 5 minutes. The 6,7,6',7'-dibenzo-derivative of the dye was likewise prepared in two stages: excess of quaternary salt proved advantageous at the second one. By condensing the 6,7-benzo-derivative of the intermediate salt, X (Y=O, R=Et, R'=Ac, X=I), with excess of 2-methylbenzoxazole ethiodide, there resulted an unsymmetrical oxatricarbocyanine, the 6,7-benzo-derivative of VIII (Y=Z=O, R=R'=Et, X=I).[15]

The selenatricarbocyanines, VIII (Y=Z=Se, R=R'=Me or Et, X=I), were prepared in yields of 21 % and 34 %, respectively, by heating an ethanolic solution of 2-methylbenzoselenazole alkiodide with 1-anilino-5-anilopenta-1,3-diene hydrochloride and sodium ethoxide for 30 seconds, followed by thorough washing of the products.[1] The bromide of the latter was prepared by reaction of the diene hydrochloride, 2-methylbenzoselenazole ethotoluene-*p*-sulphonate, and piperidine in alcohol, first at 0° and then at room temperature for several hours, and treatment with potassium bromide[10,60] and its sensitising action was described.[61] Its absorption maximum was compared with those of its methin-, trimethin-, and pentamethin-analogues.[54] As with the thiatricarbocyanines, substituents in the 5,6,5',6'-positions were said to give improved sensitising: the 5,6,5',6'-bisethylenedioxy- and 5,6,5',6'-tetraethoxy-derivatives of VIII (Y=Z=Se, R=R'=Et, X=I) were prepared by use of the hydrobromide of 1-anilino-5-anilopenta-1,3-diene, and its *NN'*-dimethyl derivative, respectively, with diethylamine or trimethylamine in ethanol as condensing agent.[56]

The *ββ'*-dimethyl derivative of VIII (Y=Z=Se, R=R'=Et, X=I) was prepared in 18 % yield by prolonged reaction of 2-methylbenzoselenazole ethiodide, 1-anilino-5-anilo-1,5-dimethylpenta-1,3-diene hydrochloride, and piperidine in ethanol. The *γ*- and *δ*-methyl derivatives were similarly prepared, by means of the appropriate diene hydrobromides.[18]

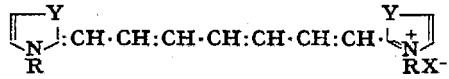
E. Selenathiatricarbocyanines

Condensation of the intermediate salt, X (Y=S, R=Et, R'=H, X=I), with 2,5,6-trimethylbenzoselenazole ethiodide gave the 5,6-di-

methyl derivative of the selenathiatricarbocyanine, VIII (Y=Se, Z=S, R=R'=Et, X=I). Its 5'-diethylamino-5-methoxy-derivative was also described.[14]

F. 2,2'-Pyridotricarbocyanines

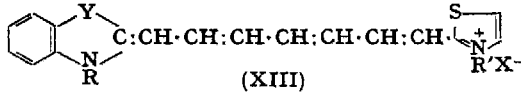
The 2,2'-pyridotricarbocyanine, XII (Y=CH:CH, R=Et, X=I), resulted in 5 % yield when 2-picoline ethiodide and 1-anilino-5-anilopenta-1,3-diene were heated with piperidine, whereas on heating with acetic anhydride the result was negative.[53] Its melting point was below those of its trimethin and pentamethin analogues.[9]



(XII)

G. Thiathiazolo- and Selenathiazolo-tricarbocyanines

By interaction of 2,5,6-trimethylbenzothiazole ethiodide, the *NN'*-dimethyl derivative of 1-anilino-5-anilopenta-1,3-diene hydrobromide, and triethanolamine in ethanol, there resulted the 5,6-dimethyl derivative of the intermediate salt, X (Y=S, R=Et, R'=Me, X=I);[13,14] condensation of this with 2,4-dimethylthiazole ethiodide and diethylamine in alcohol gave the 4',5,6-trimethyl derivative of the thiathiazolotricarbocyanine, XIII (Y=S, R=R'=Et, X=I).[14]



(XIII)

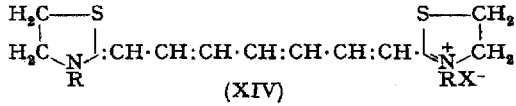
The intermediate salt, X (Y=Se, R=Et, R'=H, X=I), was similarly condensed with 2,4-dimethylthiazole ethiodide, to give the 4'-methyl derivative of the selenathiazolotricarbocyanine, XIII (Y=Se, R=R'=Et, X=I).[14]

H. Thiazolo- and Thiazolino-tricarbocyanines

The thiazolotricarbocyanine, XII (Y=S, R=Me, X=I), resulted in 10 % yield when 2-methylthiazole methiodide and 1-anilino-5-anilopenta-1,3-diene were heated with piperidine; its 4,4'-dimethyl derivative was similarly obtained in 27 % yield, but in neither instance was

condensation effected by heating with acetic anhydride.[8, 53] The melting points and sensitising maxima of both compounds were compared with those of their tri- and penta-methin analogues.[9] The sensitising action of thiazolotricarbocyanines was patented,[61] piperidine being used in their preparation.[10]

The thiazolinotricarbocyanines, XIV (R=Me or Et, X=I), were prepared in yields of 14 % and 26 %, respectively, by boiling an alcoholic solution of 2-methylthiazoline alkiodide, 1-anilino-5-anilopenta-1,3-diene hydrochloride, and sodium ethoxide for 1·5 minutes, and recrystallising the washed product from methanol.[1] By the strong base



(XIV)

method, the diene hydrochloride and 2-methylthiazoline ethotoluene-*p*-sulphonate reacted for some hours with piperidine in ethanol, after which the washed dye was converted into iodide.[10, 62] The sensitising properties of thiazolinotricarbocyanines were described[12] and patented.[61]

3. From a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, by Use of a Pyridinium Salt

A. 2,2′- and 4,4′-Tricarbocyanines

The 2,2′-tricarbocyanine, VIII (Y=Z=CH:CH, R=R′=Et, X=I), was prepared in 4 % yield by treating a solution of 2,4-dinitrophenylpyridinium chloride (1 mol.) in hot ethanol (10 c.c. per g.) with a solution of sodium (2 atoms) in ethanol, and then with a hot solution of quinaldine ethiodide (2 mols.) in ethanol (20 c.c. per g.), and allowing to cool; the product was repeatedly washed with acetone and hot ethanol and was recrystallised from methanol.[1] The same compound was prepared by boiling quinaldine ethiodide, 2-chlorobenzoxazole, and excess of pyridine in ethanol for 15 minutes, then treating with a cold solution of sodium in ethanol.[23]

The 4,4′-tricarbocyanine, IX (R=Me, X=I), was prepared by adding a cold solution of sodium in methanol to one containing lepidine methiodide and I, followed by treatment with water.[23]

B. Indotricarbocyanines

The indotricarbocyanine, VIII (Y=Z=CMe_2, R=R'=Me, X=Cl), was prepared by heating 2,4-dinitrophenylpyridinium chloride (1 mol.) with 1,3,3-trimethyl-2-methyleneindoline (2 mols.) in pyridine at 100°, pouring into water, filtering off tar, and salting out. By heating equimolecular quantities of the two reactants in acetic anhydride, there was obtained a derivative of the intermediate salt, X (Y=CMe_2, R=Me, R'=H, X=Cl), in which the phenyl group carried 2,4-dinitro-substituents.[3] The dye, VIII (Y=Z=CMe_2, R=R'=Me, X=I), was prepared by heating 2,3,3-trimethylindolenine methiodide with I and sodium acetate in acetic anhydride.[23]

C. Thia- and Selena-tricarbocyanines

The thiatricarbocyanine, VIII (Y=Z=S, R=R'=Et, X=I), was prepared in 26 % yield by treating 2,4-dinitrophenylpyridinium chloride (1 mol.) in ethanol with a solution of sodium (2 atoms) in ethanol, adding 2-methylbenzothiazole ethiodide (2 mols.) and boiling for 10 minutes; the crystalline dye was washed with water, then ether, and then acetone until the extract was pure blue.[1] It was also prepared by the action of sodium ethoxide, in the cold, on an alcoholic solution of 2-methylbenzothiazole ethiodide and I; the bromide of its *NN'*-diallyl analogue was made by use of the same pyridinium salt.[23] By another modification of the method, VIII (Y=Z=S, R=R'=Et, X=I), was prepared by treating a hot ethanolic solution of the hydrochloride of II with one of sodium, adding 2-methylbenzothiazole ethiodide, and boiling for 1 hour.[24] By yet another modification, it was made by heating 2-methylbenzothiazole ethotoluene-*p*-sulphonate (2 mols.) and finely powdered 2-iodoquinoline ethiodide (1 mol.) in pyridine at 100° for 1·5 minutes, then treating with water. Its 6,7,6',7'-dibenzo-derivative was similarly made from the appropriate benzothiazolium salt and 2-iodopyridine ethiodide in pyridine. From 2-ethylbenzothiazole ethiodide and 2-iodopyridine ethiodide in pyridine, there was prepared the $\alpha\alpha'$-dimethyl derivative of VIII (Y=Z=S, R=R'=Et, X=I).[26] The intermediate salt, IV, was produced by reaction of 2-iodoquinoline ethiodide with a large excess of cold pyridine for 12–24 hours, and could be rapidly recrystallised from water.[25]

The selenatricarbocyanine, VIII (Y=Z=Se, R=R'=Et, X=I), was made by heating 2-methylbenzoselenazole ethiodide and 2-iodo-

pyridine ethiodide with excess of pyridine for 1·5 minutes, then adding iced water.[28]

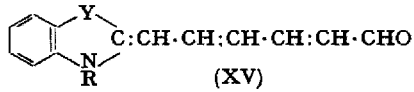
D. Thiazolinotricarbocyanines

The thiazolinotricarbocyanine, XIV (R=Me, X=I), was prepared by reaction of 2-methylthiazoline methotoluene-*p*-sulphonate, 2-iodopyridine ethiodide, and pyridine at room temperature for 5 days; it was isolated by treatment with water, and was recrystallised from methanol.[26]

4. Symmetrical and Unsymmetrical Tricarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, or from the Corresponding Methylene Base, by Condensation with a Heterocyclic Pentamethin Aldehyde

A. Thia-2′-tricarbocyanines

The 6-methyl derivative of the aldehyde, XV (Y=CH:CH, R=Et), was prepared from the 6-methyl derivative of X (Y=CH:CH, R=Et, R′=Me) by boiling with potassium hydroxide in methanol until the



(XV)

blue colour had changed to violet-red.[30] Its condensation with 2-methyl-4,5-benzobenzothiazole ethiodide was effected by boiling with acetic anhydride, and it yielded the 4,5-benzo-6′-methyl derivative of the thia-2′-tricarbocyanine, VIII (Y=S, Z=CH:CH, R=R′=Et, X=I).[29]

B. Thiatricarbocyanines

The aldehyde, XV (Y=S, R=Et), was prepared from X (Y=S, R=Et, R′=Me) in methanol by heating with an aqueous solution of potassium carbonate, and gave orange-red prisms, m.p. 158°.[30] Its condensation with 2-methylbenzothiazole ethiodide, by boiling them in acetic anhydride, gave the thiatricarbocyanine, VIII (Y=Z=S, R=R′=Et, X=I). Its 4,5-benzo-5′-methoxy-derivative was also made.[29]

C. Indoselena-, Indothia-, and Selenathia-tricarbocyanines

The aldehyde, XV (Y=Se, R=Et), was prepared from X (Y=Se, R=Et, R′=Me) by dissolving in methanol and heating with a solution

of sodium in ethanol.[30] It was boiled in acetic anhydride with 1,3,3,5-tetramethyl-2-methyleneindoline, then treated with sodium perchlorate solution, to give the 5-methyl derivative of the indoselenatricarbocyanine, VIII (Y=CMe_2, Z=Se, R=Me, R′=Et, X=ClO_4).[29]

The 5-methoxy-derivative of the indothiatricarbocyanine, VIII (Y=CMe_2, Z=S, R=Me, R′=Et, X=I), was similarly prepared from XV (Y=S, R=Et), and 5-methoxy-1,3,3-trimethyl-2-methyleneindoline in acetic anhydride.[29]

By boiling the aldehyde, XV (Y=Se, R=Et), with 6-acetylamino-2-methylbenzothiazole ethiodide in acetic anhydride, the 6-acetylamino-derivative of the selenathiatricarbocyanine, VIII (Y=Se, Z=S, R=R′=Et, X=I), resulted. In making the 5-methoxy-6′-methyl derivative of the parent dye, the condensing agent was diethylamine in ethanol.[29]

5. Symmetrical δ-Alkyltricarbocyanines from a Quaternary Salt, Having a Reactive Methyl Group, and an Aldehyde HC:C·CR:CH·CHO

A. Indotricarbocyanine

The aldehyde, HC:C·CMe:CH·CHO, was prepared by reaction of acetylene with methyl β-chlorovinyl ketone, and treatment of the product with dilute acid. To make the δ-methyl derivative of the indotricarbocyanine, VIII (Y=Z=CMe_2, R=R′=Et, X=I), an ethanolic solution of 2,3,3-trimethylindolenine ethiodide was cooled below 0°, treated with the aldehyde and triethylamine, and the mixture kept for 24 hours; the dye was crystallised from acetic acid.[31]

B. Thiatricarbocyanines

The δ-methyl derivative of the thiatricarbocyanine, VIII (Y=Z=S, R=R′=Et, X=I), was similarly synthesised from the aldehyde with 2-methylbenzothiazole ethiodide.[31]

6. Unsymmetrical δ-Alkoxytricarbocyanine from a Quaternary Salt, Having a β-(Alkylthio)vinyl Group, and a Salt Having the Group ·CH:CH·CH:CMe (OR)

A. Indothiatricarbocyanine

The δ-ethoxy-derivative of the indothiatricarbocyanine, VIII (Y=CMe_2, Z=S, R=R′=Me, X=I), was prepared by heating 2-(4-

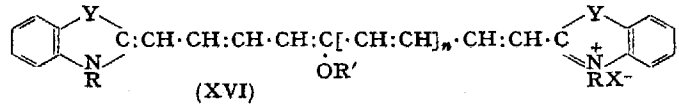
ethoxypenta-1,3-dienyl)benzothiazole methochloride and 2-β-ethylthiovinyl-3,3-dimethylindolenine methiodide with triethylamine in ethanol for 15 minutes, and treating with potassium iodide.[35]

7. ε-Acyloxy-Hepta-, -Nona-, and -Undeca-methincyanines, from a Quaternary Salt, Having a Reactive Methyl Group, with

$$R^1R^2N\cdot CH:CH\cdot CH:\underset{\displaystyle OR'}{C}[\cdot CH:CH]\cdot_{0-2}CH:\overset{+}{N}R^1R^2X^-$$

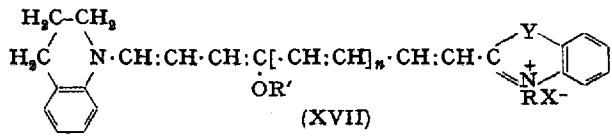
A. 2,2′- and 4,4′-Tetra- and -Penta-carbocyanines

The ε-acetoxy-2,2′-tetracarbocyanine, XVI (Y=CH:CH, n=1, R=Et, R′=Ac, X=ClO_4), was a good sensitiser.[43]



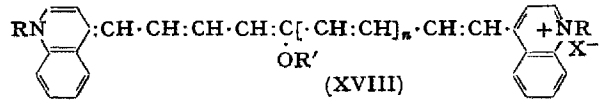
(XVI)

The ε-acetoxy-2,2′-pentacarbocyanine, XVI (Y=CH:CH, n=2, R=Me, R′=Ac, X=ClO_4), was prepared in two stages. In the first, V (n=2, R′=Ac, X=ClO_4) was condensed with quinaldine methomethylsulphate, to give XVII (Y=CH:CH, n=2, R=Me, R′=Ac, X=ClO_4);



(XVII)

the second step consisted in the reaction of this salt with quinaldine methomethylsulphate and diethylamine in pyridine, followed by treatment with alcohol.[41] The dye was a weaker sensitiser than the 4,5,4′,5′- and 6,7,6′,7′-dibenzo-derivatives of the corresponding thiapentacarbocyanine.[43]

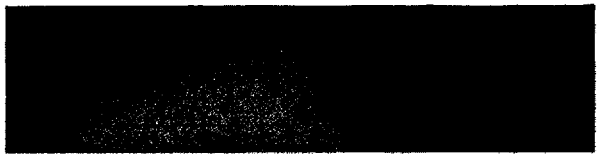


(XVIII)

The ε-acetoxy-4,4′-tetracarbocyanine, XVIII (n=1, R=Me, R′=Ac, X=ClO_4), was prepared by condensing V (n=1, R′=Ac, X=ClO_4) with lepidine methomethylsulphate by use of diethylamine in pyridine, followed by alcohol.[41]



A.



B.



C.



D.

Fig. 1. Spectrograms showing sensitising action of some polymethincyanines. (A). A. Thiaheptamethincyanine; B. Dibenzothiaheptamethincyanine; C. 4,4'-Heptamethincyanine. (B). D. ε-Acetoxythianonamethincyanine.



E.



F.



G.



H.

Fig. 1. E. ε-Acetoxy-4,5,4′,5′,-dibenzothianonamethincyanine; F. ε-Acetoxy-2,2′-nonamethincyanine; G. ε-Acetoxythia-undecamethincyanine; H. ε-Acetoxy-4,5,4′,5′,-dibenzothia-undecamethincyanine. [(A) from Brooker, Hamer, and Mees.[12] (B) from Brooker and Keyes.[43] By courtesy of the authors, the Royal Photographic Society, and the Optical Society of America]

B. Indotetracarbocyanine

The heptamethin compound, V (n=1, R′=Ac, X=Cl), was condensed with 2,3,3-trimethylindolenine methiodide in pyridine to give the ε-acetoxyindotetracarbocyanine, XVI (Y=CMe_2, n=1, R=Me, R′=Ac, X=Cl).[41]

C. Thia-tri-, -tetra-, and -penta-carbocyanines, and Selenatetracarbocyanine

Reaction of furfuraldehyde, methylaniline, and perchloric acid gave a hydroxypentamethin compound (cf. equation 12, n=0), which was acetylated by acetic anhydride at 80°, or by acetyl chloride in pyridine. The acetoxy-compound reacted with 2-methyl-6-phenylbenzothiazole methomethylsulphate in pyridine at room temperature during 30 minutes: treatment with ethanol then gave the 6,6′-diphenyl derivative of ε-acetoxythiatricarbocyanine, XVI (Y=S, n=0, R=Me, R_6=Ac, X=ClO_4). A dye which also contained 4,4′-dichloro-groups was made as well.[41]

The hydroxyheptamethin compound obtained by reaction of β-furylacraldehyde, methylaniline, and hydrochloric acid[39] (cf. equation 12, n=1) was acetylated with acetyl chloride in cooled pyridine. Its condensation with 2-methyl-6-phenylbenzothiazole methomethylsulphate gave the 6,6′-diphenyl derivative of the ε-acetoxythiatetracarbocyanine, XVI (Y=S, n=1, R=Me, R′=Ac, X=Cl). The corresponding ε-benzoxythiatetracarbocyanine was prepared by use of V (n=1, R′=COPh, X=Cl), which was made by treating V (n=1, R′=H, X=Cl) with benzoyl chloride in cold pyridine. Acylation of V (n=1, R′=H, X=ClO_4) with butyric anhydride in pyridine gave V (n=1, R′=COPr, X=ClO_4), which was condensed with 2-methylbenzothiazole ethoethylsulphate in pyridine to give XVI (Y=S, n=1, R=Et, R′=COPr, X=ClO_4).[41] The sensitising curves of XVI (Y=S, n=1, R=Et, R′=Ac, X=ClO_4) and its 4,5,4′,5′- and 6,7,6′,7′-dibenzo-derivatives were compared.[43] By use of V (n=1, R′=Ac, X=ClO_4), the 5,6,5′,6′-tetramethoxy-derivative of XVI (Y=S, n=1, R=Et, R′=Ac, X=ClO_4) was made. The heptamethin salt, V (n=1, R′=Ac, X=ClO_4), also reacted with 2-methyl-6,7-benzobenzothiazole ethoethylsulphate in pyridine and, after 1 hour, treatment with ethanol gave the 6,7-benzo-derivative of the intermediate octamethin salt, XVII (Y=S, n=1, X=ClO_4). Reaction of this salt with 6-ethoxy-2-methylbenzothiazole ethoperchlorate in pyridine gave the unsymmetri-

cal 6,7-benzo-6'-ethoxy-derivative of the ε-acetoxythiatetracarbocyanine, XVI (Y=S, n=1, R=Et, R'=Ac, X=ClO_4).[41]

The hydroxynonamethin compound, V (n=2, R'=H, X=ClO_4), prepared from 5-(2-furyl)penta-2,4-diene-1-al, 1,2,3,4-tetrahydroquinoline, and perchloric acid in cooled acetone, was acetylated with acetic anhydride in pyridine under cooling, and V (n=2, R'=Ac, X=ClO_4) was precipitated with ether. It reacted at the ordinary temperature with 2-methyl-6-phenylbenzothiazole methomethylsulphate in pyridine, to give the 6,6'-diphenyl derivative of the ε-acetoxythiapentacarbocyanine, XVI (Y=S, n=2, R=Me, R'=Ac, X=ClO_4).[41] Wedge spectrograms showing the sensitising action of the dye XVI (Y=S, n=2, R=Et, R'=Ac, X=ClO_4) and its 4,5,4',5'- and 6,7,6',7'-dibenzo-derivatives were published.[43] (See Fig. 1.) Its 5,6,5',6'-tetraethoxyderivative was made in two stages. The first consisted in the reaction of V (n=2, R'=Ac, X=ClO_4) with 5,6-diethoxy-2-methylbenzothiazole ethoethylsulphate in pyridine for 2–3 hours: alcohol precipitated the 5,6-diethoxy-derivative of XVII (Y=S, n=2, R'=Ac, X=ClO_4); this was at once warmed with more of the benzothiazolium salt in pyridine, cooled, and treated with triethanolamine and finally with alcohol.[41]

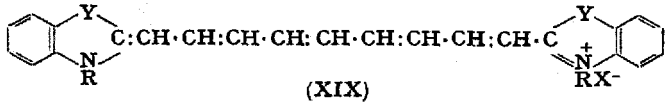
Reaction of 4-acetoxy-7-anilo-1-methylanilino-hepta-1,3,5-triene methoperchlorate with 2,5-dimethylbenzoselenazole methobromide led to the ε-acetoxyselenatetracarbocyanine, XVI (Y=Se, n=1, R=Me, R'=Ac, X=ClO_4).[41]

8. Nonamethincyanines from a Quaternary Salt, Having a Reactive Methyl Group, and a Heptamethin Salt

$$R^1R^2N\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}\overset{+}{N}R^1R^2X^-$$

A. Thia- and Selena-tetracarbocyanines

By heating together the heptamethin salt (where X=Br, $\cdot NR^1R^2$ =tetrahydroquinolyl) (see section 1), 2-methylbenzothiazole ethiodide, sodium acetate, and pyridine in methanol, followed by diethylamine, there resulted the thiatetracarbocyanine, XIX (Y=S, R=Et, X=I).



(XIX)

Its 5,6,5′,6′-tetramethyl derivative was similarly made. For making its 5,6,5′,6′-tetramethoxy-derivative, a different heptamethin salt (where X=Br, $\cdot NR^1R^2 = \cdot NMePh$) was used.[46]

The selenatetracarbocyanine, XIX (Y=Se, R=Et, X=I), was prepared in the same way as its thia-analogue.[46]

TABLE I. Some Properties of Some Symmetrical Tricarbocyanines (Formulae VIII, IX, XII, XIV; R=R′=Et, X=I)

Compound	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
VIII; Y=Z=CH:CH (2,2′-)	Bronze	219	8100	8600	—	1, 7
IX; Y=Z=CH:CH (4,4′-)	Coppery	165	9320	9800 (and 8600)	10500	7, 54, 61
VIII; Y=Z=CMe_2 (indo-)	Bright green	207	7400	7800	—	1, 7[a]
VIII; Y=Z=O (oxa-)	Blue-grey	175–177	—	7350	8300	15
VIII; Y=Z=S (thia-)	Green	211	7650	8100	8700	1, 12
VIII; Y=Z=Se (selena-)	Brilliant green	225	7700	8250	8800	1, 61
XII; Y=CH:CH (pyrido-)	—	155	—	—	—	9[a]
XII; Y=S (thiazolo-)	Green and blue needles	174	—	7900	8570	9, 10, 61[b,c]
XIV; Y=S (thiazolino-)	Steely	192	6450	7100	7600	1, 61

[a] *NN′*-dimethyl compound. [b] M.p. for *NN′*-dimethyl analogue.
[c] Sensitising for 4,4′-dimethyl derivative of *NN′*-dimethyl bromide.

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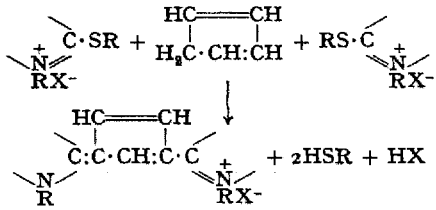
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CHAPTER IX

Cyanines in which the Odd-Numbered Carbon Chain, which Links the Nuclei, or Part of it, is Cyclic

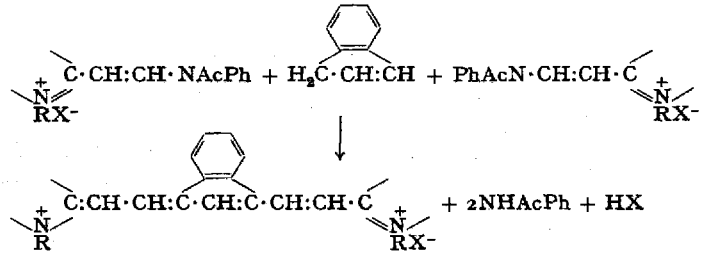
1. General Survey

Carbocyanines in which the trimethin chain formed part of a five-membered carbocyclic system were first recorded in 1933, being described as photographic sensitisers (see Table I). They were prepared by reaction of a heterocyclic quaternary salt, having an alkylthio-group, with cyclopentadiene (equation 1).[1] Instead of cyclopentadiene,



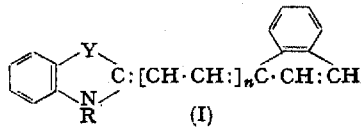
(1)

indene could be used, giving an $\alpha\alpha'$-*o*-phenylene- in place of an $\alpha\alpha'$-dimethin-substitution on the chain.[1] Five years later, it was recorded that quaternary salts having a β-acetanilidovinyl group also condensed with indene, giving heptamethincyanines with a $\gamma\gamma'$-*o*-phenylene group attached to the chain (equation 2).[2] With a strong base as condensing

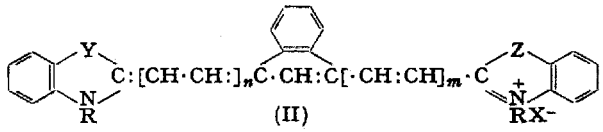


(2)

agent, it was possible to effect reaction between equimolecular amounts of indene and a quaternary salt, having either an alkylthio- or a β-acetanilidovinyl group, to give an intermediate compound, I (n=0 or 1, respectively). This could be condensed with another molecule of salt, having a similar type of reactive group or a halogeno-substituent, to give symmetrical or unsymmetrical polymethincyanines, II (n=0 or 1,



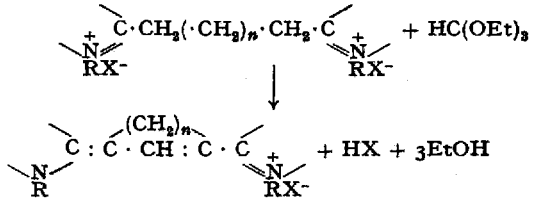
(I)



(II)

m=0 or 1), with an *o*-phenylene group on the chain; representatives of tri-, penta-, and hepta-methincyanines were described (see section 2).[3]

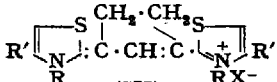
Trimethincyanines of the benzoxazole and benzothiazole series, in which the chain was made cyclic by the inclusion of one, two, or three methylene groups, with αγ-linkings, were first described in 1935 (see section 3). They were prepared by the action of ethyl orthoformate or diphenylformamidine on diquaternary salts in which two heterocyclic nuclei were linked by a polymethylene chain (equation 3; n=1,



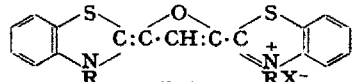
(3)

2, or 3),[4] which might carry a substituent; the αγ-carbon atoms might even be directly linked (equation 3, n=0).[5] The bases themselves were prepared by distillation of *o*-amino-phenol or -thiophenol, with a dibasic saturated aliphatic acid. In 1950, absorption data were given for six pairs of thiacarbocyanines, having one, two, three, four, five, or six methylene groups linked in the αγ-positions, and with *NN'*-dialkyl or *NN'*-diphenyl, respectively,[6,7] which dyes had been described in 1948.[8]

Data were also given for four thiacarbocyanines with a *meso*-alkyl substituent, in addition to an $\alpha\gamma$-dimethylene group: these were prepared by reaction of ethyl orthoacetate or orthopropionate with diquaternary salts of 1,4-di-(2-benzothiazolyl)-propane or -butane.[9] An intense blue colour developed on heating diquaternary salts of 1,4-di-(2-thiazolyl)butane with ethyl orthoformate in pyridine or acetic anhydride, indicating the formation of dyes, III, which were too unstable to isolate. The absorption maximum of III (R=Et, R′=Me) lay at a longer wavelength by 390 Å than that of the parent dye in which the trimethin chain was not part of a ring. This approximated to the value in the thiacarbocyanine series (see Table I); the instability



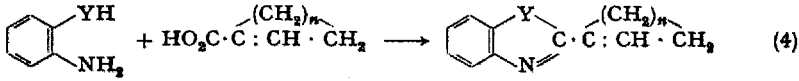
(III)



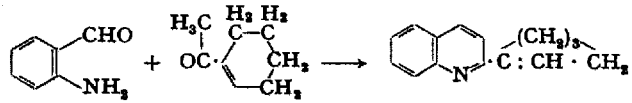
(IV)

of thiazolocarbocyanines, III, with a cyclised chain, as contrasted with the stability of the corresponding thiacarbocyanines, was attributed to lack of co-planarity of the three rings in III.[10] In 1952, *o*-aminothiophenol was condensed with diglycollyl chloride to give bases having two benzothiazole nuclei linked by the chain $\cdot CH_2 \cdot O \cdot CH_2$. Reaction of ethyl orthoformate with their diquaternary salts gave thiacarbocyanines, IV, in which oxygen was linked in the $\alpha\gamma$-positions.[11]

By a different method of approach (see section 4), in 1941, intermediate bases of the benzoxazole, benzothiazole, and benzoselenazole series were synthesised by reaction of *o*-aminophenol, and its sulphur and selenium analogues, with a 1-cyclopent(or cyclohex)ene-1-carboxylic acid (equation 4).[12] A salt of 2-(1-cyclohexenyl)quinoline was also made (equation 5).[13] Quaternary salts of these bases were condensed with other salts having an alkylthio- or β-acetanilidovinyl



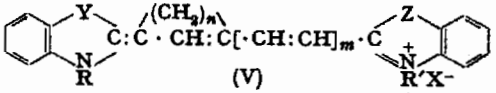
(4)



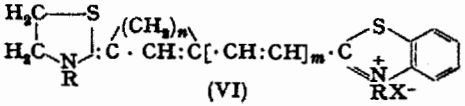
(5)

group, to give tri- and penta-methincyanines, V (n=1 or 2, m=0 or 1), in which the chain carried an $\alpha\gamma$-dimethylene or $\alpha\gamma$-trimethylene

group;[12] condensation with a salt having a 2-β-ethylthiovinyl group was also effected.[13] Similar intermediate bases of the thiazoline series were synthesised by heating β-amino-alcohols with a 1-cyclopent(or

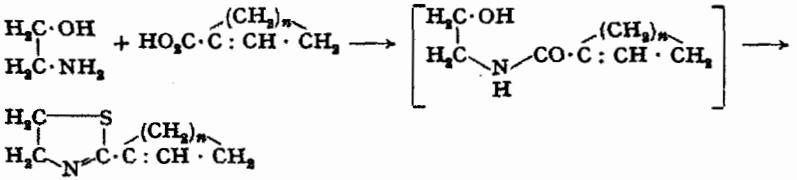


(V)



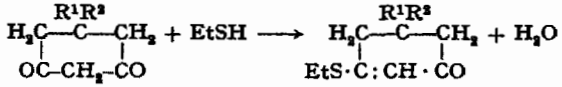
(VI)

cyclohex)ene-1-carboxylic acid, followed by treatment with phosphorus pentasulphide (equation 6). Through their salts, thiathiazolino-carbocyanines and -dicarbocyanines, VI (n=1 or 2, m=0 or 1), were prepared.[14]

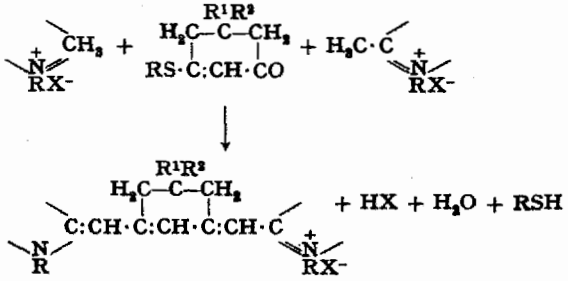


(6)

A third method of synthesising cyanines having a trimethylene group attached to the chain (see section 5) was through substituted 3-alkylthio-2-cyclohexen-1-ones, which were prepared from cyclohexan-1,3-diones by the action of ethyl mercaptan and a strong acid (equation 7).[15] Such hexenones were used in two ways. In the first place, they

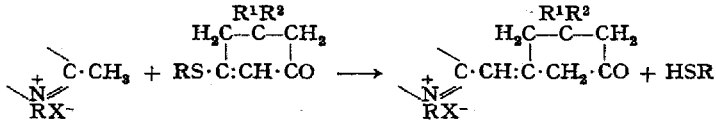


(7)



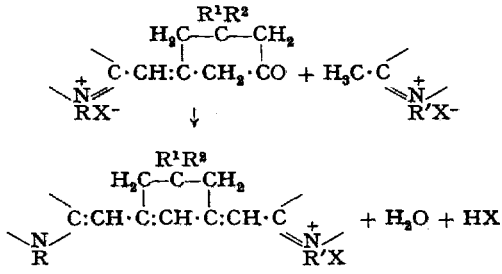
(8)

were condensed with quaternary salts, having a reactive methyl group, to give symmetrical pentamethincyanines, of the benzothiazole and benzoselenazole series, with $\beta\beta'$-trimethylene on the chain (equation 8).[16] Secondly, the hexenone was condensed with a quaternary salt, having a reactive methyl group, to give an intermediate salt (equation 9),[17]



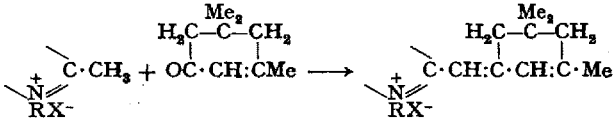
(9)

which was not isolated but was made to condense with another quaternary salt, having a reactive methyl group, to give unsymmetrical pentamethincyanines (equation 10).[18]



(10)

A different type of intermediate salt was reached by condensation of a quaternary salt, having a reactive methyl group, with a ketone, RCOMe, e.g., 3,5,5-trimethyl-2-cyclohexen-1-one (equation 11).[19] Re-

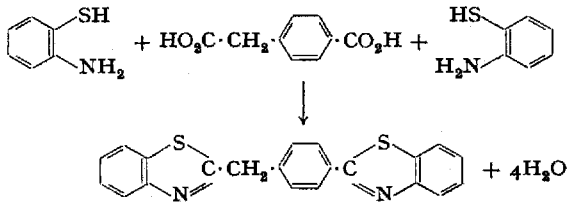


(11)

action of such a salt with another, having the group $(\cdot CH:CH)_{1-3}\cdot NAcPh$, led to hepta-, nona-, and undeca-methincyanines, in each of which three members of the chain were cyclic. Such a salt was also used to synthesise a symmetrical undecamethincyanine in which the chain comprised two carbocyclic rings (see section 6).[20]

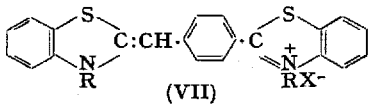
Pentamethincyanines, of the benzothiazole series, in which the chain formed part of a benzene ring, were in 1944 independently synthesised in two countries (section 7).[21,22] A di-(benzothiazolyl) base

was reached by the action of homoterephthalic acid[22] (equation 12) or chloride[21] on *o*-aminothiophenol. Elimination of acid from its di-quaternary salts gave an $\alpha\delta$-vinylenethiadicarbocyanine, VII. The absorption maximum lay at a shorter wavelength than that of the dye with an unsubstituted chain.[21,22] A base analogous to that of equation 12, but with the benzene nucleus linked through *o*- instead of *p*-positions, was synthesised but would not give a diquaternary salt.

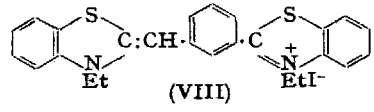


(12)

The diethiodide of a base in which the benzene nucleus was linked through *m*-positions gave VIII, which is not a cyanine. Its absorption maximum lay at a shorter wavelength by 1600 Å than that of VII (R=Et, X=I).[22]



(VII)

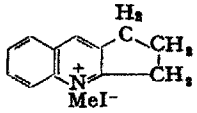


(VIII)

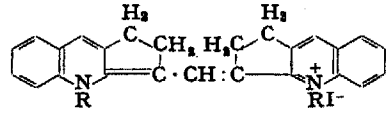
According to a publication of 1937, heterocyclic bases having a 2-β-iodoethyl group isomerised to quaternary iodides with a new ring, comprising a 2,3-dimethylene group, whence cyanines, in which nitrogen was linked to the α-position of the carbon chain by methylene, were obtainable.[23] Two years later, salts with a 2,3-tri- or 2,3-tetra-methylene group, giving rise to cyanines with nitrogen linked to the α-position by a di- or tri-methylene chain, were described. The salts were said to be obtained from a quaternary heterocyclic base, having a reactive methyl group, and a dihalogenoalkane, such as Br $(CH_2)_n$ Br (where n=2 or 3).[24] The formulae of the salts were omitted from the British complete patent specifications;[25] in the American patent, which was not published until 1952, the salts were formulated as diquaternary with an *NN'*-di- or NN'-tri-methylene chain[26] instead of being cyclic through the α-carbon to nitrogen atoms (see X-4-B).

In 1948 the condensation of dihydro-β-quinindene methiodide, IX, with 2-iodoquinoline methiodide was described, but the resultant dye

was unstable. On the other hand the salt condensed with ethyl orthoformate under special conditions to give a stable trimethincyanine, X

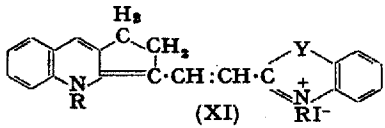


(IX)

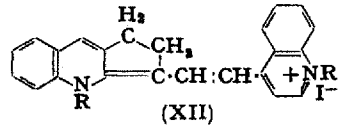


(X)

(R=Me), in which the $\alpha\alpha'$-carbon atoms of the chain formed part of homocyclic rings; the ethiodide gave X (R=Et). By heating the methiodide and 2-β-anilinovinylquinoline methiodide in acetic anhydride containing sodium acetate and pyridine there was prepared, XI (Y=CH:CH, R=Me), and its diethyl analogue was made similarly. The two analogues, XII (R=Me or Et), were likewise prepared. 2-β-Acetanilidovinylbenzoxazole methiodide and IX were condensed to



(XI)

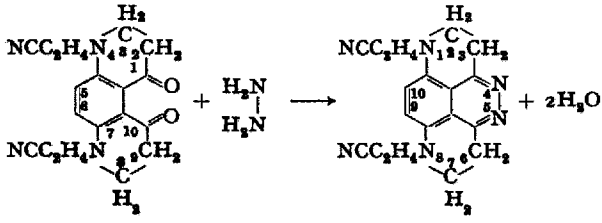


(XII)

give XI (Y=O, R=Me) and its diethyl analogue; XI (Y=S, R=Me or Et) and XI (Y=CMe_2, R=Me) were also prepared (see section 8).[27] The theory that quinaldine methiodide participated in dye condensations by initial formation of a methylene base[28] was inapplicable to dihydro-β-quinindene methiodide.[29]

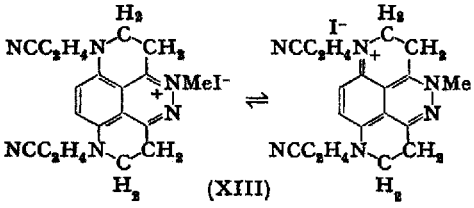
Certain cyanines with an indole or a pyrrole nucleus linked through the 3-position to another heterocyclic nucleus are considered in the next chapter (X-5-A), instead of here.

In 1953 the red 4,7-phenanthroline derivative (equation 13) was condensed with hydrazine to give the corresponding yellow hexahydrotetra-azapyrene. Because its methiodide was deep purple, it was

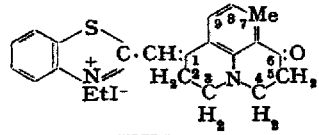


(13)

concluded that the nitrogen atom in position 4 had become quaternary and the salt, XIII, was regarded as an entirely new type of cyanine dye.[30] A little later it was found that 7-methyl-1,6-dioxojulolidine could be condensed in boiling pyridine with one molecule of 2-methylbenzothiazole ethiodide, to give XIV[31,32] but not with two molecules; this



(XIII)



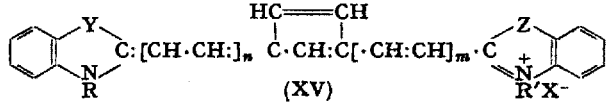
(XIV)

structure was adopted because no steric hindrance occurs at the 1-oxo-group. The cyanine showed moderate sensitising.[31] Other types of dye were also prepared (see XIII-4-E and F, and XIV-13-B). Steric hindrance prevented the condensation of 7,9-dimethyl-1,6-dioxojulolidine with 2-methylbenzothiazole ethiodide.[32]

2. Tri-, Penta-, and Hepta-methincyanines Having a Dimethin or an *o*-Phenylene Group with $\alpha\gamma$-Linkings to the Chain, by Reaction of Cyclopentadiene or Indene with a Quaternary Salt Having one of the Groups ·SR or ·CH:CH·NR¹R²

A. 2,2′-Carbocyanines

The 2,2′-carbocyanines, XV (Y=Z=CH:CH, $n=m=0$, R=R′=Me or Et, X=Br), were prepared by heating 1-methyl- or 1-ethyl-2-thiodihydroquinoline with ethyl toluene-*p*-sulphonate, followed by



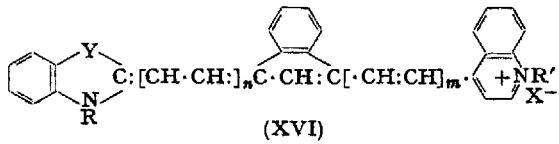
(XV)

cyclopentadiene and pyridine, and treatment with potassium bromide. The corresponding dyes, II (Y=Z=CH:CH, R=R′=Me, X=Br), were prepared by use of indene instead of cyclopentadiene.[1]

B. Indo-4′-tricarbocyanine and Thia-4′-dicarbocyanine

Reaction of 4-β-acetanilidovinylquinoline methotoluene-*p*-sulphonate with indene, pyridine, and diethylamine, led to the 4-linked

quinoline analogue of I (R=Me). Its condensation with 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide gave the indo-4′-tricarbocyanine, XVI (Y=CMe_2, n=m=1, R=R′=Me, X=I).[3]



(XVI)

Reaction of I (Y=S, n=1, R=Me) with 4-iodoquinoline methiodide, by heating with potassium carbonate in alcohol, gave the thia-4′-dicarbocyanine, XVI (Y=S, n=1, m=0, R=R′=Me, X=I).[3]

C. Thia-, Thiadi-, Thiatri-, Oxa-, and Oxatri-carbocyanines

The thiacarbocyanine, XV (Y=Z=S, n=m=0, R=R′=Me, X=Br), was prepared by heating 2-methylthiobenzothiazole methotoluene-*p*-sulphonate with cyclopentadiene and pyridine, then treating with potassium bromide. The toluene-*p*-sulphonates of its 5,6,5′,6′-bis(methylenedioxy)-, 5,6,5′,6′-tetramethoxy-, and 4,5,4′,5′-dibenzo-derivatives were also made. The *NN*′-diethyl analogues of the first three were prepared similarly. By use of indene instead of cyclopentadiene, a corresponding set of thiacarbocyanines, II (Y=Z=S, n=m=0, R=R′=Me, X=Br, I, or *p*-$SO_3 \cdot C_6H_4Me$), and derivatives was made.[1]

The intermediate compound, I (Y=S, n=0, R=Me), was prepared by heating 2-methylthiobenzothiazole methotoluene-*p*-sulphonate with indene, diethylamine, and pyridine. By its reaction with 2-methylthio-6,7-benzobenzothiazole methotoluene-*p*-sulphonate, followed by bromide, there resulted the 6,7-benzo-derivative of the thiacarbocyanine, II (Y=Z=S, n=m=0, R=R′=Me, X=Br). The intermediate compound, I (Y=S, n=1, R=Me), was prepared by heating 2-β-acetanilidovinylbenzothiazole methotoluene-*p*-sulphonate with indene, diethylamine, and pyridine, then diluting with water. By heating it with 2-methylthiobenzothiazole methotoluene-*p*-sulphonate in pyridine, and converting into bromide, it gave the thiadicarbocyanine, XV (Y=Z=S, n=1, m=0, R=R′=Me, X=Br). By heating it with 2-β-acetanilidovinylbenzothiazole ethiodide in acetic anhydride, it gave the

thiatricarbocyanine, XV (Y=Z=S, $n=m=1$, R=Me, R′=Et, X=I).[3]

The oxacarbocyanine, XV (Y=Z=O, $n=m=0$, R=R′=Me, X=I), was prepared by heating 2-methylthiobenzoxazole methotoluene-*p*-sulphonate with indene and pyridine, and converting into iodide.[1] The oxatricarbocyanine, XV (Y=Z=O, $n=m=1$, R=R′=Et, X=I), was prepared by reaction of 2-*β*-acetanilidovinylbenzoxazole ethiodide, indene, and triethylamine: its decomposition point and sensitising maximum were compared with those of the corresponding dye with an unsubstituted chain.[2]

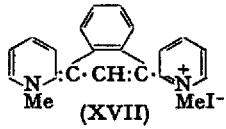
D. Indothiadi-, Indothiatri-, Oxathia-, Oxathiadi-, and Oxathiatri-carbocyanines

2-*β*-Acetanilidovinyl-3,3-dimethylindolenine methiodide on heating with indene, diethylamine, and pyridine, gave I (Y=CMe_2, $n=1$, R=Me); reaction of this with 2-methylthiobenzothiazole methotoluene-*p*-sulphonate led to the indothiadicarbocyanine, II (Y=CMe_2, X=S, $n=1$, $m=0$, R=R′=Me, X=I). The dye was alternatively prepared from I (Y=S, $n=0$, R=Me) and 2-*β*-acetanilidovinyl-3,3-dimethylindolenine methiodide, by heating them in acetic anhydride. XV (Y=CMe_2, Z=S, $n=1$, $m=0$, R=R′=Me, X=I) was also made.[3] Reaction of the above methiodide with I (Y=S, $n=1$, R=Me) in acetic anhydride gave the indothiatricarbocyanine, II (Y=CMe_2, Z=S, $n=m=1$, R=R′=Me, X=I). By heating 2-(4-acetanilidobuta-1,3-dienyl)-3,3-dimethylindolenine methiodide with indene, diethylamine, and pyridine, there resulted the intermediate compound, I (Y=CMe_2, $n=2$, R=Me); its reaction with a 2-methylthiobenzothiazolium salt gave II (Y=CMe_2, Z=S, $n=2$, $m=0$, R=R′=Me, X=I).[3]

By heating I (Y=S, $n=0$, R=Me) with 2-methylthiobenzoxazole methotoluene-*p*-sulphonate in alcohol, followed by iodide, there resulted the oxathiacarbocyanine, XV (Y=O, Z=S, $n=m=0$, R=R′=Me, X=I). By heating I (Y=S, $n=1$, R=Me) with the same benzoxazolium salt in pyridine, there was obtained the oxathiadicarbocyanine, XV (Y=O, Z=S, $n=0$, $m=1$, R=R′=Me, X=*p*-$SO_3 \cdot C_6H_4Me$). Reaction of 2-*β*-acetanilidovinylbenzoxazole alkiodide with I (Y=S, $n=1$, R=Me) in acetic anhydride gave the oxathiatricarbocyanines, XV (Y=O, Z=S, $n=m=1$, R=Me or Et, R′=Me, X=I).[3]

E. 2,2′-Pyridocarbocyanine

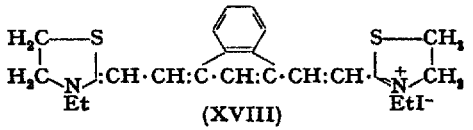
The 2,2′-pyridocarbocyanine, XVII, was obtained on heating 2-methylthiopyridine methotoluene-*p*-sulphonate with indene.[1]



(XVII)

F. Thiazolinotricarbocyanine

The thiazolinotricarbocyanine, XVIII, was prepared by heating together 2-β-acetanilidovinylthiazoline ethiodide, indene, and triethylamine. Its decomposition point and sensitising maximum were compared with those of the parent dye having an unsubstituted chain.[2]



(XVIII)

3. Trimethincyanines, in which the $\alpha\gamma$-Positions are Linked, either Directly, or Through a Chain of One to Six Methylene Groups, or Through Oxygen, by Reaction of Alkyl Orthoformate with a Diquaternary Salt, Having Nuclei Joined by $\cdot CH_2\cdot(CH_2)_n\cdot CH_2\cdot$ or by $\cdot CH_2\cdot O\cdot CH_2\cdot$

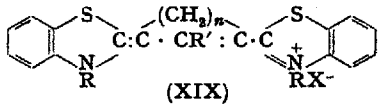
A. 2,2′-Carbocyanines

The $\alpha\gamma$-methylene-2,2′-carbocyanine, V (Y=Z=CH:CH, n=1, m=0, R=R′=Et, X=I), was prepared by boiling 1,3-di-(2-quinolyl)-propane diethiodide with ethyl orthoformate and pyridine for 3–4 hours, and precipitating with ether. A derivative in which the methylene group was replaced by a benzylidene group was similarly prepared from 2-phenyl-1,3-di(2-quinolyl)propane, being precipitated by water.[5]

B. Thia-, Oxa-, and Selena-carbocyanines

1,4-Di-(2-benzothiazolyl)butane diethiodide reacted with diphenylformamidine on boiling with sodium acetate in acetic anhydride to give the $\alpha\gamma$-dimethylenethiacarbocyanine, V (Y=Z=S, n=2, m=0, R=R′=Et, X=I).[4,5] The corresponding ethane diethiodide, on heating

with ethyl orthoformate in pyridine, gave a thiacarbocyanine in which the $\alpha\gamma$-positions were directly linked.[5] Values for absorption maxima and extinction coefficients were given for six pairs of thiacarbocyanines, V (Y=Z=S, n=3, 4, 5, or 6, m=0, R=R′=Me or Ph),[6,7] which had been prepared earlier.[8] The 6,6′-dimethoxy-derivative of V (Y=Z=S, n=2, m=0, R=R′=Et, X=ClO_4) resulted in 44 % yield by boiling 1,4-di[-2-(6-methoxybenzothiazolyl)]butane diethiodide with ethyl orthoformate in pyridine for 15 minutes, and converting into perchlorate. The 5,5′-dimethoxy-derivative, as iodide, was obtained in 31 % yield by boiling the corresponding butane diethiodide with ethyl orthoformate in acetic anhydride for 35 minutes. The 4,4′-dimethoxy-derivatives of V (Y=Z=S, n=2 or 3, m=0, R=R′=Et, X=I) were also prepared, in yields of 23 % and 51 %. The absorption maxima of the 6,6′-, 5,5′-, and 4,4′-dimethoxy-derivatives of V (Y=Z=S, n=2, m=0, R=R′=Et) lay at 6180 Å, 6150 Å, and 6040 Å, respectively,[33] as against 6010 Å for the parent dye (Table I). That of the 4,4-dimethoxy-derivative of V (Y=Z=S, n=3, m=0, R=R′=Et, X=I) lay at 5880 Å,[33] as against 5650 Å for the parent dye (Table I). Two *NN*′-dicyclohexyl dyes, V (Y=Z=S, n=1 or 2, m=0, R=R′=C_6H_{11}, X=I or ClO_4), were prepared in yields of 28 % and 50 %.[34] Absorption maxima were given for a series of $\alpha\gamma$-dimethylene dyes in which the *NN*′-dialkyl groups were diMe, diEt, diPr, di-Pr^i, di-Bu, di-Bu^i, di-CH_2CO_2H, di-CH_2CH_2OH, di-$CH_2CH_2CO_2Me$, and di-CH_2CH_2OAc: they lay between 5970 and 6100 Å.[35] The *meso*-substituted thiacarbocyanines, XIX (n=1, R=Ph, R′=Me or Et, X=I), were prepared in



(XIX)

yields of 30 % and 26 %, by 30 minutes' boiling of ethyl orthoacetate, or orthopropionate, with 1,3-di-(2-benzothiazolyl)propane di(phenochloride) and acetic anhydride, treatment with potassium iodide, then with ether, and recrystallisation from alcohol. The analogue, XIX (n=2, R=Et, R′=Me, X=I), was prepared by 15 minutes' boiling of 1,4-di-(2-benzothiazolyl)butane di-(ethotoluene-*p*-sulphonate) and ethyl orthoacetate in acetic anhydride, but the corresponding *meso*-ethyl analogue was too unstable to be isolated. XIX (n=2, R=Ph, R′=Me, X=I) was likewise unstable, but was obtained in 9 % yield.[9]

In preparing the thiacarbocyanines, IV (R=Et or Ph, X=I), from the diethiodide or dipheniodide of di-(2-benzothiazolylmethyl)oxide, boiling was for 1 hour with ethyl orthoformate and acetic anhydride, and recrystallisation was from alcohol. The yields were 31 % and 30 %, respectively.[11]

1,4-Di-(2-benzoxazolyl)butane diethiodide was heated with ethyl orthoformate in pyridine to give the $\alpha\gamma$-dimethyleneoxacarbocyanine, V (Y=Z=O, n=2, m=0, R=Et, X=I); an analogue, V (n=3), was prepared from the corresponding pentane,[4] and another, V (n=0) from 1,2-di-(2-benzoxazolyl)ethane di-(ethoethylsulphate), followed by potassium iodide.[5]

The $\alpha\gamma$-dimethyleneselenacarbocyanine, V (Y=Z=Se, n=2, m=0, X=I), was prepared by heating together 1,4-di-(2-benzoselenazolyl)-butane diethiodide, ethyl orthoformate, and pyridine.[5]

C. Thiazolocarbocyanines

Diquaternary sulphonates of 1,4-di-(2-thiazolyl)butanes were heated with ethyl orthoformate in pyridine or acetic anhydride. The four thiazolocarbocyanines, III (R=Et, R′=Me and R=Et, Pr^n, or Bu^n, R′=Ph), were too unstable to isolate but their absorption maxima were determined.[10]

4. Tri- and Penta-methincyanines with $\alpha\gamma$-Dimethylene or -Trimethylene on the Chain, from a Quaternary Salt, Having a Cyclopentenyl or Cyclohexenyl Group, and a Salt Having an ·SR, ·CH:CH·NR^1R^2, or ·CH:CH·SR Group

A. Thia-2′-carbo- and Thia-2′-dicarbo-cyanines

Distillation of *o*-aminothiophenol with cyclohex-1-ene carboxylic acid anhydride gave 2-cyclohexenylbenzothiazole (equation 4; Y=S, n=3). This and 2-methylthioquinoline were heated with methyl toluene-*p*-sulphonate at 160–180° for 3·5 hours, and the resultant salt mixture was boiled with pyridine for 30 minutes, and treated with potassium iodide, giving the $\alpha\gamma$-trimethylenethia-2′-carbocyanine, V (Y=S, Z=CH:CH, n=3, m=0, R=R′=Me, X=I).[12]

2-Cyclohexenylbenzothiazole methotoluene-*p*-sulphonate was boiled with 2-β-acetanilidovinylquinoline ethiodide in pyridine for 20

minutes, then treated with iodide, to give the $\alpha\gamma$-trimethylenethia-2'-dicarbocyanine, V (Y=S, Z=CH:CH, n=3, m=1, R=Me, R'=Et, X=I).[12] The $\alpha'\gamma'$-dimethylene thia-2'-dicarbocyanine, V (Y=CH:CH, Z=S, n=3, m=1, R=R'=Me, X=I), was prepared by heating the methotoluene-*p*-sulphonates of 2-cyclohexenylquinoline and of 2-ethylthiovinylbenzothiazole with pyridine and triethylamine, and converting into iodide.[13]

B. Thia-, Thiadi-, and Oxa-carbocyanines

The $\alpha\gamma$-trimethylenethiacarbocyanine, V (Y=Z=S, n=3, m=0, R=R'=Me, X=Br), was prepared by heating 2-cyclohexenylbenzothiazole and 2-methylthiobenzothiazole with methyl toluene-*p*-sulphonate, boiling the salts with pyridine, and converting the dye into bromide; use of 3-ethyl-2-thiobenzothiazoline, in place of the methylthio-base, gave the *NN'*-ethylmethyl analogue of the dye. The $\alpha\gamma$-dimethylenethiacarbocyanine, V (Y=Z=S, n=2, m=0, R=R'=Me, X=Br), and its 5,6-dimethoxy-derivative were also made.[12]

By heating 2-cyclohexenylbenzothiazole methotoluene-*p*-sulphonate and 2-β-acetanilidovinylbenzothiazole ethiodide with pyridine, and converting into iodide, there resulted the $\alpha\gamma$-trimethylenethiadicarbocyanine, V (Y=Z=S, n=3, m=1, R=Me, R'=Et, X=I).[12]

2-Cyclopentenylbenzoxazole was prepared by boiling *o*-aminophenol and cyclopentenylcarboxylic acid anhydride for 1 hour and then distilling. This and 2-methylthiobenzoxazole were heated with methyl toluene-*p*-sulphonate, and the resultant salts with pyridine, to give the $\alpha\gamma$-dimethyleneoxacarbocyanine, V (Y=Z=O, n=2, m=0, R=R'=Me, X=I).[12]

C. Indothiadi-, Oxathia- and Selenathia-carbocyanines

To obtain the $\alpha'\gamma'$-trimethyleneindothiadicarbocyanine, V (Y=S, Z=CMe_2, n=3, m=1, R=R'=Me, X=I), 2-hexenylbenzothiazole methotoluene-*p*-sulphonate and 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide were heated together in pyridine, then treated with potassium iodide.[12]

The oxathiacarbocyanine, V (Y=O, Z=S, n=2, m=0, R=R'=Me, X=I), was prepared by heating the methotoluene-*p*-sulphonates of 2-cyclopentenylbenzoxazole and 2-methylthiobenzothiazole with pyridine, and converting into iodide. Its 6',7'-benzo-, 5,6-dimethyl-, and 4',5'-benzo-5,6-dimethyl-derivatives were also made. The dye, V (Y=O,

Z=S, n=3, m=0, R=R′=Me, X=I), was made from the methotoluene-p-sulphonates of 2-cyclohexenylbenzoxazole and 2-methylthiobenzothiazole; the *NN′*-ethylmethyl analogue was made by replacing the latter base by 3-ethyl 2-thio-benzothiazoline.[12]

The selenathiacarbocyanine, V (Y=Se, Z=S, n=3, m=0, R=R′=Me, X=Br), was prepared from the methotoluene-p-sulphonates of 2-cyclohexenylbenzoselenazole and 2-methylthiobenzothiazole by boiling with pyridine.[12]

D. Thiathiazolino-carbo- and -dicarbo-cyanines

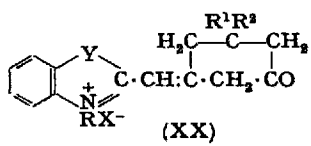
The thiathiazolinocarbocyanine, VI (n=3, m=0, R=R′=Me, X=I), was prepared by heating 2-cyclohexenylthiazoline and 2-methylthiobenzothiazole with methyl toluene-p-sulphonate at 160–180° for 3 hours, boiling with pyridine for 30 minutes, and treating with iodide. Its 4,5-dimethoxy- and 6,7-benzo-derivatives were made, also the bromide of the $\alpha\gamma$-dimethylene analogue.[14]

The thiathiazolinodicarbocyanine, VI (n=3, m=1, R=R′=Me, X=I), was prepared by boiling 2-cyclohexenylthiazoline methotoluene-p-sulphonate and 2-β-acetanilidovinylbenzothiazole methiodide in pyridine for 20 minutes, and converting into iodide.[14]

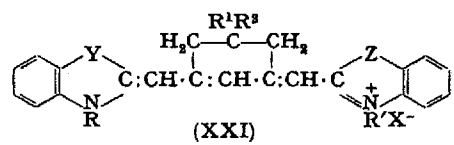
5. Pentamethincyanines, Having a $\beta\beta'\cdot CH_2\cdot CR^1R^2\cdot CH_2\cdot$ Group, from a Quaternary Salt, Having a Reactive Methyl Group, with a 3-Alkylthio cyclohex-2-en-1-one, or with an Intermediate Salt

A. Thia-2′- and Thia-4′-dicarbocyanines

Fusion of 3-ethylthiocyclohex-5,5-dimethyl-2-en-1-one, 2-methylbenzothiazole, and methyl toluene-p-sulphonate, followed by heating with acetic anhydride, and treatment with potassium iodide, gave XX (Y=S, R=R^1=R^2=Me, X=I) (equation 9).[17] This salt condensed with quinaldine ethiodide, on boiling them with triethylamine in pyridine, to give the thia-2′-dicarbocyanine, XXI (Y=S, Z=CH:CH, R=R^1=R^2=Me, R′=Et, X=I) (equation 10).[18]

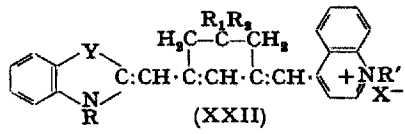


(XX)



(XXI)

The thia-4'-dicarbocyanine, XXII (Y=S, R=R'=R¹=R²=Me, X=I), was similarly prepared, through lepidine methotoluene-*p*-sulphonate.[18]



(XXII)

B. Thia- and Selena-dicarbocyanines

The thiadicarbocyanine, XXI (Y=Z=S R=R'=R¹=R²=Me, X=I), was prepared (equation 8) by heating together, at 100° for 2 hours, 3-ethylthio-5,5-dimethylcyclohex-2-en-1-one, 2-methylbenzothiazole, and methyl toluene-*p*-sulphonate, boiling with triethylamine in pyridine for 30 minutes, and converting into iodide; the *NN'*-diethyl analogue, and the 5,5'-dichloro- and 5,5'-dimethyl derivatives of that were also prepared; so also were XXI (Y=Z=S, R=R'=Et, R¹=H, R²=Me or Ph, X=I), the 5,5'-dichloro-derivative of the former, the 5,5'-dimethyl derivative of the latter, and, as bromide, the analogue with an unsubstituted $\alpha\gamma$-trimethylene chain.[16]

The selenadicarbocyanine, XXI (Y=Z=Se, R=R'=Et, R¹=R²=Me, X=I), was prepared by fusion of 2-methylbenzoselenazole, 3-ethylthio-5,5-dimethylcyclohex-2-en-1-one, and ethyl toluene-*p*-sulphonate, followed by boiling with triethylamine in pyridine and conversion into iodide.[16]

C. Selenathiadicarbocyanines

The selenathiadicarbocyanine, XXI (Y=Se, Z=S, R=R'=R¹=R²=Me, X=I), resulted on heating XX (Y=S, R=R¹=R²=Me, X=I) with 2-methylbenzoselenazole methotoluene-*p*-sulphonate and triethylamine in pyridine, and converting into iodide.[18]

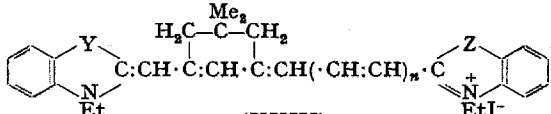
6. Hepta-, Nona-, and Undeca-methincyanines, Having a $\beta\delta$ $\cdot CH_2 \cdot CR^1R^2 \cdot CH_2 \cdot$ Group, and an Undecamethincyanine Having Two Such, Through Quaternary Salts, Having the Group

$$\begin{array}{l} H_2C \cdot CR^1R^2 \cdot CH_2 \\ \quad\quad | \quad\quad\quad | \\ \cdot CH{:}C \cdot CH{=\!=}C \cdot Me \end{array}$$

A. Heptamethincyanines of the Thia-, Oxa-, Selena-, and Oxathia-Series

By condensation of a quaternary salt substituted as in equation 11[19] with one of the same series but having a 2-β-acetanilidovinyl sub-

stituent, by heating with triethylamine in pyridine or ethanol, there resulted tricarbocyanines of the types XXIII (n=1, Y=Z=S, Se, or O); the oxathiatricarbocyanine, XXIII (n=1, Y=S, Z=O), was also described.[20]



(XXIII)

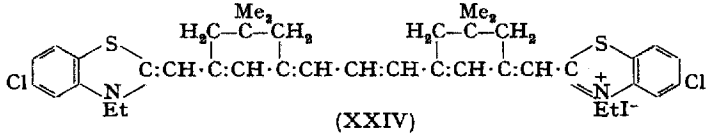
B. Nonamethincyanines of the Thia-Series

By condensation of quaternary salts substituted as in equation 11[19] with 2-(4-acetanilido-1,3-butadienyl)benzothiazole ethiodide, XXIII (n=2, Y=Z=S) and a 6,7-benzo-derivative were prepared. An analogue of the former having a 5-methylcyclohexenylidene ring, attached by chains in the 1- and 3-positions, was also described.[20]

C. Undecamethincyanines of the Thia-Series

By condensation of a benzothiazolium, and of a 4,5-benzobenzothiazolium salt, substituted as in equation 11[19] with 2-(6-acetanilidohexa-1,3,5-trienyl)benzothiazole ethiodide, there was obtained XXIII (n=3, Y=Z=S).[20]

By heating a 5-chlorobenzothiazolium salt, which was substituted as in equation 11, with diethoxymethyl acetate in pyridine (cf. IV, 13), there was obtained the symmetrical undecamethincyanine, XXIV, in which two cyclohexenyl components entered into the chain.[20]



(XXIV)

7. Pentamethincyanines, by Removal of Acid from a Diquaternary Salt, which has the Nuclei Linked by $\cdot CH_2 \cdot C_6H_4 \cdot$

A. Thiadicarbocyanines

The base of equation 12 was heated with ethyl sulphate and the diquaternary salt converted into di-iodide. Its suspension in methanol

was treated with 10 % ammonia at 20–25° and the thiadicarbocyanine, VII (R=Et, X=I), was salted out, in 74 % yield, by sodium iodide: recrystallisation from methanol gave a 37 % yield. The *NN'*-dimethyl analogue was prepared similarly.[21]

8. Cyanines in which One or More Dihydro-β-quinindene Nuclei are Involved in the Chain

The chain-substituted trimethincyanine, X (R=Me), was prepared by heating dihydro-β-quinindene methiodide with sodium formate, ethyl orthoformate, and pyridine in acetic anhydride for 15 minutes. Its diethyl analogue was prepared similarly except that use of sodium formate was unnecessary and heating was for 1 hour. To obtain the two dyes, XI (Y=CH:CH, R=Me or Et), 2-β-anilinovinylquinoline alkiodide, and dihydro-β-quinindene alkiodide were boiled in acetic anhydride containing pyridine and sodium acetate for 1 hour, and the reaction mixture was treated with water. The 6-methyl derivative of the former was prepared from the corresponding 6-methylquinolinium salt. The two dyes, XII (R=Me or Et), were also made. To obtain XI (Y=O, R=Me or Et), 2-β-acetanilidovinylbenzoxazole alkiodide was boiled with dihydro-β-quinindene alkiodide and sodium acetate in acetic anhydride for 1 hour, and the mixture treated with water. The two sulphur analogues, XI (Y=S, R=Me or Et), were similarly made. To obtain XI (Y=CMe_2, R=Me), 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide and dihydro-β-quinindene methiodide were boiled for 1 hour in acetic anhydride containing potassium acetate and pyridine.[27]

Although regarded as chain-substituted trimethincyanines, the dyes may be named as in the following examples:

X (R=Me) is bis-3-(4-methyldihydro-β-quinidene)methincyanine iodide.

XI (Y=O, R=Et) is [2-(3-ethylbenzoxazole)] [3-(4-ethyl-dihydro-β-quinindene)]dimethincyanine iodide.

XII (R=Me) is [3-(4-methyldihydro-β-quinindene)] [4-(1-methylquinoline)]dimethincyanine iodide.

Some particulars of some of the dyes[27] are given in Table III.

TABLE I. Some Properties of Thiacarbocyanines in which $\alpha\gamma$-Substituents Make the Chain Cyclic (In Formulae, Y=Z=S, R=R′=Et, X=I)

Nature of substituent	Formula	Appearance of crystals	M.p., °C (decomp.)	Absorption maximum (Å)	Bathochromic shift on substitution (Å)	Sensitising (Å) maximum	Sensitising (Å) Extent	Ref.
none	—	steel-blue prisms	269	5570	—	5900 (and 5330)	6600	36, 37
·CH:CH	XV (n=m=0)	yellow	265[a]	—	—	5000	5300	1
o·C_6H_4·	II (n=m=0)	red needles	226–228[a]	—	—	5700	5900	1
$\alpha\gamma$-link	V (n=m=0)	dark red	—	5600	30	5900	—	5
CH_2	V (n=1, m=0)	—	—	5580	10	—	—	6, 7
$(CH_2)_2$	V (n=2, m=0)	bluish needles	—	6010	440	6400	6800	4, 6, 7
$(CH_2)_3$	V (n=3, m=0)[b,c]	dark green	234	5650	80	6600	7000	6, 7, 12
$(CH_2)_4$	V (n=4, m=0)[b]	—	—	5750	180	—	—	6, 7
$(CH_2)_5$	V (n=5, m=0)[b]	—	—	5630	60	—	—	6, 7
$(CH_2)_6$	V (n=6, m=0)[b]	—	—	5580	10	—	—	6, 7
O	IV	minute, dark	198	5550	—20	—	—	11

[a] Decomp. not recorded. [b] R=R′=Me. [c] X=Br.

TABLE II. Some Properties of Thiadicarbocyanines in which Part of the Chain is Cyclic (In Formulae, Y=Z=S, R=R′=Et, X=I)

Nature of substituents	Formula	Appearance of crystals	M.p., °C (decomp.)	Sensitising (Å) Maximum	Extent	Ref.
none	—	green needles	253	7000	—	38, 39
αγ-·CH:CH·	XV ($n=1$, $m=0$)[a,b]	blue needles	215[c]	6500	—	3
αδ-·CH:CH·	VII	bronze	225–227	6000	6900	19
αγ-$(CH_2)_3$	V ($n=3$, $m=1$)[d]	bluish green	243	7200	7800	12
βδ-·CH_2·CMe_2·CH_2·	XXI ($R^1=R^2=Me$)	green	190	6980	—	16
βδ-·CH_2·CHMe·CH_2·	XXI ($R^1=H$, $R^2=Me$)	light green	248	6950	—	16
βδ-·CH_2·CHPh·CH_2·	XXI ($R^1=H$, $R^2=Ph$)	dark green	264	7100	—	16

[a] *NN′*-dimethyl. [b] X=Br. [c] Decomp. not recorded. [d] R=Me, R′=Et.

TABLE III. Concerning Cyanines in which One or More Dihydro-β-quinindene Nuclei are Involved in the Chain (Ref. 27). (In the Formulae, R=Me)

Formula	Appearance of crystals	M.p. (°C)	% Yield	Solvent used for recrystallisation
X	bronze platelets	268[a]	20	pyridine
XI (Y=CH:CH)	violet plates	272–273	30	pyridine
XI (Y=O)	dark violet prisms	267–268	60 (crude)	pyridine
XI (Y=S)	dark green plates	271	60	pyridine
XI (Y=CMe_2)	brown	264–265	90	spirit
XII	green platelets	264–265	60 (crude)	pyridine

[a] Decomp. recorded.

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CHAPTER X

Variations in the Nuclei which Enter into Cyanine Molecules

1. General Survey

The length of the chain which joins the two nuclei in a cyanine is of paramount importance, as is also the nature of the nuclei, and these have been adopted as the basis for classification. From the first, chemists have been interested in the substituents which may be introduced into the nuclei, so that this way of variation has largely been dealt with, as instances arose, in the preceding chapters. In addition, the introduction of other special groups is considered here (section 2). Variations in the anion (section 3) and variations in the groups attached to nitrogen (section 4) are also dealt with. Interesting modifications of the *N*-alkyl group (section 4-A) extend to the introduction of *NN'*-alkylene groups (section 4-B) and this includes Isoquinoline Red as well as much newer types of dyes. Chemists writing in 1920 regarded it as obvious that the nitrogen atoms of cyanines must carry alkyl groups, in order to allow the formation of dyes capable of existence in alkaline solution.[1] Since then, cyanines with one or more *N*-aryl groups have been made (section 4-C). Other dyes, with *NN'*-diH structures, have been described in the literature as cyanines. Although in agreement with the opinion expressed in 1945, that these *NN'*-diH dyes are not strictly cyanines,[2] the author has found it convenient to include them here (section 4-D). In cyanines, the benzothiazole nucleus was the first to have its nitrogen atom linked by a chain to the carbocyclic ring, but later such a 3,4-bridge was introduced in other nuclei, also the corresponding 1,8-bridge in quinoline nuclei (section 4-E).

The usual methods of preparing cyanines have been applied to interesting and unusual nuclei (section 5). Nuclei with nitrogen as the only hetero-atom include 1- and 3-linked isoquinoline, also acridine, acenaphthenopyridine, 2*H*-pyrroline, 3-linked indole, and 2- and 3-linked

pyrrole (section 5-A). Dimethincyanines with one 3-linked indole nucleus and di- and tetra-methincyanines having one 3-linked pyrrole nucleus are also included (section 5-A), though, as an extra part of the chain joining the nitrogen atoms is cyclic, they also belong in the preceding chapter. Amongst nuclei having two nitrogen atoms as the only hetero-atoms (section 5-B), 1,3-diazines are represented by the quinazoline, pyrimidine, and perimidine nuclei, 1,4-diazines by pyrazine and quinoxaline, and 1,2-diazines by phthalazine and pyridazine. A 1,2-diazole nucleus and a 1,3-diazole nucleus have also been introduced into cyanines. Other cyanines have complex nuclei such as 1,7-phenanthroline, naphthyridine, or indolo(3',2'-3,4)quinoline, in which there are two nitrogen atoms but in different rings. Cyanine dyes having nuclei with three nitrogen atoms as hetero-atoms are those with a 1,2,4-triazole or a triazolo[4,3a]quinoline nucleus (section 5-C). Nuclei with four nitrogen atoms as hetero-atoms have also been introduced into cyanine molecules and comprise the *s*-triazolo[2,3-a]pyrimidine, the tetrazolo[a]-quinoline, and the simple tetrazole nucleus (section 5-D).

Nuclei with one nitrogen and one sulphur as hetero-atoms include certain complex benzothiazoles, also six-membered rings such as perinaphtho-1,3-thiazine, 3,1,4- and 1,4,2-benzothiazine, and dihydro-1,3,4-thiazine (section 5-E). Nuclei with two nitrogen atoms and one sulphur, that were introduced into cyanines, were 1,2,4- and 1,3,4-thiadiazoles and, with two nitrogen atoms and one oxygen, the 1,3,4-oxadiazole nucleus (section 5-G). Complex nuclei with one nitrogen and two sulphur atoms comprised five types of thionaphthenothiazoles (section 5-I), and others with two nitrogen atoms and two sulphur atoms comprised benzobisthiazoles (section 5-J).

In Table I there are brought together some properties of symmetrical trimethincyanines having pairs of these unusual nuclei. Table II contains data for methincyanines, each of which has a quinoline nucleus linked through its 2-position to an unusual nucleus: in order to cover a wider field, the second nuclei are so selected as to be different from those in Table I.

2. Introduction of Certain Substituents

As early as 1932, cyanines were made in which tetrahydrobenzo-derivatives of the usual heterocyclic nuclei were employed. The examples included thia-2'-, and thia-4'-cyanines, also thiacarbo-, including

meso-alkylthiacarbo-, thiadicarbo-, and thiatricarbo-cyanines, in which one or more tetrahydro-4,5- or -6,7-benzobenzothiazole nuclei figured. Samples were produced to prove that tetrahydrobenzo-quinoline, -benzoselenazole, -benzoxazole, or -indolenine nuclei could also be used.[3] The preparation of various types of dyes from 2-methyltetrahydro-benzothiazolium or -benzoselenazolium salts was later described.[4] In 1942, cyanines having a 4-thienylthiazole nucleus were described as strong sensitisers and examples of thiazolo-2'-, thiazolocarbo-, and *meso*-alkylthiazolocarbo-cyanines were given.[5] In 1950, cyanines with a 4-benzofurylthiazole nucleus were claimed; examples with one such nucleus were of the thiazolo-2'-, thiathiazolo-, selenathiazolo-, and thiazolo-2'-carbocyanine types: examples with two such nuclei were of the thiazolo- and thiazolotri-carbocyanine types.[6] A carbocyanine with a 4-furylthiazole and a 6,7-benzobenzoselenazole nucleus was patented.[7]

The good sensitising of cyanines with a 5-phenylbenzoxazole nucleus was found to be improved if the 5-phenyl group was substituted: examples included oxa-2'-cyanines, and oxa-, oxathia-, oxathiazolino-, and oxathiazolo-carbocyanines.[8] Dyes with substituted phenyl in the 5- or 6-position of the benzothiazole nucleus were likewise found valuable, as instanced by a thiacarbocyanine and a trinuclear dye.[9]

Two 6,7,6',7'-methylenedioxy-groups were introduced into a 2,2'-carbocyanine molecule so long ago as 1920[10] and, in 1932, 6,7-ethylenedioxy-groups were introduced into 2,4'- and 4,4'-cyanines and into 2,2'-carbocyanines.[11] Cyclic hydrocarbondioxy-ring structures were claimed to confer on thia- and selena-carbocyanines non-wandering properties, together with a desirable sensitising gap in the green; the examples comprised a selenathiacarbocyanine, and symmetrical and unsymmetrical thiacarbocyanines.[12]

6-Fluoro-2-methylbenzothiazole was synthesised and hence dyes of the thia-2'-cyanine, unsymmetrical thiacyanine, and thia-2'-carbocyanine types, having a 6-fluoro-substituent. 6,6'-Difluoro-substituents were introduced into dyes of the thiacyanine, thiacarbocyanine, *meso*-alkylthiacarbocyanine, thiadi- and thiatri-carbocyanine types, also into a styryl dye and a dimethinmerocyanine. The dyes were less soluble in alcohol and had higher melting points than the unsubstituted parent dyes, but the absorption maxima were scarcely affected.[13] 5,5'-Difluoro-groups were introduced into a thiacarbocyanine and into two *meso*-alkylthiacarbocyanines. One 5-trifluoromethyl group was intro-

duced into a thiacyanine, a thiacarbocyanine, and a thia-2'-carbocyanine, also into a styryl dye and a dimethinmerocyanine, and two such groups entered into the molecules of dyes of the thiacarbocyanine, *meso*-alkylthiacarbocyanine, and thiadi- and thiatri-carbocyanine types. Again, the substituents scarcely affected the absorption maxima.[14] A thiacyanine having one 6-trifluoro(methylthio)-group was prepared, also a styryl dye and a merocyanine with one such nucleus; a thiacarbocyanine with two such nuclei was also made.[15] One trifluoro-(methylthio)-group was introduced into the 5-position of a thiacyanine and into the 5- or 6-position of a thiadicarbocyanine; three thiacarbocyanines, of which two were *meso*-substituted, showed a bathochromic shift of 70–100 Å on introduction of 5,5'- or 6,6'-diSCF_3 groups,[16] but with 5,5'- or 6,6'-di-(trifluoromethoxy) groups the shift was 0–40 Å.[17]

2-Methylbenzothiazoles with a 6-thio- or a 6-isothio-carbamidogroup, such as $Ph\cdot CH_2\cdot NH\cdot \overset{\overset{S}{\cdot\cdot}}{C}\cdot NH\cdot$, $Ph\cdot CH_2\cdot N{:}C(SEt)\cdot NH\cdot$, $H_2C{:}CH\cdot CH_2\cdot NH\cdot \overset{\overset{S}{\cdot\cdot}}{C}\cdot NH\cdot$, and $H_2C{:}CH\cdot CH_2\cdot N{:}C(SEt)\cdot NH\cdot$, were synthesised, and hence dyes containing such groups; these comprised four thia-4'-cyanines, each with one substituent, and, with two, four thiacarbocyanines, eight *meso*-alkylthiacarbocyanines, four thiadicarbocyanines, and four thiatricarbocyanines: the yields were 23–44 %, 34–55 %, 10–38 %, 39–81 %, and 16–41 %, respectively, in the five classes. It was hoped to combine chemical and spectral sensitising in the one dye molecule, but the compounds did not show chemical sensitising properties. The absorption of the substituted thiacarbocyanines lay at a shorter wavelength than that of the corresponding 6,6'-diaminoanalogues.[18]

The presence in a thiacarbocyanine molecule of an unsaturated group in the 5- or 6-position, or of two such groups in the 5,5'- or 6,6'-positions, resulted in bathochromic shifts of absorption.[19]

Thirteen symmetrical thiacarbocyanines having 5,5'(or 6,6')-bis-(arylazo)-substituents were prepared by the pyridine and ethyl orthoformate method from salts which 5(or 6)-arylazo-2-methylbenzothiazoles gave with methyl sulphate; two *meso*-ethyl derivatives were also made. A thiacyanine, a thiacarbocyanine, and a *p*-dimethylaminostyryl salt, each having one 5(or 6)-arylazobenzothiazole nucleus were described, also a 2,2'-carbocyanine with two 6-(*p*-dimethylaminophenylazo)quinoline nuclei. As the absorption spectra had one intense band,

it was concluded that the azo groups and polymethin chain formed a single chromophore.[20]

3. Variations in the Anion

It was recognized at a very early date (see II-1-B) that, whilst the nature of the anion did not affect the sensitising action of a cyanine, it had an important influence on the solubility. Iodides have often been especially suitable for characterising new dyes, because of their comparatively low solubility and good crystallising power, but alkylsulphates, on the other hand, because of their greater solubility, were sometimes more acceptable for adding to photographic emulsions. Alkyl toluene-*p*-sulphonates have long been used because they are less toxic than alkyl sulphates whilst, like them, giving dyes more soluble than the iodides. According to a recent patent, symmetrical and unsymmetrical oxa-, thia-, and selena-carbocyanines, with one or more cyclohexanesulphonate anions, are sensitisers with the advantage of enhanced solubility; the examples included also dyes of the *meso*-alkylthia- or -thiazolo-carbocyanine types, and of the oxathia-, selena-2′-, and thiazolino-carbocyanine types.[21] Similarly the n-butanesulphonate anion has been introduced into the molecules of methin- and trimethincyanines; examples included a thiacyanine and a selena-2′-cyanine, oxacarbocyanines, and *meso*-alkylthia- and *meso*-alkylthiazolo-carbocyanines. The ester is non-toxic and the dyes so soluble that they may be added from aqueous solutions.[22]

To convert a less soluble cyanine or quaternary salt, such as iodide, into a more soluble one, the standard procedure of heating with the appropriate silver salt in alcohol was improved upon by heating in the presence of a phenol[23] or a primary amine.[24] Yields varying from 43–96 % resulted.[23,24]

Various cyanine carboxylates, such as formate, acetate, phenylacetate, benzoate, and salicylate, were prepared by treating the dye chlorides with potassium formate, *etc.*, but some of the reactions were reversible.[25] A satisfactory separation must depend on the desired salt being appreciably less soluble than the chloride.

The erythrosinates of various cyanines were prepared by treating dye iodides with sodium erythrosinate; they were fairly good sensitisers with complex absorption spectra.[26]

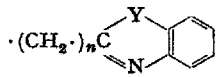
4. Variations in the Groups Attached to the Nitrogen Atoms

A. Modified *N*-Alkyl Groups

As early as 1920, a series of symmetrical 2,2'-carbocyanines with various *NN'*-dialkyl groups included one with *NN'*-di-(*β*-phenoxyethyl) groups.[10] In 1937 symmetrical and unsymmetrical carbocyanines of various series were described, in which *NN'*-diaralkyl groups were present: this replacement of the *NN'*-dialkyl groups caused a bathochromic shift of about 100 Å in the absorption maxima. Instead of alkyl iodides for preparing the quaternary salts, compounds such as $PhCH_2Br$, $p\text{-}NO_2 \cdot C_6H_4 \cdot CH_2Br$, $p\text{-}MeO \cdot C_6H_4 \cdot CH_2Br$, $p\text{-}Me \cdot C_6H_4 \cdot CH_2Br$, and $PhCH_2CH_2Br$ were used.[27] Subsequently one or two *N*-aralkyl groups were introduced into the molecules of 2,2'-, 2,4'-, 4,4'-, thia-2'-, and thia-4'-cyanines, of 2,2'-, 4,4'-, and thiacarbocyanines, and of thiatricarbocyanines: the sensitising action of the 1,1'-dibenzyl-4,4'-carbocyanines was outstanding.[28] Cyanines having a *m*- or *p*-carboxyaralkyl group attached to one or both nitrogen atoms were non-staining dyes, which sensitised at about the same wavelength, but more strongly, than those in which the *N*-aralkyl group was not substituted; examples included compounds of the thia-2'-cyanine and oxa- and oxathiazolo-carbocyanine types.[29]

Cyanines with hydroxyalkyl groups on one or both nitrogen atoms proved good sensitisers; in sensitising for longer wavelengths, the tendency to fog was reduced. The quaternary salts were made by treating a heterocyclic base with an alkylene bromohydrin, followed by potassium iodide. They were used in the preparation of cyanines of various types, such as 2,2'-, 2,4'-, and thia-2'-cyanines, and 2,2'-, 4,4'-, and thia-carbocyanines, and also thiadi- and thiatri-carbocyanines.[30] Carbocyanines having a benzimidazole nucleus with one *N*-acetoxyalkyl group were patented as sensitisers; in the sixteen examples, the other nucleus was indolenine, benzoselenazole, or thiazoline.[31] Carbocyanines, and di- and tri-carbocyanines having at least one *N*-alkyl group substituted by alkoxy-, acyloxy-, carboxy-, or acyl- were useful for sensitising to the longer wavelengths. Substances such as *β*-ethoxyethyl toluene-*p*-sulphonate, *β*-bromoethyl acetate, bromoacetic acid and chloroacetone were caused to react with heterocyclic bases, and treatment with potassium iodide gave quaternary iodides having the groups $\cdot CH_2 \cdot CH_2 \cdot OEt$, $\cdot CH_2 \cdot CH_2 \cdot O_2CMe$, $\cdot CH_2CO_2H$, and $\cdot CH_2 \cdot COMe$, respectively, attached to nitrogen. Such salts were used in the

preparation of 2,2′-, 2,4′-, and thia-2′-cyanines, and 2,2′-, 4,4′-, and thia-carbocyanines, also thiatricarbocyanines.[32] A patent covering the preparation of carbocyanines by use of a salt having a 2-β-alkylthiovinyl group (V-10) included examples in which one group attached to a heterocyclic nitrogen atom was $\cdot CH_2CH_2CO_2H$, $CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2Me$, or $(\cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N^+Me_2Et)ClO_4^-$.[33] Cyanines in which at least one nitrogen atom carried one of the groups $\cdot CH_2 \cdot CH_2 \cdot OPh$, $\cdot CH_2 \cdot CH_2 \cdot SPh$, or $\cdot CH_2 \cdot CH_2 \cdot SePh$ showed the advantages of increased solubility and non-staining, yet, because of their increased bulk, had the non-wandering properties that are important in multi-layer coatings.[34] Other non-diffusing sensitisers, with high solubility, were characterised by having on one nitrogen atom the group, I (Y=O, S, or Se, n=1 or 2),

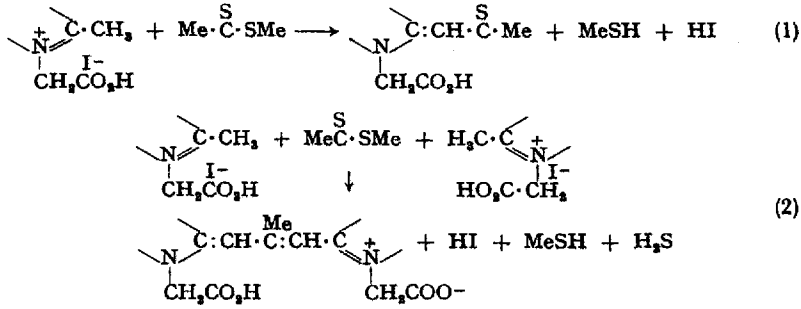


(I)

which might have a 5,6-methylenedioxy-substituent; the examples included a thia-2′-cyanine, oxathia- and thia-carbocyanines, merocyanines, a trinuclear and a styryl dye.[35] Thiacarbocyanines with the group, I (Y=S, n=1), on both nitrogen atoms sensitised at a longer wavelength by 60–70 Å than those with *NN′*-dimethyl groups.[36] It was claimed that methincyanines having one tetrahydrofurfuryl group attached to nitrogen were better sensitisers than those with alkyl. The examples, however, were all trimethincyanines; they comprised an oxathiazolino- and a thia-carbocyanine, each with one *N*-tetrahydrofurfuryl group, besides symmetrical *meso*-alkylthiacarbocyanines, and a thiadicarbocyanine, with two such groups.[37] Another modification consisted in the introduction of an *N*-carbamylmethyl group. For instance, heating 2-methylbenzothiazole with chlorodiethylacetamide and a trace of sodium iodide at 100° for 10 days gave the quaternary chloride having the group $\cdot CH_2CONEt_2$ attached to nitrogen; another such group was $\cdot CH_2CONH_2$. Salts of this kind reacted with orthoesters in pyridine to give symmetrical thia- and 4,4′-carbocyanines, also *meso*-alkyl dyes of both types, and 4,4′-hepta- and -nona-methincyanines, all of them with two such groups, and, with one such, there were prepared oxathia-, oxa-4′-, and thia-4′-carbocyanines.[38]

In the benzothiazole and benzoselenazole series, condensation of a quaternary salt, having a reactive methyl group and an *N*-carb-

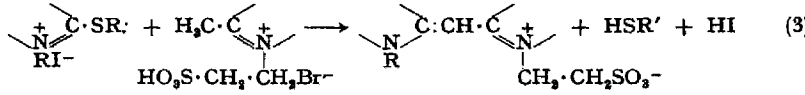
oxyalkyl group, $\cdot(CH_2\cdot)_{1-4}CO_2H$, with a dithiocarboxylic ester, S:CR(SR'), gave, simultaneously, a thioketone (equation 1) and an anhydro *meso*-substituted carbocyanine hydroxide, having a zwitterion (equation 2). The examples of dyes included *meso*-methyl- and *meso*-ethyl-thia- and -selena-carbocyanines. Condensation was effected by heating with triethylamine in pyridine; the yields of thioketones varied from 5–26 % and of dyes from 17–58 %.[30]



(1)

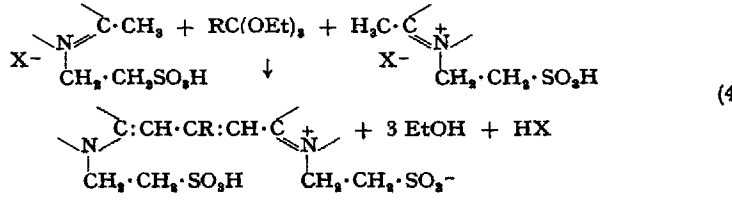
(2)

Whereas cyanines having one *N*-carboxyalkyl group have been described, quaternary salts with an *N*-sulphoalkyl group gave rise to dyes with a zwitterion. Such salts were prepared by heating a heterocyclic base with compounds such as *p*-sulphobenzyl bromide, at 160° for 12 hours, or 2-bromomethane sulphonic acid. Condensation, in pyridine, of such a salt, having a reactive methyl group, with another salt having an alkylthio-group (cf. II-4) gave, for instance, a thiacyanine (equation 3).



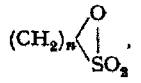
(3)

There were also prepared dyes of the thia-2'-, thia-4'-, and 2,4'-cyanine types, and a thia-4'-carbocyanine, where one of the reacting salts had an *N*-sulphoalkyl group. Reaction of ortho-esters with such salts gave symmetrical thiacarbocyanines, including *meso*-alkyl dyes (equation 4), and a thiadicarbocyanine of this type was also prepared.[40]



(4)

According to an independent discovery, reaction of an alkane sultone

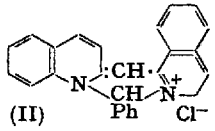


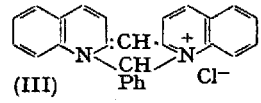
where n is at least 3,[41] with a heterocyclic base, having a reactive group, gave a betaine. These were used in the preparation of dyes of the thia-2′-cyanine, symmetrical and unsymmetrical thiacarbocyanine, including *meso*-alkyl derivatives, and selenathiacarbocyanine types, also of a styryl and a trinuclear dye.[42]

B. *NN*′-Alkylene Groups, which may be Substituted

A patent of 1882 described the production of red and violet dyes, with a reddish yellow fluorescence, by heating a quinoline or pyridine base with benzotrichloride.[43] Such bases were derived from coal tar: neither pure quinoline nor pure quinaldine gave rise to a dye, but their mixture did. Other benzotrihalides gave less soluble dyes.[44] The yield from coal tar quinoline was only 5 % but, in addition, 50 % of the quinoline was recoverable, and that recovered quinoline gave a smaller yield of dye, which was known as Quinoline Red. Whereas heating pure quinoline and pure quinaldine with benzotrichloride gave a very small yield,[45] in 1886 isoquinoline was synthesised,[46] and in 1887 it was found that an 11 % yield of dye resulted on heating isoquinoline, quinaldine, and benzotrichloride with zinc chloride: the name Isoquinoline Red was used for this[45] but, when the preparation was patented, the earlier name was used.[47] A mixture of the dye with cyanine was applied in the preparation of "azaline" plates.[47, 48] In 1912 the preparation of Isoquinoline Red by heating isoquinoline, quinaldine, and zinc chloride at 100°, adding benzotrichloride, and finally heating at 150°, was described: the reaction mixture was made alkaline with lime water, unchanged bases were removed by steam distillation, and the residue was acidified with hydrochloric acid to give the dye, which resulted in 25–30 % yields. It was established that a related dye is obtainable from quinoline, quinaldine, zinc chloride, and benzotrichloride, but in much smaller yield. Work on the oxidative breakdown of Isoquinoline Red led to formula II, in which there is an *NN*′-benzylidene group.[49] Isoquinoline Red was prepared from pure isoquinoline, derived from coal tar, quinaldine, and benzotrichloride, by heating with anhydrous

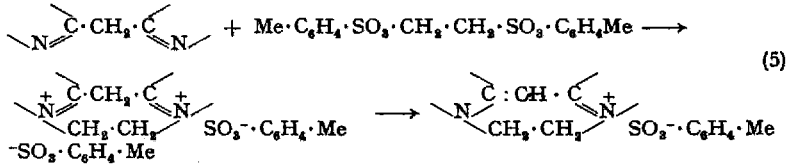
aluminium chloride at 150–155° for 1 hour. After purification, it was finally recrystallised from boiling water, with addition of hydrochloric acid, and resulted in 23% yield. By use of the 6-methyl and 6-ethyl derivatives of quinaldine, there were also made the 6′-methyl and 6′-ethyl derivatives of Isoquinoline Red.[50] A few years later, a different dye, the true Quinoline Red, was synthesised from di-(2-quinolyl)-methane by heating with excess of benzylidene chloride at 100° and then with pyridine at 150–160°.[51] Although its absorption was like that of 2,2′-cyanine, it differed in showing yellowish red fluorescence. Consideration of the various possible formulae led to the adoption of III,


(II)

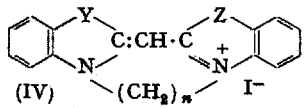

(III)

having an *NN′*-benzylidene group. Di-(2-quinolyl)methane also gave fluorescent dyes with methylene iodide or with ethylene dibromide, whence it was concluded that the ring containing two nitrogen atoms, whether it be six- or seven-membered, is the cause of the fluorescence.[52]

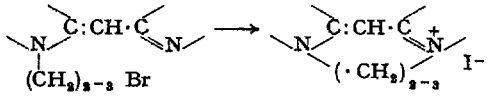
Salts obtained by heating a 2-methyl heterocyclic base with a dihalogenoalkane were described in 1939 and were then believed to have a 2,3-tri- or a 2,3-tetra-methylene group (see IX-1).[53] In a patent specification, however, they were formulated as diquaternary with an *NN′*-di- or an *NN′*-tri-methylene chain.[54] In 1949 symmetrical *NN′*-alkylene methincyanines were synthesised by heating a di-heterocyclylmethane with an alkylene arylsulphonate, $ArSO_3(\cdot CH_2)_{2-3}\cdot SO_3Ar$, at 150–200°, followed by treatment with an acid-binding agent, such as triethylamine in methanol. The reaction is indicated in equation 5.


(5)

Examples included the 2,2′-, oxa-, and thia-cyanines, IV (Y=Z= CH:CH, O, or S, n=2), and yields, after recrystallisation, were 5%,

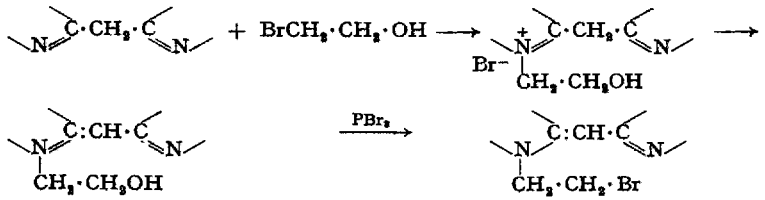

(IV)

8 %, and 38 %, respectively.[55] The benzimidazolocyanines, IV (Y=Z=NEt, n=1 or 2), were made.[56] A method for preparing both symmetrical or unsymmetrical methincyanines consisted in heating an *N*-bromoalkylenecyanine base at 170° for 4 hours, then treating with sodium iodide (equation 6).



(6)

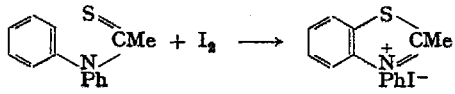
It was applied to the preparation of two thiacyanines, IV (Y=Z=S n=2 or 3), the latter as bromide, and a thia-2'-cyanine, (Y=S, Z=CH:CH, n=2). A base required as starting point was prepared from di-(2-benzothiazolyl)methane as indicated in equation 7.[57]



(7)

C. *N*-Aryl Groups

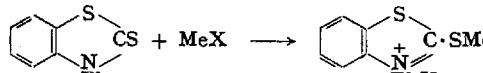
The first mention of *NN'*-diphenyl groups in a cyanine molecule appeared in 1942, when 2-methylbenzothiazole pheniodide and *o*-nitropheniodide, also 2-β-acetanilidovinylbenzothiazole pheniodide and 2-methylthiobenzothiazole phenotoluene-*p*-sulphonate were used. Dyes with *NN'*-diphenyl groups were a thiacyanine, prepared by the little-used malonic acid method (II-6-D), a thiacarbocyanine, and a thiadicarbocyanine; the *NN'*-di-(*o*-nitrophenyl) analogue of the last was also made. Dyes with one *N*-phenyl or *N*-*o*-nitrophenyl group were pairs of thia-4'-cyanines, -carbocyanines, and -dicarbocyanines, also styryl dyes.[58]



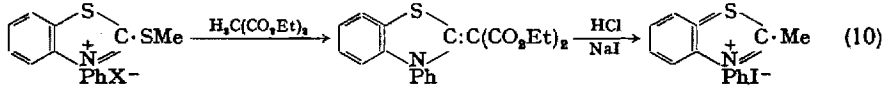
(8)

2-Methylbenzothiazole pheniodide was prepared in low yield (equation 8) by heating thioacetyldiphenylamine with iodine and sodium acetate in 90 % acetic acid, and reducing the resultant tri-iodide with sulphur dioxide in ethanol.[59,60] The ring-closure was later effected

with bromine in chloroform,[61] and an *NN'*-diphenylthiacarbocyanine was described.[62] Further, 2-oxo-3-phenylbenzothiazoline[63] was converted into the 2-thio-compound, which on heating with alkyl toluene-*p*-sulphonate gave the 2-alkylthio-3-phenylbenzothiazolium salt (equation 9).[64] This, by the stages of equation 10, gave the corresponding 2-methyl salt.[65] A third method, which gave a 28 % yield of 2-methylbenzothiazole pheniodide, consisted in treating *o*-thioldiphenylamine

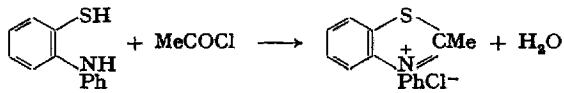


(9)



(10)

with acetyl chloride (equation 11) and converting the salt into iodide. The corresponding 2-ethyl-, 2-propyl-, and 2-benzyl-iodides were similarly made, in yields of 80 %, 45 %, and 28 %, respectively. From 2-methylbenzothiazole pheniodide, the ortho-ester method gave an 80 % yield of 3,3'-diphenylthiacarbocyanine iodide; its *meso*-methyl and -ethyl derivatives were prepared in yields of 56 % and 40 %. Its

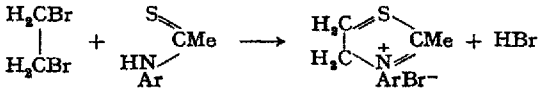


(11)

$\alpha\gamma$-dimethyl and -diethyl derivatives were prepared in yields of 72 % and 6 %. Its $\alpha\gamma$-diphenyl derivative resulted in 25 % yield when the medium was acetic anhydride but condensation did not take place in pyridine. Its $\alpha\gamma$-dibromo-derivative was prepared in 17 % yield, as bromide, and its $\alpha\gamma$-dibromo-β-methyl derivative in 22 % yield. Styryl compounds were also made.[66] Absorption data were given for these thiacarbocyanines as well as for unsymmetrical thiacarbocyanines with one or more *N*-phenyl groups: some also had an α- or $\alpha\gamma$-substituents.[67] A thiacyanine having one *N*-phenyl group was prepared in 60 % yield by the method (cf. II-5) involving 2-imino-3-phenylbenzothiazoline.[68] *p*-Toliodides of 2-alkyl-6-methylbenzothiazole were condensed with ortho-esters in pyridine to give 6,6'-dimethylthiacarbocyanines, some of which had $\alpha\gamma$-dimethoxy- or -dimethyl, or a β-methyl, -ethyl, or -phenyl substituent.[69] 2-Alkylbenzothiazole cyclohexiodides were syn-

thesised and were condensed with ortho-esters in pyridine to give 3,3'-di-(cyclohexyl)thiacarbocyanine iodide, and its *meso*-methyl and -ethyl derivatives, the last being as perchlorate; also the perchlorates of its $\alpha\gamma$-dimethyl and -dimethoxy-derivatives.[70]

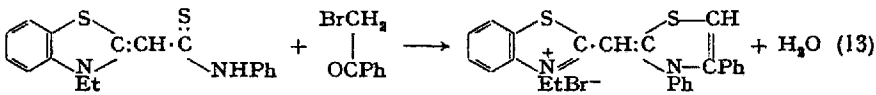
NN'-Diarylthiazolinocarbocyanines, including those with a *meso*-methyl or -ethyl group, were prepared, by the ortho-ester and pyridine method, from 3-aryl-2-methylthiazolinium salts.[71] These salts were synthesised by condensing ethylene dibromide with *N*-thioacetylarylamine (equation 12). An *N*-phenyl or an *N*-α-naphthyl group was thus introduced.[72]



(12)

Sensitising by some types of cyanine containing a 4-methyl-3-phenyl(or *p*-chlorophenyl)-thiazole nucleus was patented.[62] Condensation of 2,4-dimethylthiazole pheno(or α-naphtho)-perchlorate with ethyl orthoformate in pyridine gave 14 % and 9 % yields of the *NN'*-diarylthiazolocarbocyanines. Analogues in which each diphenyl group had a *p*-methoxy- or *p*-dimethylamino-substituent were described. An *NN'*-diphenylthiazolocarbocyanine was prepared in 17 % yield. Two thiathiazolocarbocyanines were made, one having *N*-phenyl, and the other *N*-α-naphthyl, in the thiazole nucleus. An unsymmetrical thiazolocarbocyanine was accompanied by another dye.[73] A thiazolo-2'-cyanine having one *N*-phenyl group was prepared by fusing 4-methyl-3-phenyl-2-thiothiazoline, 2-methylbenzothiazole, and methyl toluene-*p*-sulphonate, then boiling with pyridine.[74]

Methincyanines with an *N*-arylthiazole nucleus were synthesised by heating a 2-arylamino-2-thioethylidene compound with an α-halogenoketone, (e.g., equation 13).[75] This dye might be called [2-(3-ethylbenzothiazole)][2-(3,4-diphenylthiazole)]methincyanine bromide.

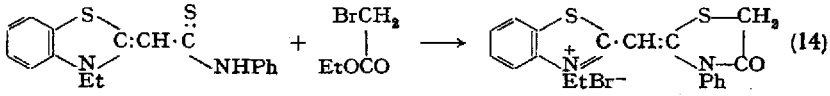


(13)

The examples comprised dyes of the thiazolocyanine, thiazolo-2'- and thiazolo-4'-cyanine, and of the indo-, selena-, thia-, and thiazolinothiazolocarbocyanine types.[75]

Methincyanines with a 3-aryl-4-thiazolidone nucleus were syn-

thesised by heating a 2-arylamino-2-thioethylidene compound with a halogeno-ester, (e.g., equation 14), and converting to iodide.[76] Alternatively, a halogeno-acid could be used.[77] The name [2-(3-ethylbenzothiazole)][2-(4-oxo-3-phenylthiazoline)]methincyanine bromide describes the dye of equation 14. The 4,5-benzo-derivative of the bromide

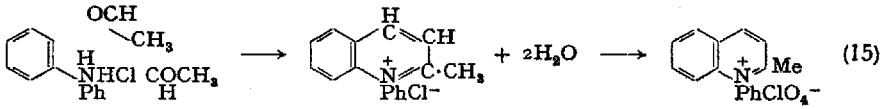


(14)

was made, also the thiazolino-2′-cyanine, as perchlorate.[76] Such dyes could be converted into certain types of trinuclear dyes (XV-5-A and B). Diazotised amines coupled with dyes such as that of equation 14, in the 5-position, to give azo dyes.[78]

The preparation of salts such as the phenoperchlorates of 2,3,3-trimethylindolenine and 2-β-acetanilidovinyl-3,3-dimethylindolenine made possible the synthesis of a symmetrical indocarbocyanine having *NN′*-diphenyl groups, whilst one 3,3-dimethyl-*N*-phenylindolenine nucleus was introduced into a styryl dye, a dimethinpyrrolo-dye[79] and into six unsymmetrical carbocyanines, for which optical data were given.[80]

Quinaldine phenoperchlorate was synthesised in 1951 from diphenylamine hydrochloride and paraldehyde in dioxane (equation 15).[81] Instead of paraldehyde, there could be used acetaldehyde, aldol, or crotonaldehyde and an oxidising agent was advantageous.[82] From the



(15)

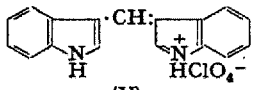
salt there were prepared an *NN′*-diphenyl-2,2′-carbocyanine, also an indo-2′- and a thia-2′-carbocyanine in which the quinoline nucleus had an *N*-phenyl group.[81] Seven other *N*-arylquinaldinium, or substituted quinaldinium salts were synthesised, in which the aryl group was phenyl, *o*- or *p*-tolyl, or α- or β-naphthyl, the yields varying from 10–25 %.[83] A series of *NN′*-diaryl-2,2′-carbocyanines, mostly perchlorates, comprised dyes with *NN′*-diphenyl, *NN′*-di-*o*- or *NN′*-di-*p*-toluidyl-, or *NN′*-di-α-, or -β-, naphthyl groups, including derivatives with 6,6′-dimethyl, or 5,6,5′,6′- or 7,8,7′,8′-dibenzo-substituents: two dyes had a *meso*-methyl group. The presence of an *N*-aryl group activated the 2-methyl group of the quinaldinium salt, hence its reaction

with ethyl orthoacetate. Replacement of the *NN'*-diethyl groups of a 2,2'-carbocyanine by *N,N'*-diphenyl or *N,N'*-dinaphthyl groups gave bathochromic shifts of 100–120 Å and 140–180 Å, respectively.[84] These *N*-aryl groups were also introduced into the molecules of nine thia-2'-carbocyanines. The intensity of absorption of each was less than that of the corresponding pairs of symmetrical carbocyanines.[85] The same *N*-arylquinaldinium perchlorates were used in the preparation of nine indo-2'-carbocyanines. As in the other series, an additional phenylene in the *N*-aryl group had little effect on the absorption.[86] 5,6-Benzoquinaldine *p*-tolochloride was used in the preparation of a symmetrical 2,2'-carbocyanine, also of a 2,4'- and a thia-2'-cyanine, a styryl dye, and an indo-2'- and a thia-2'-carbocyanine, all iodides; absorption data were given.[87] The syntheses of *N*-arylquinaldinium salts having 7,8-benzo-, 8-hydroxy-, or 8-methyl substituents were described, and of various symmetrical and unsymmetrical carbocyanines prepared from them, also of styryl compounds.[88] Quinaldine *m*-nitrophenoperchlorate gave an *NN'*-di-(*m*-nitrophenyl)-2,2'-carbocyanine. One such group was introduced into the molecules of a 2,4'-cyanine and of an indo-2'- and thia-2'-carbocyanine; yields were 41–57 %.[89]

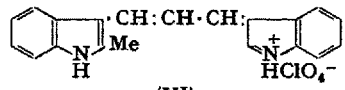
D. *NN'*-diH Structure

Dyes with the *NN'*-diH structure, although not true cyanines, cannot be omitted.

The compound V, which gave a red methanolic solution, was described in 1911 as obtained by dissolving indole in very little alcohol and treating with ethyl orthoformate and the calculated amount of



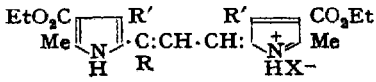
(V)



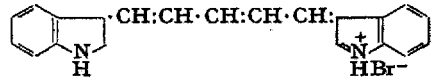
(VI)

acid. 2,5-Dimethylindole could be used similarly, also 5-methyl-2-phenylpyrrole, whilst 3-methylindole gave a violet-red dye.[90] In 1925, the trimethin dye, VI, was obtained in 60% yield by heating 2-methylindole for 1 hour with 1,1-diethoxyprop-2-yne and excess of perchloric acid; its 5,5'-dimethyl derivative was also described, and the sodium salts of both. An 80 % yield of VII (R=H, R'=Me, X=Cl) was obtained by heating 3-carbethoxy-2,4-dimethylpyrrole with 1,1-diethoxyprop-

2-yne in alcoholic hydrochloric acid.[91] Just as the ring of pyridine cyanobromide could be ruptured by certain amines (see VIII-1), so it could be ruptured by α-methylindole, and its derivatives, and the pentamethin dye, VIII, was described in 1913.[92]

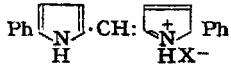


(VII)



(VIII)

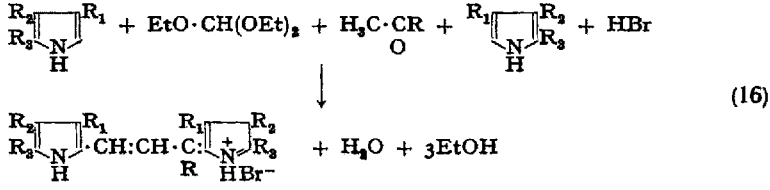
In 1929 the methin dye, IX (X=Cl), occurred as a by-product in the synthesis of 2-formyl-5-phenylpyrrole from 5-phenylpyrrole, zinc cyanide, and hydrochloric acid.[93] In 1944, the 3,3′-diphenyl- and 4,4′-dicarbethoxy-5,5′-dimethyl analogues of IX (X=Br) were prepared by



(IX)

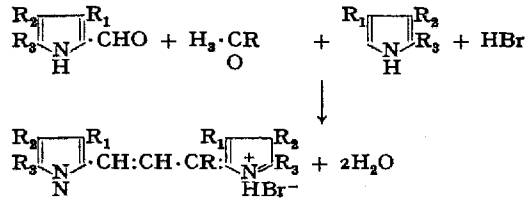
the action of ethyl orthoformate and hydrobromic acid in acetic acid on the appropriate pyrrole. The trimethin dye, VII (R=H, R′=Ph, X=Br), was prepared from 4-carbethoxy-5-methyl-3-phenylpyrrole by two routes; the first involved heating it with 1,3,3-triethoxyprop-1-ene and hydrobromic acid; the second consisted in heating it with 4-carbethoxy-2-formyl-5-methyl-3-phenylpyrrole, acetaldehyde diethyl acetal, and hydrobromic acid.[94]

It was found that a mixture of a substituted pyrrole, ethyl orthoformate, hydrobromic acid, and acetone gave a blue colour, which was attributed to an α-methyltrimethin-dye (equation 16): ten such compounds were thus prepared. To confirm the structure, four were syn-



(16)

thesised from a pyrrole, a ketone, a 2-formylpyrrole, and acid (equation 17). Groups introduced into the α-position on the chain were methyl, ethyl, isobutenyl, phenyl, *p*-methoxyphenyl, and 2-naphthyl.[94]

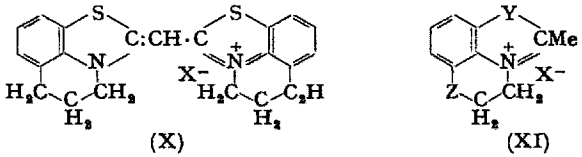


(17)

In 1950 absorption data for two thiacyanine analogues having the *NN'*-dihydro-structure were recorded[95] but without any indication of the method of preparation.

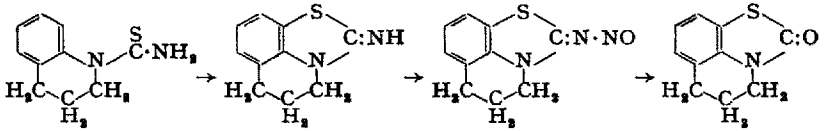
E. Heterocyclic Nitrogen Atom Linked by a Chain to Second Ring

A thiacyanine, X (X=I or ClO_4), having 3,4,3',4'-bis(trimethylene) groups dates from 1931. It was prepared by the method (II-6-A) in which methyl magnesium iodide acted on the 2-oxobenzothiazoline:

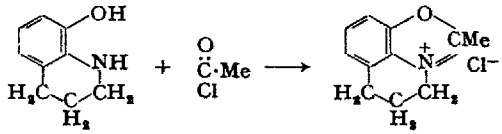


(X) (XI)

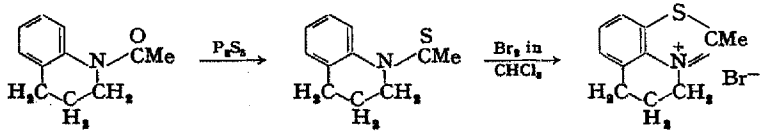
that was synthesised as indicated in equation 18.[96] In 1940 the preparation of salts such as XI (Y=O or S, Z=CH_2) was patented. The benzoxazolium salt was obtained in 80% yield by heating 8-hydroxy-1,2,3,4-tetrahydroquinoline with excess of acetyl chloride in a sealed



(18)



(19)



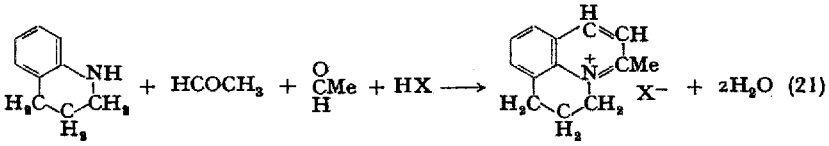
(20)

tube at 100° for 14 hours (equation 19), and the benzothiazolium salt similarly. Alternatively the latter could be prepared as indicated in equation 20. The salts were used in the preparation of dyes of the thiacarbocyanine, *meso*-methyl- or -ethyl-thiacarbocyanine, and thiatricarbocyanine types, with two 3,4-trimethylene groups, also of the following types with one such group: thia-2′-cyanine, *meso*-ethylselenathiacarbocyanine, and *meso*-ethylthiacarbocyanine.[97] Supersensitising by a pair of dyes in which at least one had one or both heterocyclic nitrogen atoms linked to a second ring was patented. Besides dyes with 3,4-trimethylene-benzoxazole or -benzothiazole nuclei, others with a 1,8-trimethylenequinoline nucleus were claimed, also dyes derived from salts, XI (Y=O, S, or CH:CH, Z=O). The dyes described had only one nucleus of the special structure and were of the 2,2′- or thia-2′-cyanine types, also oxathiazolo-, *meso*-alkyl-thia-, or -selenathiacarbocyanines.[98] A thiacarbocyanine with a *meso*-methylthio-group and with one 3,4-trimethylene group was prepared by the method (VI-15) involving a 3,4-trimethylenebenzothiazolium salt having a 2-·CH:CMe(SMe) group.[99] Trimethincyanines having a 3,4-trimethylenebenzimidazole nucleus were good sensitisers; in the examples, the other nucleus was benzoselenazole, indolenine, or thiazoline.[100]

The method used for the synthesis of 2-methylbenzothiazole pheniodide (section 4-C) was also applied to the synthesis of XI (Y=S, $Z=CH_2$). The salt was used in the preparation of a 3,4,3′,4′-bis(trimethylene)thiacarbocyanine[59,60] and there were also described an oxathiacarbocyanine and a thia-2′-cyanine each with one 3,4-trimethylene group.[59] Methin-, trimethin-, and pentamethin-cyanines, having at least one 3,4-trimethylenebenzothiazole nucleus, were patented as sensitisers.[101] The β-ethyl, αγ-dimethyl, and αγ-diethyl derivatives of 3,4,3′,4′-bis(trimethylene)thiacarbocyanine iodide were prepared in yields of 6 %, 20 %, and 12 % by the ethyl orthoformate and pyridine method, also its αγ-methylene and -dimethylene derivatives.[102]

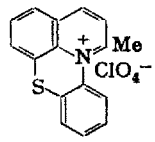
In 1953, methin- and trimethin-cyanines with a 1,8-bridge in a 2-linked quinoline nucleus were described. The 1,8-linking could be made through such groups as di- or tri-methylene, *o*-phenylene, *o*-cyclopentylene or -hexylene. The malonic acid method (II-6-D) was used for a 2,2′-cyanine with two 1,8-dimethylene groups. Other dyes with two 1,8-bridging groups were exemplified by 2,2′- and 4,4′-carbocyanines. Dyes with one 1,8-bridging group were of the 2,2′-, 2,4′-, and thia-2′-cyanine types, and of the oxa-2′-, oxa-4′-, *meso*-ethylthia-2′-, and

thia-4′-carbocyanine types, also dimethinmerocyanines and styryl dyes.[103] The 2-methyl salts were prepared by condensing the acid addition salt of an aromatic secondary amine, e.g., tetrahydroquinoline, with acetaldehyde, paraldehyde, aldol, or crotonaldehyde, in the presence of an oxidising agent, e.g., ferric chloride or *m*-nitrobenzene (equation 21). Used in place of tetrahydroquinoline, indoline led to a



(21)

1,8-dimethylene-, 2,3-trimethyleneindoline to a 1,8-*o*-cyclopentylene- and carbazole to a 1,8-*o*-phenylene bridge;[104] use of phenothiazine gave XII, where the 1,8-bridge is part of a thiazine nucleus.[103]

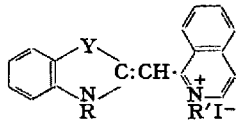


(XII)

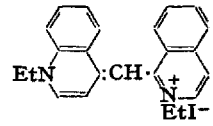
5. Use of Unusual Nuclei

A. Nuclei with Nitrogen as the One Hetero-Atom

It was noted in 1886 that isoquinoline differed from quinoline in that its quaternary salts did not condense with those of lepidine or quinaldine to give cyanine dyes.[105] Although in 1934 a 9 % yield of dye was, on the contrary, obtained by the action of alkali on the ethiodides of isoquinoline and quinaldine, the reaction did not appear to be general. However, 1-iodoisoquinoline alkiodides were prepared at that time and, by an extension of the 2′-cyanine condensation (II-2) gave rise to various types of dyes, which were conveniently described as 1′-cyanines. Thus condensation with quinaldinium salts gave five dyes of the 2,1′-cyanine type, XIII (Y=CH:CH), yields varying from 23–70 %. Condensation of the ethiodides of 1-iodoisoquinoline and lepidine, by use of triethylamine in ethanol, followed by recrystallisation, gave a 56 % yield of XIV.[106] By use of 2-methylbenzothiazolium salts, four thia-1′-cyanines, XIII (Y=S), were prepared in yields of



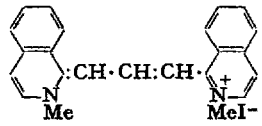
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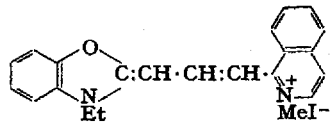
(XIV)

40–52 %,[106,107] whilst ethiodides of 2-methylbenzoselenazole and 1-iodoisoquinoline gave XIII (Y=Se, R=R'=Et). By reaction of 2,4-dimethylthiazole ethiodide and 1-iodoisoquinoline methiodide, a thiazolo-1'-cyanine was made. Comparing 2,2'- with 2,1'-cyanine, 2,4'- with 4,1'-cyanine, thia-2'- with thia-1'-, and selena-2'- with selena-1'-cyanine, i.e., pairs of dyes in which the carbon chain joining the nitrogen atoms is of the same length, the colours were similar, but the sensitising properties of cyanines with isoquinoline nuclei were poor compared with those of cyanines with quinoline nuclei.[106] Later on, the 6-chloro- and 6-bromo-derivatives of the thia-1'-cyanines, XIII (Y=S, R=R'=Et, X=I), were prepared in 52 % and 56 % yields, by means of potassium carbonate as condensing agent.[108] Twenty years later, the *meso*-methyl and -phenyl derivatives of the thia-1'-cyanine, XIII (Y=S, R=R'=Et), the former as perchlorate, were prepared, in yields of 72 % and 36 %, by use of 2-ethyl- or 2-benzyl-benzothiazole ethiodide and triethylamine in ethanol.[109]

In 1922 it was recorded that the methyl group in 1-methylisoquinoline and its salts is highly reactive and the methiodide was used to give a styryl dye and an anil.[110] In 1950 1-methylisoquinoline methiodide was condensed with iodoform under the influence of potassium hydroxide in ethanol,[111] or with diethoxymethyl acetate by heating with triethylamine in pyridine for 3 hours[112] to give the symmetrical 1,1'-carbocyanine, XV; the yields were 51 %[111] and 47 %.[112]



(XV)

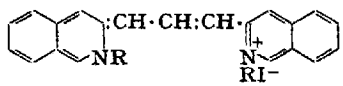


(XVI)

The methiodide reacted with 2-β-acetanilidovinylbenzoxazole ethiodide, by heating with triethylamine in pyridine, to give the oxa-1'-carbocyanine, XVI, in 28 % yield, and a thia-1'-carbocyanine was also

described.[111] Symmetrical 1,1′-carbocyanines, having two 3,4-dihydroisoquinoline nuclei, were prepared from 1-methyl-3,4-dihydroisoquinolinium salts by use of alkyl orthoformate.[113]

The observation in 1922 of the reactivity of the methyl group in 1-methylisoquinoline and its salts was coupled with that of its non-reactivity in 3-methylisoquinoline and this was correlated with the single-bond linkage between the nitrogen and the carbon atom in position 3.[110] This conclusion was accepted for nearly thirty years: it was then re-examined, because reactivity of the 3-methyl group was expected on account of its conjugation with the nitrogen atom round the periphery of the pyridine ring; further, according to modern theory, the linkage between nitrogen and the carbon atom in position 3 is a double bond in one of the three most probable contributing structures. It was found that 3-methylisoquinoline alkiodides, judged by their formation of styryl dyes (see XIII-1), or of dimethincyanines having a pyrrole nucleus (see below), would be rated as highly reactive, whereas other types of reaction would lead to the opposite conclusion: thus they failed to give methincyanines with 2-iodoquinoline ethiodide, or to condense with ethyl orthoformate in pyridine.[114] Boiling 3-methylisoquinoline alkiodide with ethyl orthoformate in isoquinoline for 45 minutes gave a 2 % yield of XVII (R=Me or Et);[114,115] an alternative

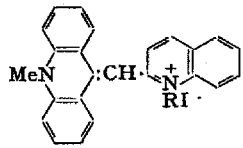


(XVII)

method was to heat with ethyl isoformanilide in nitrobenzene for 5 minutes.[114] It was concluded that the reactivity of the methyl group in 3-methylisoquinolinium salts depended on whether sufficiently basic conditions for liberation of the methylene base were applied. Since 3-methylisoquinolinium salts did not yield carbocyanines by reaction with trihalogenomethane and caustic alkali, intervention of a competing reaction, the formation of a carbinol base, was postulated.[114] The carbocyanine, XVII (R=Et), absorbed at a shorter wavelength than the corresponding 2,2′-carbocyanine, and even than the 2,2′-pyridocarbocyanine, of which it is the 4,5,4′,5′-dibenzo-derivative. For the uncharged 3-linked isoquinoline ring, one structure of the Kekulé type might written, but for the positively charged form three structures: hence high basicity was expected. It was confirmed by the absorption

maxima of the styryl dye and of the dimethincyanine with a pyrrole nucleus. From the data, it was concluded that the 2-ethyl-3-linked isoquinoline ring is the most basic yet met with. The remarkable observation that the dimethyl dye, XVII (R=Me), absorbs at a shorter wavelength by 340 Å than the diethyl dye, XVII (R=Et), was not explained.[116]

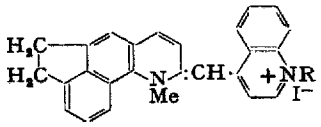
According to a patent of 1929, the methylene base from 9-methylacridine methiodide was one of those that gave on reaction with formic acid and acetic anhydride (see IV-7) a trimethincyanine.[117] The methiodide, however, gave a negative result in several normal cyanine condensations: e.g., it did not react with quinoline methiodide and sodium hydroxide in aqueous alcohol, nor did it give a carbocyanine by reaction with ethyl orthoformate in pyridine[118] or in acetic anhydride[119] but was found to do so in acetic acid.[120] Although it did not condense with 2-iodoquinoline alkiodide by the usual procedure (II-2) of boiling with potassium hydroxide in ethanol, reaction occurred when water was the medium. The resultant dyes, XVIII (R=Me or Et), may



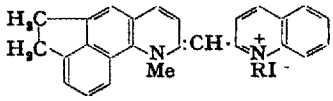
(XVIII)

be designated 2′,3′-benzo-2,4′-cyanines, but each showed one broad absorption band at about the same position as the stronger of the two narrow absorption bands characteristic of the parent 2,4′-cyanine. The two substances, XVIII, were not sensitisers.[118] 9-Methylacridine methiodide was caused to react with 4-β-acetanilidovinylquinoline ethiodide, by heating with potassium acetate in acetic acid, to give an acridino-4′-carbocyanine. Similarly it condensed with quaternary salts having a 2-β-anilinovinyl group to give trimethincyanines in which the second nucleus was a 2-linked quinoline or pyridine, oxazole, benzoxazole, thiazole, or indolenine.[120]

2-Methylacenaphthenopyridine methiodide was condensed with quinoline alkiodide to give the two 2,4′-cyanines, XIX (R=Me or Et), and with 2-iodoquinoline alkiodide to give the two 2,2′-cyanines, XX (R=Me or Et), all poor sensitisers; the latter reaction was abnormal in proceeding better in water than in ethanol.[118]

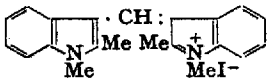


(XIX)

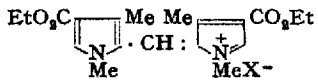


(XX)

The preparation of a methincyanine with indole nuclei was suggested in 1911, when it was mentioned that, besides indole itself (see X-4-D), *N*-alkylindole reacted with ethyl orthoformate and acid.[90] In 1940 such a methincyanine, XXI, was prepared in 35 % yield by fusing 1,2-dimethylindole and 3-formyl-1,2-dimethylindole, and adding



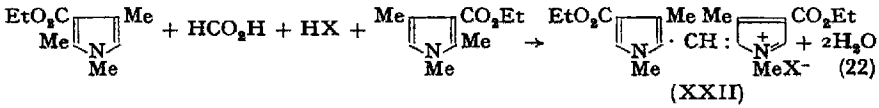
(XXI)



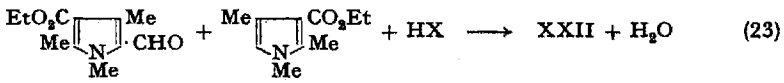
(XXII)

hydrochloric acid (cf. V-8), dissolving the product in ethanol, precipitating with sodium iodide, and recrystallising from methanol.[121] In 1956 symmetrical and unsymmetrical trimethincyanines, which might be α-substituted, and which had two 3-(1-alkyl-2-arylindole) nuclei, were patented as sensitisers for photographic emulsions for giving direct positives.[122]

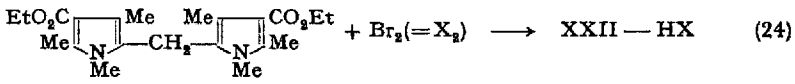
The first true cyanines having monocyclic 2-linked pyrrole nuclei, XXII (X=Cl, Br, or ClO_4), were synthesised in 1942 by reaction of a pyrrole, unsubstituted in the 2-position, with formic acid (equation 22), or by reaction of one molecule of pyrrole with one of a 2-formylpyrrole



(22)



(23)

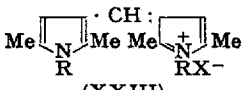


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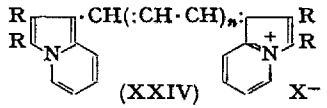
and acid (equation 23), or, thirdly, by the action of bromine on a 2,2′-dipyrrylmethane (equation 24).[123] It was not until 1945 that they were

named cyanines.[2] More precisely, they are 2,2′-pyrrolocyanines. In 1956 certain methin-, trimethin-, and pentamethin-cyanines of this type, with two 3,5-diphenylpyrrole nuclei, were described as useful anti-halation dyes.[124] Compounds such as 1-alkyl-2-formylmethylene-pyrrolidine or 5-methyl-2*H*-pyrroline ethiodide were used in the preparation of numerous sensitising trimethincyanines having one 2*H*-pyrroline nucleus; a trimethincyanine with two such nuclei, and a methincyanine with one, also sensitised (cf. XIII-1-M.1 and XIV-10-C.1a).[125]

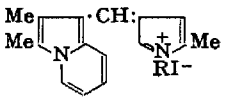
In 1945, 3,3′-pyrrolocyanines were described. Thus *N*-ethyl-2,5-dimethylpyrrole was caused to react with ethyl orthoformate and hydrochloric acid (cf. IV-6) to give the methincyanine, XXIII (R=Et); the *N*-phenyl-base reacted more smoothly with the corresponding 3-formylpyrrole to give XXIII (R=Ph). The method of preparing methincyanines in this series is similar to that which gives trimethincyanines when applied to quaternary salts having a reactive methyl



(XXIII)



(XXIV)

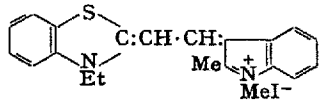


(XXV)

group. The absorption maxima of the pyrrolocyanines lay at a shorter wavelength than that of a 2,2′-pyridocyanine, although the latter has a shorter resonating chain. The corresponding trimethin analogues were obtained by reaction of the pyrrole bases with 1,3,3-triethoxy-prop-1-ene and acid (cf. VII-2); the vinylene shifts were 940 and 925 Å. The dyes were useful for anti-halation. Besides those with simple pyrrole nuclei, methin- and trimethin-cyanines with two pyrrocoline nuclei were patented, such as XXIV (n=0 or 1, R=Me, X=I or Br), both of which gave blue methanolic solutions. Unsymmetrical methincyanines were also claimed: e.g., XXV (R=$\cdot(CH_2)_{11}Me$) was prepared from 2,3-dimethylpyrrocoline, 1-dodecyl-3-formyl-2,5-dimethylpyrrole, and hydrochloric acid in aqueous alcohol, followed by sodium iodide.[126] The trimethincyanine, XXIV (n=1, R=Ph), was prepared by boiling 2,3-

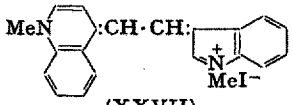
diphenylpyrrocoline, 1,3,3-trimethoxyprop-1-ene, potassium bromide, and acetic acid.[127] Subsequently 2,2′-dialkyl (or diphenyl)-5,5′-dialkyl-3,3′-pyrrolocyanines were prepared by heating a pyrrole, unsubstituted in the 3-position, with excess of formic acid. As the dyes were decolorised by weakly alkaline solutions and were photographically inert, they were suitable for anti-halation layers.[128] Other 3,3′-pyrrolocyanines, for this purpose, had *NN*′-di(carboxymethyl) groups, besides alkyl groups in the 2,2′,5,5′-positions: they were made by reaction of the pyrrole with excess of ethyl orthoformate at room temperature for 1 hour, or with excess of formic acid by boiling for 5 minutes, followed by treatment with acid.[129]

In 1912 dimethin dyes with one 3-linked indole nucleus, having an *N*H group, were prepared by condensing quinaldinium or lepidinium salts with 3-formyl-2-methylindole, by boiling with piperidine in methanol; 2- and 4-picolinium and 9-methylacridinium salts condensed likewise.[130] In 1940 a true dimethincyanine was prepared from 2-methylbenzothiazole ethotoluene-*p*-sulphonate and 3-formyl-1,2-dimethylindole by boiling them in acetic anhydride for 5 minutes, the product being converted by sodium iodide into XXVI, which was obtained in 87 % yield and was recrystallised from methanol. It was obtained in theoretical yield by boiling the anhydronium base having

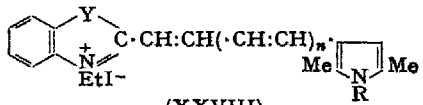


(XXVI)

an *N*-ethylbenzothiazoline nucleus with excess of methyl iodide in nitrobenzene for 4 hours, and in 39 % yield by boiling the anhydronium base having a 1,2-dimethylindole nucleus (see XI-6) with excess of ethyl iodide for 6 hours. The dimethincyanine, XXVII, was similarly



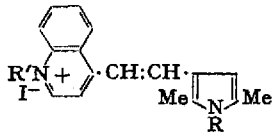
(XXVII)



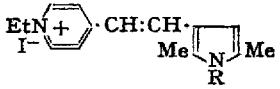
(XXVIII)

prepared from lepidine methiodide and 3-formyl-1,2-dimethylindole in acetic anhydride, and was also made from each of two isomeric bases (see XI-6) by boiling with methyl iodide in nitrobenzene.[131]

Dimethincyanines with one 3-linked pyrrole nucleus were described in 1945. For instance, heating 2-β-acetanilidovinylbenzoxazole ethiodide with 1-ethyl(or phenyl)-2,5-dimethylpyrrole in acetic anhydride for 5 minutes, and recrystallising from ethanol, gave a 43% (or 26%) yield of XXVIII (Y=O, n=0, R=Et or Ph). A benzothiazole analogue, XXVIII (Y=S, n=0, R=Et), was similarly made; it, and the corresponding *N*-phenyl compound, were also prepared from 2-methylbenzothiazole ethiodide by heating with 1-ethyl(or phenyl)-3-formyl-2,5-dimethylpyrrole and piperidine in ethanol for 45 (or 30) minutes, and recrystallising from methanol (or ethanol), both yields being 32%. The pairs of indolenine analogues, XXVIII (Y=CMe_2, n=0, R=Et or Ph) (yields 50% and 16%), of 4-quinoline analogues, XXIX (R=Et or Ph, R'=Et) (yields 39% and 25%), and of 4-pyridine analogues, XXX (R=Et or Ph) (yields 32% and 5%), were similarly made.[2] Such dimethincyanines, also their analogues with an indole or



(XXIX)



(XXX)

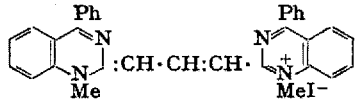
pyrrocoline, instead of a pyrrole, nucleus proved useful filter dyes. Examples included one compound with a 2-quinoline nucleus and another, where the pyrrole nucleus had an *N*H-structure.[131] Two particular dimethincyanines, *viz.* the 6'-methoxy-[132] and the 6'-dimethylamino-[133] derivatives of XXIX (R=Ph, R'=Me), as chloride or iodide, were found useful in treating worm infestations. A dimethinpyrrolothiacyanine with the zwitterionic group $\overset{+}{N}{=}CH_2CH_2SO_3^-$ (section 4-A) was readily soluble in mild alkali.[134]

The two tetramethin dyes, XXVIII (Y=O, n=1, R=Et or Ph), were prepared by boiling 1-ethyl(or phenyl)-2,5-dimethylpyrrole, 2-(4-ethoxy-1,3-butadienyl)benzoxazole ethiodide, and acetic anhydride for 5 minutes, and recrystallising from ethanol (or methanol), the yields being 33% and 16%. The corresponding pair, XXVIII (Y=S, n=1, R=Et or Ph), was made similarly, in yields of 71% and 32%. The absorption data of the unsymmetrical di- and tetra-methinpyrrolocyanines were remarkable; each of the four dyes, XXVIII (Y=O, R=Et or Ph, n=0 or 1), absorbed at a shorter wavelength than either of the two related symmetrical dyes.[2]

Methin dyes, such as XXIII, have been called pyrrolocyanines and their trimethin analogues have been called pyrrolocarbocyanines; a dimethin dye, such as XXVIII (Y=O, n=0), has been named an oxa-pyrrolocarbocyanine.[2] With this exceptional series, however, it seems far better to use the unequivocal systematic nomenclature. Thus, XXVIII (Y=O, n=0, R=Ph) would be [2-(3-ethylbenzoxazole)]-[3-(2,5-dimethyl-1-phenylpyrrole)] dimethincyanine iodide.

B. Nuclei, Including Complex Nuclei, with Two Nitrogen Atoms as the Only Hetero-Atoms

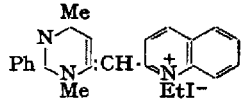
As early as 1922 it was noted that the condensation of ethyl orthoformate (IV-6) or of 1,3,3-triethoxyprop-1-ene (VII-2) with a salt having a reactive methyl group might be applied to an alkyl halide of 3-alkyl(or aryl)-4-oxo-3,4-dihydroquinazoline.[135] Ten years later, 2-methyl-4-phenylquinazoline methiodide was condensed with ethyl orthoformate in pyridine to give the carbocyanine, XXXI. This differed



(XXXI)

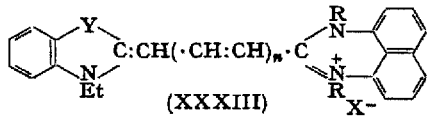
from a 2,2′-carbocyanine in having two equal absorption bands and in being photographically inert.[136] In 1933 methincyanines were prepared by heating a diazine, such as 4-methylthioquinazoline or 2,4-di(methylthio)-pyrimidine with a heterocyclic base, having a reactive methyl group, and ethyl toluene-p-sulphonate (cf. II-4).[137] Since exchange of radicals might occur (see II-A), the nature of the N-alkyl group in the diazine nucleus is doubtful. Moreover it remained undetermined whether the 1- or the 3-nitrogen atom became quaternary: this applied also to a carbocyanine prepared from 2,4-dimethylquinazoline ethiodide and ethyl orthoformate in pyridine.[137] Both 2-methylthioquinazoline and 2,4-di-(methylthio)pyrimidine were condensed with indene and methyl (or ethyl) toluene-p-sulphonate (cf. IX-2).[138] A salt of each base was also used in the malonic acid method (II-6-D) of synthesising symmetrical methincyanines.[139] In 1949, pyrimido-2′-cyanines, such as XXXII, were patented as useful therapeutics for worm infestations. This compound was prepared from 4,6-dimethyl-2-phenylpyrimidine

methiodide and 2-iodo(or 2-arylthio)-quinoline ethiodide with triethylamine in ethanol.[140] In 1950 photo-sensitising trimethincyanines and a methincyanine, each having a 3-alkyl-4-oxohexahydroquinazoline nucleus, were patented[141] (cf. XIII-1-M.1 and XIV-10-C.1b).



(XXXII)

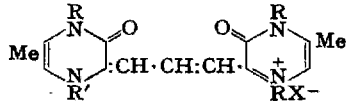
A study of 1-alkylperimidine, which comprises a six-membered nucleus with nitrogen atoms in the 1,3 positions, was published in 1955.[142, 143] This type of base was converted into quaternary salts by means of alkyl toluene-*p*-sulphonates. From these salts and the 2-*β*-acetanilidovinyl derivatives of other heterocyclic salts, with triethylamine in ethanol, three trimethincyanines, XXXIII (n=1, Y=O, R=Et, X=ClO_4 and n=1, Y=S or CH:CH, R=Me, X=I), were prepared. A methincyanine, XXXIII (n=0, Y=S, R=Et, X=I), was prepared



(XXXIII)

by heating the ethotoluene-*p*-sulphonates of 1-ethyl-2-methylperimidine and 2-ethylthiobenzothiazole with triethylamine in ethanol.[143] Condensation of a 2-methylperimidinium salt with ethyl orthoformate could not be brought about.[142] Merocyanines (see XIV-1) and trinuclear dyes (see XV-3-E) were also made.

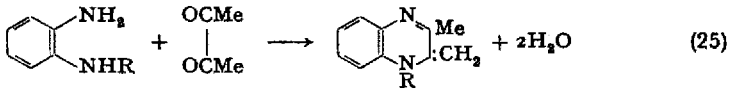
In 1936 the action of alkyl halides on 2,5-dimethyl- and 1,2,5-trimethyl-6-oxodihydropyrazine gave quaternary salts of these bases.



(XXXIV)

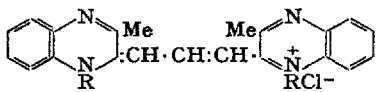
From them by use of ethyl orthoformate in acetic anhydride, there were prepared the carbocyanines, XXXIV (R=H or Me, R'=Me, X=Cl, Br, or I and R=H, R'=Et, X=Br or I), which were photographic sensitisers.[144]

2,3-Dimethylquinoxaline was converted into its methiodide with difficulty and an early attempt to condense this salt with quinoline methiodide (II-1) was unsuccessful.[145] Subsequently 2-methylene-1,2-dihydroquinoxalines were synthesised (equation 25), and were caused

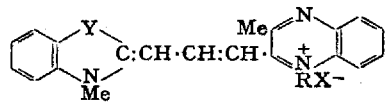


(25)

to react with sodium formate in acetic anhydride (IV-6-A) to give carbocyanines, XXXV (R=Me or Ph). The methylene bases also condensed with *N*-alkylindolines having the group :CH·CHO (cf. V-8) to give the indoquinoxalinocarbocyanines, XXXVI (Y=CMe_2, R=Ph, Me,

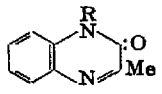


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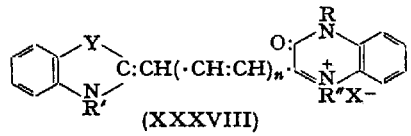


(XXXVI)

·$CH_2CH_2SO_3H$, ·CH_2Ph, or *p*-C_6H_4OEt), two of which had a 6-amino- or 6-chloro-substituent in the quinoxaline nucleus. They were reddish blue, blue, or greenish blue, and all desensitised strongly.[146] In 1942 it was recorded that 2,3-dimethylquinoxalinium salts could be formed when alkyl sulphonic esters or, better, alkyl sulphates, were used. Thus XXXVI (Y=CMe_2, R=Me or Ph, X=I or $MeCO_2$, respectively) were prepared by use of the formylmethyleneindoline: the condensing agent was boron trifluoride. By reaction of quaternary salts having the group ·CH:CH·NMePh (cf. V-6) with 2,3-dimethylquinoxalinium salts in pyridine, or in acetic anhydride with sodium acetate, there were prepared the dyes, XXXVI (Y=O or CH:CH, X=I or Cl, respectively). Condensation of 3-methyl-2-methylene-1-phenyldihydroquinoxaline with sodium formate in cold acetic anhydride containing acetyl chloride gave XXXV (R=Ph), or the corresponding acetate, contaminated by another dye.[147] Alkyl sulphates were used to make quaternary salts of the 3-oxodihydroquinoxalines, XXXVII (R=H or Me): no appreciable

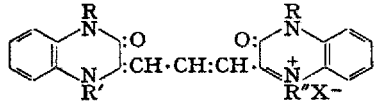


(XXXVII)



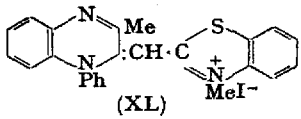
(XXXVIII)

N-alkylation of the former took place. Reaction with 2-*β*-anilinovinylquinoline methiodide gave the trimethincyanine, XXXVIII (n=1, Y=CH:CH, R=R′=R″=Me, X=I); the base from this methiodide was condensed with the methomethylsulphate of XXXVII (R=Ph), by use of pyridine in acetic anhydride, to give XXXVIII (n=1, Y=CH:CH, R=Ph, R′=R″=Me, X=SO_4Me). By interaction of 2-*β*-acetanilidovinylbenzoxazole methiodide, sodium acetate in acetic anhydride, and the methomethylsulphate of XXXVII (R=H), there was prepared XXXVIII (n=1, Y=O, R=H, R′=R″=Me, X=I). Thia-analogues, XXXVIII (n=1, Y=S, R=H or Me, R′=R″=Et, X=I), were prepared similarly; the base from *β*-methylanilinovinylbenzothiazole methiodide reacted with the methomethylsulphate of XXXVIII (R=Ph) and pyridine in acetic anhydride, followed by sodium chloride, to give XXXVIII (n=1, Y=S, R=Ph, R′=R″=Me, X=Cl). The compounds, XXXVIII (n=1, Y=CMe_2, R=H, Me, or Ph, R′=R″=Me, X=SO_4Me), were reached by condensing the methomethylsulphate of XXXVII (R=H, Me, or Ph) with 2-formylmethylene-1,3,3-trimethylindoline in acetic anhydride, and were sometimes converted into chlorides. The symmetrical carbocyanines, XXXIX (R=H, Me, or Ph,

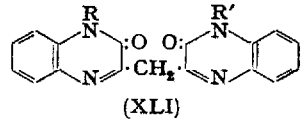


(XXXIX)

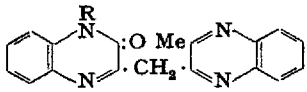
R′=R″=Me, X=SO_4Me), were prepared from the methomethylsulphates of XXXVII (R=H, Me, or Ph): for the first, diphenylformamidine in acetic anhydride was used, for the second and third, ethyl orthoformate and a little concentrated sulphuric acid in methanol. The compounds were described as useful dyes for acetate silk and tannin-mordanted cotton.[148, 149] The methincyanine, XXXVIII (n=0, Y=S, R=R′=R″=Me, X=I), was prepared by heating the methomethylsulphate of XXXVII (R=Me) with 2-methylthiobenzothiazole methiodide in pyridine. The same methiodide with 3-methyl-2-methylene-1-phenyldihydroquinoxaline in ethanol gave, as one product, the methincyanine XL. Fourteen disubstituted methanes, belonging to one of the four types XLI, XLII, XLIII, and XLIV (Y=CH:CH, O, or S), were synthesised. They gave intense colours in sulphuric acid but could not be converted into quaternary salts[150] which might have yielded methincyanines (see II-6-B).



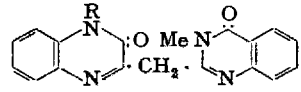
(XL)



(XLI)

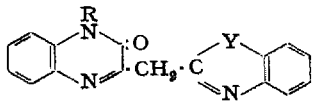


(XLII)

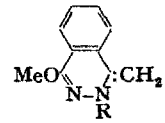


(XLIII)

In 1936 two methylene bases, XLV (R=*m*- or *p*-$C_6H_4NO_2$), having a 3,4-dihydrophthalazine nucleus were prepared: the methylene group was found to be reactive, like that in the methylene bases derived from

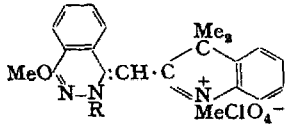


(XLIV)

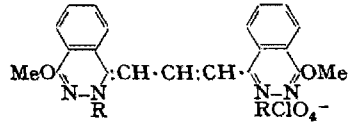


(XLV)

2-methylindoleninium or quinaldinium salts. By heating such a base with 3,3-dimethyl-2-(oximinomethyl)indolenine methoperchlorate at 100° for 1 hour there resulted the methincyanine, XLVI (R=*p*-$C_6H_4NO_2$). By heating a mixture of methylene base and its perchlorate with ethyl orthoformate or diphenylformamidine in acetic anhydride, the symmetrical carbocyanines, XLVII (R=*m*- or *p*-$C_6H_4NO_2$), were prepared.

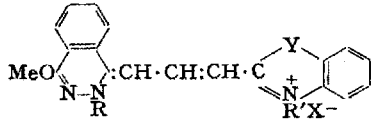


(XLVI)



(XLVII)

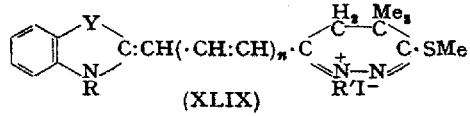
Reaction of methylene base with 2-*β*-acetanilidovinyl-3,3-dimethylindoline perchlorate in boiling acetic anhydride for 6 minutes gave the indophthalazinocarbocyanine, XLVIII (Y=CMe_2, R=*p*-$C_6H_4NO_2$, R'=Me, X=ClO_4); an analogue in which the 3-*N*-aryl group of the



(XLVIII)

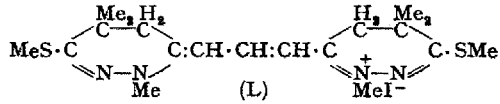
phthalazine nucleus was 2,6-dichloro-4-nitrophenyl was also made. In a derivative of the phthalazinothiacarbocyanine, XLVIII (Y=S, R=Et, X=I), the benzothiazole nucleus had a 6-chloro-substituent and the *N*-aryl group of the phthalazine nucleus was again 2,6-dichloro-4-nitrophenyl. All the dyes desensitised to some extent[151] but this may be entirely due to the nitro-groups and not to the phthalazine nucleus.

Another 1,2-diazine, pyridazine, was introduced into cyanine and merocyanine molecules in 1954. The methincyanine, XLIX (n=0, Y=S, R=Et, R′=Me, X=I), was prepared from 2-ethylthiobenzothiazole ethiodide, 4,4,6-trimethyl-3-(methylthio)dihydropyridazine methiodide,[152] and triethylamine in ethanol, by boiling for 2 hours. An *NN*′-dimethyl analogue was made by heating the appropriate bases with methyl toluene-*p*-sulphonate and boiling the resultant salt mixture with pyridine. Benzoxazole and 2-linked quinoline analogues of the first dye, and the 4-linked quinoline analogue of the second were isolated as perchlorates. Trimethincyanines having one dihydropyridazine nucleus were of the types XLIX (n=1, Y=S, O, or CMe_2), and one



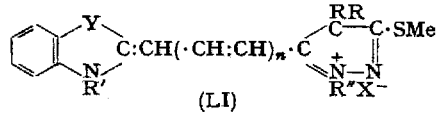
(XLIX)

with a 4-linked quinoline nucleus. The symmetrical carbocyanine, L, was also made.[153] Quaternary salts of substituted dihydropyridazines and pyridazines were used in the synthesis of methin- and trimethincyanines.[154]



(L)

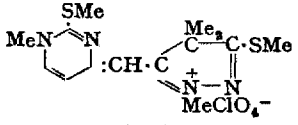
Turning to five-membered ring systems, the 1,2-diazole, pyrazolenine, was introduced into the molecules of cyanine and merocyanine sensitising dyes. The methincyanine, LI (n=0, Y=S, R=R′=R″=Me,



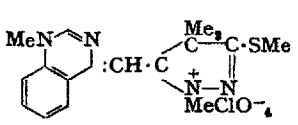
(LI)

X=I), was prepared by fusing 2-methylthiobenzothiazole and 4,4,5-trimethyl-3-methylthiopyrazolenine with methyl toluene-*p*-sulphon-

ate, boiling the salts with pyridine, and treating with sodium iodide. Methincyanines in which the other nucleus was a 1,3-diazine, as in LII or LIII, were also described. The unsymmetrical trimethincyanine LI (n=1, Y=S, R′=Et, R=R″=Me, X=I) was prepared and the corresponding benzoxazole and indolenine dyes, LI (Y=O or CMe_2) were isolated as perchlorates. There were also prepared LI (Y=

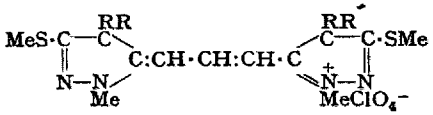


(LII)

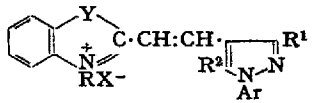


(LIII)

CH:CH, n=1, R=R′=R″=Me, X=ClO_4) and the 4-quinoline analogue. The symmetrical carbocyanine, LIV (R=Me), was prepared from 4,4,5-trimethyl-3-methylthiopyrazolenine methotoluene-p-sulphonate and

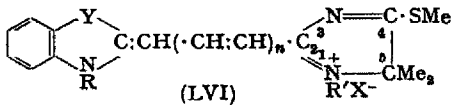


(LIV)



(LV)

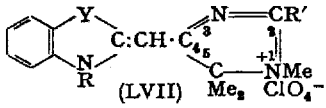
ethyl orthoformate in pyridine; so similarly was LIV (R=Et).[155] Dimethincyanines of type LV, prepared by reaction of a quaternary salt, having a reactive methyl group, and a 1-aryl-4-formylpyrazole, were described as useful for dyeing fibres.[156]



(LVI)

Methincyanines with a 1,3-diazole nucleus, namely a 5,5-disubstituted-4-alkylthioimidazolenine nucleus, were described in 1952. Thus reaction of quaternary salts of 5,5-dimethyl-2,4-di(methylthio)-imidazolenine and 2-methylbenzothiazole, by heating in pyridine, followed by sodium perchlorate, gave LVI (n=0, Y=S, R=R′=Me, X=ClO_4). Analogues of the types LVI (n=0, Y=O, Se, CMe_2, or CH:CH) were made, besides others in which the second nucleus was a thiazole, thiazoline, or 4-linked quinoline; the 5,5-dimethyl groups might be replaced by diethyl, diphenyl, cyclopentamethylene, or cyclo-

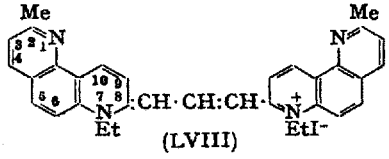
tetramethylene.[157] Such unsymmetrical methincyanines were alternatively prepared by reaction of a quaternary salt of a 5,5-disubstituted-4-alkylthio-2-methylimidazolenine[158] with a quaternary salt having an alkylthio-group; these imidazolenine salts also gave rise to unsymmetrical trimethincyanines of the types LVI (n=1, Y=O, S, CMe_2, or CH:CH, R=Me or Et, R′=Me, X=ClO_4), also an analogue with a 4-linked quinoline nucleus; instead of the 5,5-dimethyl groups, there might be a cyclopentamethylene group[159] On the other hand, 5,5-disubstituted-2-alkyl-4-alkylthioimidazolenine salts condensed, in the 4- instead of in the 2-position, with salts having a reactive methyl group, to give unsymmetrical cyanines such as LVII (Y=O, S, CMe_2, or



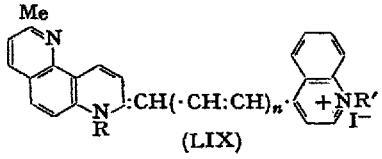
(LVII)

CH:CH, R=Me or Et), also analogues with a 4-linked quinoline nucleus. The group in the 2-position might be Me, Et, Ph, or ·CH_2Ph, whilst instead of the 5,5-dimethyl groups there might be 5,5-diethyl or a -cyclopentadiene group.[160] A methincyanine with one 1,2- and one 1,3-diazole nucleus was described.[155]

Complex bases having two nitrogen atoms, but in different rings, have also been used for making cyanine dyes. 2,8-Dimethyl-1,7-phenanthroline had been synthesised from *m*-phenylenediamine, and in 1934 its ethiodide was condensed with ethyl orthoformate in acetic anhydride, to give the carbocyanine, LVIII, for which absorption and sensitising data were given.[161] Ten years later the preparation of unsymmetrical cyanines from a salt with one so-called 1,5-phenanthroline nucleus, having a reactive group in the 2-position was patented, but the base was not formulated: it was, presumably, the same as in the earlier



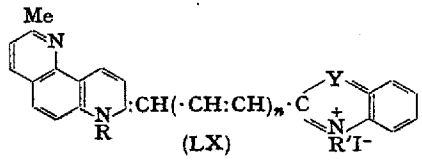
(LVIII)



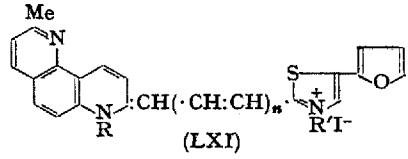
(LIX)

work. Methincyanines described were of the types LIX (n=0), LX (n=0, Y=O, S, Se, or CH:CH), LXI (n=0), and LXII; trimethincyanines were of the types LIX (n=1), and LX (n=1, Y=O, CMe_2, or S);

pentamethincyanines were of the types LX (n=2, Y=CMe_2 or S), and LXI (n=2). Sensitising properties were described.[162]

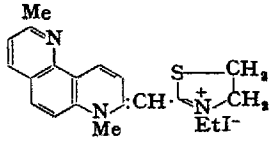


(LX)

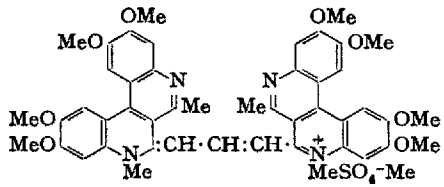


(LXI)

The symmetrical carbocyanine, LXIII, having complex nuclei, was synthesised by the pyridine and ethyl orthoformate method, in the hope that it would have anti-malarial power.[163]

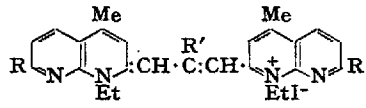


(LXII)



(LXIII)

In 1953 naphthyridine derivatives were recorded as giving high yields of carbocyanines, especially in acid media. Thus 7-acetylamino-2,4-dimethylnaphthyridine ethiodide on boiling with ethyl orthoformate in acetic anhydride gave a 90 % yield of LXIV (R=NHCOMe,

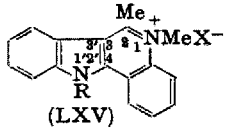


(LXIV)

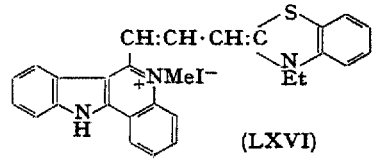
R'=H) but in an alkaline medium the yield was only 20 %. The analogue, LXIV (R=OMe, R'=H), was also made. *Meso*-methyl- and *meso*-ethyl-derivatives of the first dye were prepared. For comparison with LXIV (R=NHCOMe, R'=H, Me, or Et), the corresponding carbocyanines were prepared from 7-acetylamino-2,4-dimethylquinoline ethiodide. Chromatographic purification was carried out in both series and besides the principal absorption maximum attributed to the dyes with 2,2'-linkings, secondary maxima were attributed to the corresponding dyes with 2,4'- and 4,4'-linkings. As compared with the dyes having two quinoline nuclei, those with two naphthyridine nuclei

absorbed at a longer wavelength by nearly 200 Å. Merocyanines and trinuclear dyes were also made.[164]

2-Methylindolo(3′,2′-3,4)quinoline[165] was converted into its metho-toluene-*p*-sulphonate, LXV (R=H, X=$C_7H_7SO_3$); the corresponding 1′-methyl derivative, LXV (R=Me, X=$C_7H_7SO_3$), was also made: these salts were used for preparing cyanines. More rapid condensation and higher yields were usually obtained from the latter than from the former but, exceptionally, the trimethincyanine, LXVI, was prepared



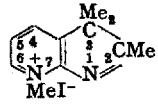
(LXV)



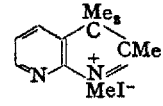
(LXVI)

from the former by reaction with 2-*β*-acetanilidovinylbenzothiazole ethiodide, whereas the latter did not give a satisfactory product. Other compounds that were prepared were of the styryl, anil, and azadimethincyanine types[166] (see XIII-1, XIII-2.B, and XII-7).

2,3,3-Trimethyl-3*H*-1,7-diazaindene gave two methiodides, LXVII and LXVIII, whence different series of cyanines and merocyanines were prepared; their absorption data were discussed.[167]



(LXVII)



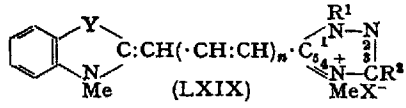
(LXVIII)

C. Nuclei with Three Nitrogen Atoms as Hetero-Atoms

In 1950 the 2,1,3-triazole nucleus was introduced into the molecules of dimethincyanines belonging to the azacyanine class (see XII-10).[168]

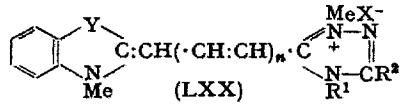
Three years later it was shown that a 5-methyl-1,2,4-triazole became quaternary at the nitrogen atom in position 4, the 5-methyl group being thereby activated.[169,170] Methincyanines having one such nucleus were LXIX (*n*=0, Y=S, R^1=R^2=Me, X=ClO_4) and LXIX (*n*=0, Y=S, R^1=Ph, R^2=Me, X=I). Trimethincyanines with a 1,2,4-triazole nucleus were of the types LXIX (*n*=1, Y=O, S, CMe_2, or

CH:CH, X=I or ClO_4), also a 4-linked quinoline analogue. Substituents in the 1-position of the triazole nucleus might be Me, Ph, or *p*-C_6H_4Cl, and in the 3-position Me, ·SMe, ·SEt, or ·SCH_2Ph.[169] Subsequently

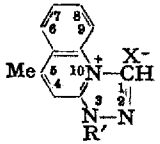


(LXIX)

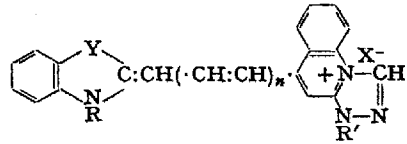
5-methyl-1,2,4-triazoles having a substituent on the 4-*N*-atom were made: on salt formation, the 1-*N*-atom became quaternary. Methincyanines with such a nucleus were LXX (*n*=0, Y=S, R^1=R^2=Ph, X=ClO_4; and *n*=0, Y=CH:CH, R^1=R^2=Ph, X=I). Trimethincyanines were of the types LXX (*n*=1, Y=O, S, CMe_2, or CH:CH), or with a 4-linked quinoline nucleus.[171]



(LXX)



(LXXI)



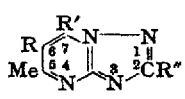
(LXXII)

In 1954 methin- or trimethin-cyanines having a triazolo[4,3-a]-quinoline nucleus were prepared from quaternary salts such as LXXI. Unsymmetrical methincyanines with this nucleus were LXXII (*n*=0, Y=S or CH:CH, R=R′=Et, X=ClO_4). An unsymmetrical trimethincyanine was LXXII (*n*=1, Y=S, R=R′=Et, X=ClO_4).[172]

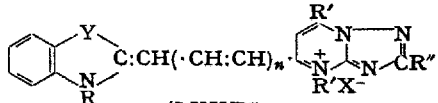
D. Nuclei with Four Nitrogen Atoms as Hetero-Atoms

Unsymmetrical cyanines, in which one nucleus had four nitrogen atoms, namely the *s*-triazolo[2,3-a] pyrimidine nucleus, were described in 1948. The starting points were quaternary salts of bases such as LXXIII having a reactive 5-methyl(or ethyl) group: twenty-two such bases were described. The nine examples included (a) methincyanines, LXXIV (*n*=0, Y=CH:CH or S), the latter dye being *meso*-substituted; (b) trimethincyanines, LXXIV (*n*=1, Y=S), including one with a

meso-ethyl group; (c) pentamethincyanines, LXXIV (n=2, Y=S or O), the latter compound having a *meso*-methyl group; (d) heptamethincyanines of the type LXXIV (n=3, Y=S), and its thiazoline analogue,



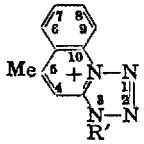
(LXXIII)



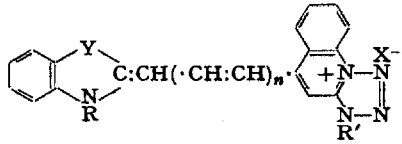
(LXXIV)

but the former dye had a *meso*-ethyl and an α-methyl group, being prepared from 5,7-diethyl-*s*-triazolo[2,3-a]pyrimidine ethiodide. The compounds were described as excellent sensitisers and appreciably water-soluble.[173]

Quaternary salts, LXXV, of 5-methyltetrazolo[a]quinoline were prepared in 1954. This nucleus was introduced into unsymmetrical methincyanines, LXXVI (n=0, Y=S or CH:CH, R=R′=Et, X=I), and into a trimethincyanine, LXXVI (n=1, Y=O, R=R′=Et, X=I).[172]

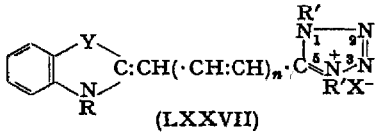


(LXXV)

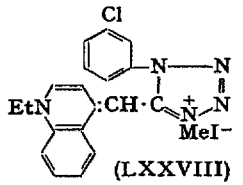


(LXXVI)

Simple 5-methyltetrazoles were converted into tetrazolium salts. These were used in the preparation of methincyanines, such as LXXVII (n=0, Y=S, R=R¹=Me, R¹=Ph, X=I, and n=0, Y=CH:CH, R=R′=Me, R¹=*p*-C_6H_4Me, X=I), and LXXVIII.[174] Various trimethincyanines of the types LXXVII (n=1, Y=O, S, Se, or CMe_2,



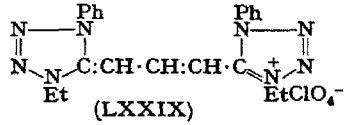
(LXXVII)



(LXXVIII)

X=I or ClO_4) were prepared.[174, 175] The 1-substituent might be Me, Ph, C_6H_{11}, *o*- or *m*-C_6H_4Cl, *p*-C_6H_4Me, *p*-C_6H_4OMe, *p*-C_6H_4Br, or 3,4- or

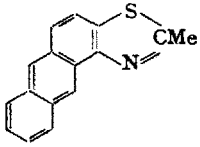
3,5-$C_6H_3Me_2$.[174] From 5-methyl-1-phenyl-1,2,3,4-tetrazole ethiodide there was prepared the symmetrical tetrazolocarbocyanine, LXXIX.[175]



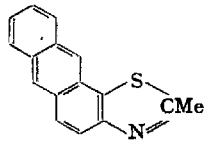
(LXXIX)

E. Nuclei with One Nitrogen and One Sulphur as Hetero-Atoms

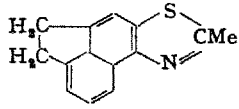
In 1931, the use of complex thiacarbocyanines, which might be *meso*-substituted, for sensitising to red light was patented. The ortho-ester method was used for the dyes, which were prepared from alko-alkylsulphates or alkotoluene-*p*-sulphonates of five bases, three of which, LXXX–LXXXII, had one nitrogen and one sulphur as hetero-



(LXXX)



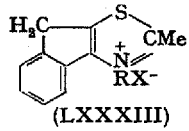
(LXXXI)



(LXXXII)

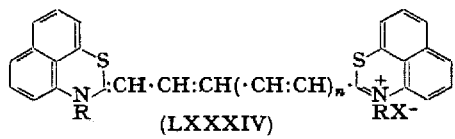
atoms (see also sections 5-F and G).[176] By the methods previously described (II-2, 1, and 3 respectively) these salts were also used for the preparation of complex thia-2′-, thia-4′-, and thiacyanines.[177] In other patents, two examples of unsymmetrical thiadicarbocyanines had as one nucleus LXXXI or LXXXII,[178] and two examples of unsymmetrical thiatricarbocyanines had as one nucleus LXXX or LXXXII.[179] In 1946 quaternary salts of LXXX and LXXXI were used in the preparation of complex thia-4′-cyanines and of thia-, thiadi-, and thiatri-carbocyanines. The dinaphthothiacarbocyanines had their absorption maxima at a longer wavelength by 615–635 Å than had the corresponding thiacarbocyanines. They were less good sensitisers than the dibenzothiacarbocyanines: because of their greater molecular weight, they were liable to coagulate in aqueous solution.[180] One acenaphthenothiazole nucleus, LXXXII, was introduced into the molecules of methin- and trimethin-cyanines, and of a styryl dye, and two such into a symmetrical tri- and penta-methincyanine. The absorption maxima lay at longer wavelength than corresponding dyes with a 4,5-benzo-

benzothiazole nucleus.[181] It was recorded in 1938 that a complex salt, LXXXIII, reacted with 2-iodoquinoline methiodide to give an easily soluble violet dye, which depressed sensitivity, did not sensitise, and caused fog, and was not regarded as being a thia-2'-cyanine.[182] This requires confirmation.

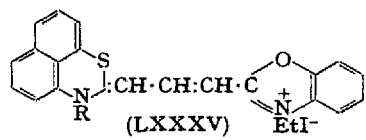


(LXXXIII)

Interesting nuclei containing one nitrogen and one sulphur atom in a six-membered ring have been used in the preparation of cyanines. In 1931 2-methylperinaphtho-1,3-thiazine was synthesised[183] but quaternary salts were not readily prepared. However from the methiodide and ethiodide there were made the carbocyanines, LXXXIV (n=0, R=Me or Et, X=I), which were devoid of sensitising action.[184] Subsequently, by short heating with ethyl orthoformate and pyridine, pure specimens of both dyes, free from solvent of crystallisation, were prepared. By use of methyl sulphate for salt formation, the carbocyanine, LXXXIV (n=0, R=Me, X=SO_4Me), was obtained in 53 %



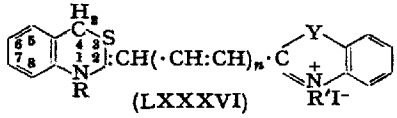
(LXXXIV)



(LXXXV)

yield. A 30 % yield of the dicarbocyanine, LXXXIV (n=1, R=Me, X=I), was obtained from the methiodide, 1-anilino-3-anilo-1,3-prop-1-ene hydrochloride, and potassium acetate in acetic anhydride, by reaction at 0° for 7 days. Alcoholic solutions of the carbocyanines and dicarbocyanine were reversibly bleached by alkali. By condensing 2-methylperinaphtho-1,3-thiazine with quaternary salts having a 2-β-acetanilidovinyl group, there were prepared the bases of unsymmetrical carbocyanines (see XI-7-C). By heating one of these with methyl or ethyl iodide, there were made the carbocyanines, LXXXV (R=Me or Et), which were weak sensitisers.[185]

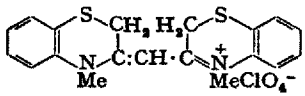
In 1942 attempts to convert 2-methyl-3,1,4-benzothiazine into quaternary salts were unsuccessful; the base, however, was condensed with quaternary salts, having a 2-β-acetanilidovinyl group, to give the bases of unsymmetrical carbocyanines (see XI-7-B). By heating two of these with ethyl iodide, the carbocyanines, LXXXVI (n=1, Y=O or



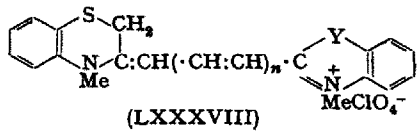
(LXXXVI)

S, R=R′=Et), were prepared. They were good sensitisers.[186] 2-Methylthio- and 2-ethylthio-3,1,4-benzothiazine were converted into the methiodide and ethiodide, respectively. In this series the exchange of radicals already noted (see II-4-A) was liable to occur. By condensation of the salts with others having a reactive methyl group, there were prepared four types of methincyanines, *viz.*, LXXXVI (n=0, Y=O, S, or CH:CH, R=R′=Et) and the analogue with a 4-linked quinoline nucleus, also derivatives of the first and second having a 6,7-benzo-substituent in the benzoxazole or benzothiazole nucleus. The methincyanine, LXXXVI (n=0, Y=CH:CH, R=R′=Me), was prepared, not only by the above method, but also by heating a base, having the alkyldihydro-structure either in the quinoline or in the 3,1,4-benzothiazine nucleus (see XI-7-A), with methyl sulphate and converting into iodide.[187] The method of heating together 2-ethylthio-3,1,4-benzothiazine, ethyl toluene-p-sulphonate, and a heterocyclic base having a reactive methyl group (see II-4-A) led,[188] in this series, not to methincyanines, but to the hydriodides of their bases. Absorption and sensitising data were given for the dyes, which comprised some powerful sensitisers.[187]

1,4,2-Benzothiazine is such a weak base that it cannot be converted into quaternary salts by the usual methods. However in 1951 such salts were synthesised from *N*-alkyl(or aryl)-*o*-aminothiophenols and α-halogenoketones.[189] In that year the symmetrical methincyanine, LXXXVII, was prepared by heating quaternary salts of 3-methyl- and 3-methylthio-1,4,2-benzothiazine with anhydrous sodium acetate in ethanol.[190] The unsymmetrical methincyanine, LXXXVIII (n=0,

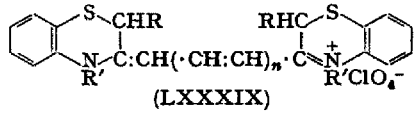


(LXXXVII)



(LXXXVIII)

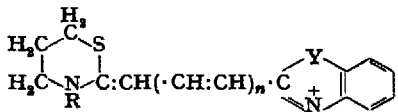
Y=S), (cf. ref. 188) was prepared either from methomethylsulphates of 3-methyl-1,4,2-benzothiazine and 2-methylthiobenzothiazole, or, alternatively, from the same salts of 3-methylthio-1,4,2-benzothiazine and 2-methylbenzothiazole. The unsymmetrical trimethincyanines, LXXXVIII (n=1, Y=S or CH:CH), were prepared from 3-methyl-1,4,2-benzothiazine methoperchlorate and a salt having a β-acetanilidovinyl group. Heating 3-methyl-1,4,2-benzothiazine methoperchlorate with ethyl orthoformate in acetic anhydride containing pyridine gave the symmetrical carbocyanine, LXXXIX (n=0, R=H, R′=Me), but



(LXXXIX)

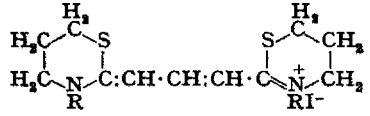
it was accompanied by another dye, which was identified as the isomeric $\alpha\gamma$-dimethylthiacarbocyanine. Similarly 3-methyl-1,4,2-benzothiazine phenoperchlorate gave LXXXIX (n=0, R=H, R′=Ph), together with the isomeric $\alpha\gamma$-diphenylthiacarbocyanine. The symmetrical carbocyanines, LXXXIX (n=0, R=Et or CO_2Et, R′=Me), were prepared from the methoperchlorates of 2-ethyl- or 2-carbethoxy-3-methyl-1,4,2-benzothiazine, respectively. A dye which resulted by heating 1,4,2-benzothiazine methoperchlorate with ethyl orthoformate and acetic anhydride containing pyridine proved to be 3,3′-dimethylthiacarbocyanine perchlorate; similarly 3-phenyl-1,4,2-benzothiazine methoperchlorate gave the $\alpha\gamma$-diphenyl derivative of this thiacarbocyanine. The absorption maxima of carbocyanines with 1,4,2-benzothiazine nuclei lay at a shorter wavelength than those with benzothiazole nuclei. By boiling 3-methyl-1,4,2-benzothiazine methoperchlorate with 1-anilino-3-aniloprop-1-ene hydrochloride and acetic anhydride containing pyridine for 1 minute, the dicarbocyanine, LXXXIX (n=2, R=H, R′=Me), resulted in 57% yield. All these dyes were readily decolorised by alkali.[190]

In 1943 the simple dihydro-1,3,4-thiazine nucleus was introduced into the molecules of various kinds of cyanines. Methincyanines of the types, XC (n=0, Y=O, S, Se, or CH:CH, R=R′=Et), and the

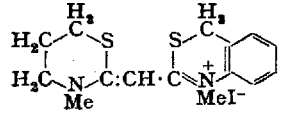


(XC)

4-linked quinoline analogue were prepared, also dyes with *N*-methyl groups, and numerous derivatives of the second type, by heating a 2-alkylthiodihydro-1,3,4-thiazine alkiodide with a quaternary salt having a reactive methyl group; the same alkyl group was used in the alkylthio as in the alkiodide, because exchange of radicals (see II-4-A) might occur. Through 2-methyldihydro-1,3,4-thiazine alkiodide, by heating with ethyl orthoformate in pyridine, the two carbocyanines, XCI (R=Me or Et), were prepared: their absorption maxima lay at a



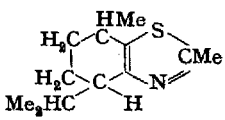
(XCI)



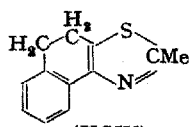
(XCII)

longer wavelength, by 175 Å and 165 Å, than those of the corresponding thiazolinocarbocyanines. By heating 2-methyldihydro-1,3,4-thiazine methiodide with a quaternary salt, having a 2-β-acetanilidovinyl group, and triethylamine in ethanol, the two unsymmetrical carbocyanines, XC (n=1, Y=O or S, R=Me, R′=Et), were prepared in yields of 19 % and 13 %.[191] From 2-methyldihydro-1,3,4-thiazine methiodide and 3-methylthio-1,4,2-benzothiazine methiodide, by boiling with triethylamine in ethanol, an 11 % yield of the unsymmetrical methincyanine, XCII, was obtained.[187]

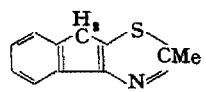
Quaternary salts of substituted 2-methylthiazoles, such as 2-methyl-4,5-tri(or penta)-methylenethiazole served to introduce one such nucleus into the molecule of various types of cyanines.[192,193] So, similarly, were used quaternary salts of complex 2-methylthiazoles, such as XCIII, XCIV, and XCV,[194–196] and salts of others, such as XCVI and XCVII, with a spirocyclic substituent.[197,198] The sensitising properties of these dyes and of styryl and dimethinmerocyanine dyes with the same nuclei (cf. XIII-1-M.5; XIV-10-C.1a) were recorded.[192–198]



(XCIII)

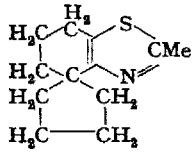


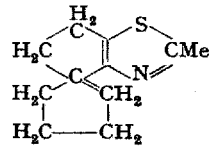
(XCIV)



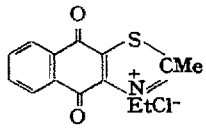
(XCV)

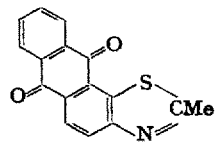
The ethochloride, XCVIII, of 2-methylnaphthoquinono[2,3-d]thiazole was synthesised and was used in the preparation of various unsym-


(XCVI)


(XCVII)

metrical cyanines, and of a styryl salt, with one nucleus of this kind, also of a tri- and a penta-methincyanine with two such nuclei.[199] 2-Methylanthraquinono[1,2-d]thiazole, XCIX, was synthesised and

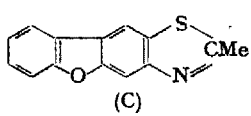

(XCVIII)

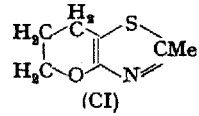

(XCIX)

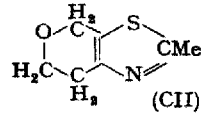
converted into its methochloride and methiodide; one complex nucleus was introduced into a methin- and a trimethin-cyanine, a styryl compound, and a *p*-dimethylaminoanil, and two of them into a symmetrical trimethincyanine.[200]

F. Complex Nuclei with a Nitrogen, an Oxygen, and a Sulphur as Hetero-Atoms

Complex thiacarbocyanines described as useful for sensitising to red light (section 5-E) included those prepared from quaternary salts of the base C,[176] and a thia-2'-cyanine from such a salt was also made.[177]


(C)


(CI)

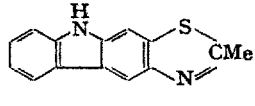

(CII)

Quaternary salts of two types of 2-methyldihydropyranothiazole, CI and CII, were used to introduce one such nucleus into various kinds of cyanines[201–203] (cf. XIII-1-M.6 and XIV-10-C.1f).

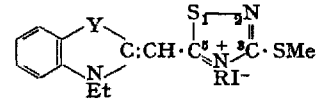
G. Nuclei, Including Complex Nuclei, with Two Nitrogen Atoms and One Sulphur or One Oxygen as Hetero-Atoms

Salts of a complex base, CIII, having two nitrogen atoms and one sulphur, were used in 1931 for preparing trimethin-[176] and methincyanines.[177]

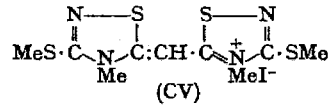
In 1933 a methincyanine, CIV (Y=S), was prepared by heating 3,5-di(methylthio)-1,2,4-thiadiazole and 2-methylbenzothiazole with ethyl toluene-*p*-sulphonate, followed by pyridine and potassium iodide. Similarly, from the thiadiazole and quinaldine there was prepared CIV (Y=CH:CH).[137] The malonic acid method (see II-6-D) was applied to the synthesis of the symmetrical methincyanine, CV.[139] 3,5-Di-(methylthio)-1,2,4-thiadiazole was also heated with alkyl toluene-*p*-sulphonate and cyclopentadiene or indene (see IX-2) to give symmetrical carbocyanines with an $\alpha\gamma$-dimethylene or -*o*-phenylene group,



(CIII)



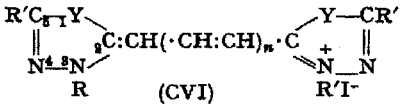
(CIV)



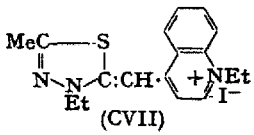
(CV)

respectively.[138] By reaction of a 2-(1-cyclopentenyl)-benzoxazole or -benzothiazole (see IX-4) with 3,5-di(methylthio)-1,2,4-thiadiazole and methyl toluene-*p*-sulphonate, there were prepared unsymmetrical carbocyanines with one benzoxazole, or one benzothiazole, nucleus and one 3-methylthio-1,2,4-thiadiazole nucleus, and with $\alpha\gamma$-dimethylene attached to the chain.[204]

Dyes with a 5-methyl-1,3,4-thiadiazole nucleus were claimed in 1934 to be powerful sensitisers with high solubility in water. The examples comprised the symmetrical carbocyanine, CVI (n=1, Y=S, R=Et, R′=Me), which was obtained, together with the neocyanine (see XV-3-A), by boiling 2,5-dimethyl-1,3,4-thiadiazole ethiodide with ethyl orthoformate in acetic anhydride; also its *meso*-methyl derivative, and the dicarbocyanine, CVI (n=2, Y=S, R=Et, R′=Me). Reaction of 2,5-dimethyl-1,3,4-thiadiazole ethiodide with quinoline ethiodide and



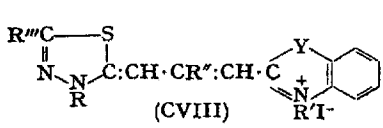
(CVI)

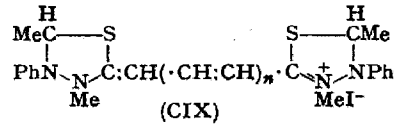


(CVII)

sodium ethoxide in ethanol gave the thiadiazolo 4′-cyanine, CVII; a thiadiazolo-2′-carbocyanine, CVIII (Y=CH:CH, R=R′=Et, R″=H,

R‴=Me), was also described. Although dyes with a 1,3,4-oxa- or -selena-diazole nucleus were claimed, there was no example of either.[205] In 1937 cyanine dyes prepared from quaternary salts of 4-aryl-2,5-dimethyldihydro-1,3,4-thiadiazole were described as useful sensitisers for

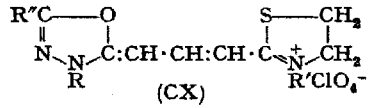

(CVIII)


(CIX)

both silver bromide and silver chloride emulsions. Examples were the symmetrical carbocyanine and dicarbocyanine, CIX (n=1 or 2), and the *meso*-methyl derivative of the former. A 2′-carbocyanine with one such dihydro-1,3,4-thiadiazole nucleus and one 7,8-benzoquinoline nucleus was also described.[206] A *meso*-methoxycarbocyanine was prepared by condensing a benzothiazolium salt having the group 2-CH:CMe(OMe) (see VI-15) with 2,5-di(methylthio)1,3,4-thiadiazole methiodide;[99] the sensitising properties of a *meso*-ethoxy analogue were described.[207] By heating a benzoxazolium or benzothiazolium salt, having the group 2-CH:CMe_2 (see VI-15) with 2,5-di(methylthio)-1,3,4-thiadiazole ethiodide and triethylamine in ethanol, there were prepared unsymmetrical *meso*-methylcarbocyanines with a benzoxazole or benzothiazole nucleus and a 3-ethyl-5-methylthio-1,3,4-thiadiazole nucleus.[208] Sensitising by *meso*-substituted unsymmetrical carbocyanines having one 5-SR-1,3,4-thiadiazole nucleus was patented. Examples included CVIII (Y=O, R=R′=Et, R″=Me, R‴=SMe) and the *meso*-ethyl analogue of the *NN*′-dimethyl dye; in five other compounds, CVIII (Y=S), the *meso*-substituent was Me, ·OMe, ·OEt, or ·SMe; the 5-substituent was ·SCH_2Ph in one instance, otherwise ·SMe.[209] In later patents, there were described methincyanines having a 5-methylthio-1,3,4-thiadiazole nucleus together with a 4,4-dimethyl-3-methylthio-1,2-diazole nucleus,[155] or with a 4,4-dimethyl-3-methylthiopyridazine nucleus,[153] also a 5-benzylthio-1,3,4-thiadiazole nucleus together with a 3-methylbenzothiazole nucleus. Trimethincyanines of the types CVIII (Y=O, S, CMe_2, or CH:CH, R=H, R and R′=Me or Et, X=I) were described, also a thiazoline and a 4-linked quinoline analogue; the 5-R‴ group might be ·SMe, ·SEt, ·SPr^i, or ·SCH_2Ph, and the nucleus other than thiadiazole might be substituted.[210]

In 1941 it was claimed that carbocyanines with a 5-furyl-1,3,4-oxadiazole nucleus were better sensitisers than analogues with a

5-methyl group. In all three examples, CX ($R''=C_4H_6O$), the other nucleus was thiazoline; the method (see V-8) consisted in condensing 5-furyl-2-methyl-1,3,4-oxadiazole alkiodide with a base having a 2-formylmethylene group. The dyes were good sensitisers for chloride emulsions and readily washed out.[211] Chloride emulsions sensitised by an unsymmetrical carbocyanine with a 5-phenyl-1,3,4-oxadiazole

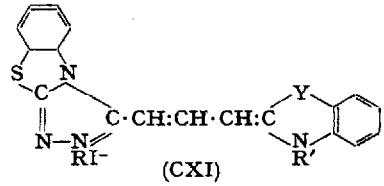


(CX)

nucleus were also better than those sensitised by a 5-methyl dye. They were similarly prepared, and besides examples where the second nucleus was thiazoline, there were others where it was benzothiazole, 2-linked quinoline, or 3,3-dimethylindolenine; the phenyl group might be substituted.[212]

H. Complex Nuclei with Three Nitrogen Atoms and One Sulphur as Hetero-Atoms

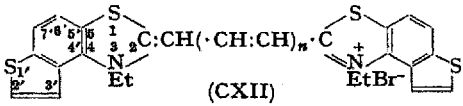
The sensitising properties of unsymmetrical carbocyanines of the types CXI (Y=O, S, or Se), in which a triazole ring had a fused-on benzothiazole nucleus, were described.[213]



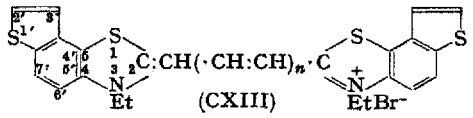
(CXI)

I. Complex Nuclei with One Nitrogen and Two Sulphur Atoms as Hetero-Atoms

In 1937 the syntheses from 4- or 5-aminothianaphthene of 2-methylthianaphtheno-(4′,5′,4,5)-thiazole and of 2-methylthianaphtheno-(4′,5′,5,4)-thiazole, respectively, were described. The ethoethylsulphates of the bases were condensed with ethyl orthoformate in pyridine to give the symmetrical carbocyanines, CXII ($n=1$) and CXIII ($n=1$),

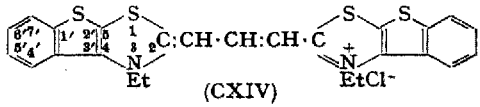


(CXII)

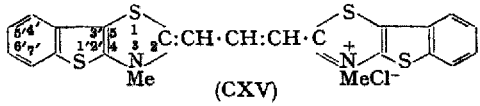


(CXIII)

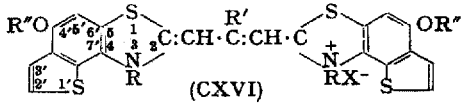
respectively, of which the sensitising maxima were at 6150 Å and 6100 Å. For the penta- and hepta-methincyanines, CXIII (n=2 or 3), the sensitising maxima were at 7150 Å and 8300 Å, respectively. A salt of the second base was also condensed with the ethiodide of 1-ethyl-6-methyl-2-thiodihydroquinoline to give a complex thia-2'-cyanine.[214] Ten years later, the preparation and sensitising of symmetrical and unsymmetrical carbocyanines with a thianaphtheno-(2',3',5,4)- or -(2',3',4,5)-thiazole nucleus were patented. The two examples, CXIV and CXV, were both symmetrical.[215] In 1948 symmetrical carbocyanines, including *meso*-alkyl derivatives, CXVI, characterised by



(CXIV)



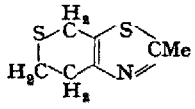
(CXV)



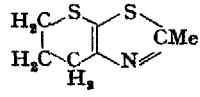
(CXVI)

having 4'-alkoxythianaphtheno-(7',6',4,5)-thiazole nuclei, were described as photographic sensitisers; CXVI (R=R'=R"=Me, X= $\cdot SO_3C_7H_7$) had a broad sensitising maximum from 5600 Å to 6600 Å.[216]

Quaternary salts of two types of dihydrothiopyranothiazole, each having a 2-methyl group, CXVII and CXVIII, were used in the synthesis of various sensitising cyanine dyes[203, 217, 218] (cf. XIII-1-M.8 and XIV-10-C.1i).



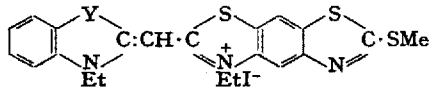
(CXVII)



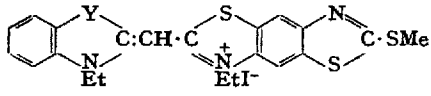
(CXVIII)

J. Complex Nuclei with Two Nitrogen and Two Sulphur Atoms as Hetero-Atoms

In 1940 there was described the preparation of dithiolbenzobisthiazoles from *m*- and *p*-phenylenediamines and from 1,3-diamino-4-methylbenzene, by heating under pressure with carbon disulphide and sulphur; the corresponding di(methylthio)-derivatives were converted into quaternary salts, which were condensed with others having a reactive methyl group to give methincyanines, having a (methylthio)-benzobisthiazole nucleus: these were photographic sensitisers. Through quaternary salts of the base derived from *m*-phenylenediamine, the dyes, CXIX (Y=S, Se, O, or CH:CH), also a 4-linked quinoline analogue, and 5-methyl derivatives of the first two, were prepared.

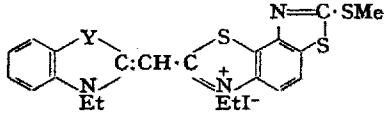


(CXIX)



(CXX)

The base derived from *p*-phenylenediamine entered into the molecules of CXX (Y=S or Se), of a 4-linked quinoline analogue, of a 5-methyl-*meso*-methyl derivative of the second dye, and of the 5,6-benzo-derivative of CXX (Y=CH:CH). The base derived from the toluylenediamine was used in the preparation of CXXI (Y=S, CH:CH, O, or Se),

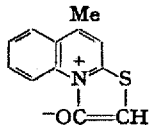


(CXXI)

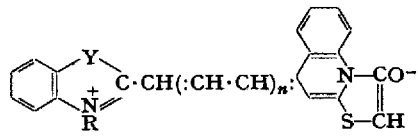
and the 4-linked quinoline analogue, of the 4,5-benzo-derivative of the first dye, as ethoethylsulphate, and of the 5,6-benzo-derivative of the second.[219]

K. Nucleus Giving Rise to Non-ionised Cyanine Dyes

It was recorded in 1951 that, like 2-pyridylthioacetic acid,[220] 2-quinolylthioacetic acids, unsubstituted in the 8-position, are converted into unimolecular anhydro-compounds, to which cyclic *meso*-ionic structures were assigned[221] (equation 26). The anhydro-compound, CXXII, prepared from 2-(4-methylquinolylthio)acetic acid,[221] was found to give rise to cyanine dyes by virtue of its reactive methyl group. These were similar to merocyanines (see Chapter XIV) in that they are non-ionised. They were described as useful sensitisers.[221]

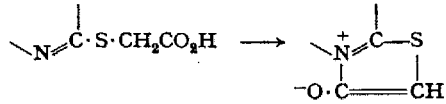


(CXXII)



(CXXIII)

The methincyanine, CXXIII (n=0, Y=CH:CH, R=Et), was prepared by boiling CXXII and 2-phenylthioquinoline ethotoluene *p*-sulphonate with triethylamine in pyridine for 10 minutes and treating



(26)

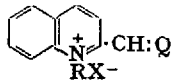
with methanol; the yield, after dissolving in pyridine and precipitating with methanol, was 33 %. Its analogue, CXXIII (n=0, Y=S, R=Et), was obtained in 34 % yield by reaction of CXXII and 2-ethylthiobenzothiazole ethoethylsulphate. The 4,5- and 6,7-benzo-derivatives of CXXIII (n=0, Y=O, R=Me) were similarly made.[222]

In the trimethincyanine series, there was prepared CXXIII (n=1, Y=O, R=Et) by boiling CXXII and 2-*β*-acetanilidovinylbenzoxazole ethiodide with triethylamine in pyridine, precipitating with ether, and purifying as before; its 6,7-benzo-derivative was made similarly, as were CXXIII (n=1, Y=S, R=Et), obtained in 40 % yield, the 4,5-benzo- and 5-chloro-derivatives of the last, and CXXIII (n=1, Y=Se, R=Et). The *meso*-methyl and *meso*-phenyl derivatives of the 4,5-benzo-derivative of CXXIII (n=1, Y=S, R=Et or Me, respectively) were prepared by use of appropriate benzothiazolium salts having the group ·CH:CR(SR′) (where R=Me or Ph, R′=Et or Me, respectively).[222]

TABLE I. Some Properties of Symmetrical Carbocyanines with Unusual Nuclei

Nature of nuclei	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
3-linked isoquinoline	XVII (R=Et)	brownish red needles	7330	—	—	5800	114, 115
3-linked pyrrole	Trimethin analogue of XXIII (R=Et)	red; silvery reflex	220–222	4425	—	—	2
pyrrocoline	XXIV (R=Me, X=Br)	blue green crystals	273–274	—	—	—	127
quinazoline	XXXI	greenish red needles	270[a]	5900 6300	—	—	136
dihydroquinoxalone	XXXIX (R=R'=Me, X=SO_4Me)	green	227[a]	5980 6520	—	—	148
pyridazine	L	deep purple needles	282	—	5800	6100	153
1,2-diazole	LIV (R=Me)	deep blue needles	255	—	5700 6100	6200	155
1,7-phenanthroline	LVIII	—	—	6300	6600	7300	161
naphthyridine	LXIV (R=NHCOMe, R'=H)	dark blue leaflets[b]	291–294[b]	6570	—	—	164
perinaphtho-1,3-thiazine	LXXXIV (n=0, R=Et, X=I)	green needles	212	5400	—	—	184, 185
dihydro-1,3,4-thiazine	XCI (R=Et)	deep red	243	4600	4850	5200	191

[a] Decomp. not recorded. [b] Data for product before purification.

TABLE II. Some Properties of Unsymmetrical Methincyanines 

Derivation of nucleus Q	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
acridine	XVIII (R=Me)	bronze lustre	250–265	5500	—	—	118
acenaphthenopyridine	XX (R=Et)	brownish red	201	5450	5100 5700	6400	118
2-linked 1,3-diazole	LVI (n=0, Y=CH:CH, R=Et, R′=Me, X=ClO_4)	red needles	263[a]	—	4400 4700	5100	157
4-linked 1,3-diazole	LXIX (Y=CH:CH, R=Et, R′=Me)	orange needles	277[a]	—	5200	5400	160
1,2,4-triazole	LXX (n=0, Y=CH:CH, R=R′=Ph, X=I)	orange	200[a]	—	—	—	171
triazolo[4,3-a]-quinoline	LXXII (n=0, Y=CH:CH, R=R′=Et, X=ClO_4)	maroon	217–218	—	—	—	172
s-triazolo[2,3-a]-pyrimidine	6-MeO-derivative of LXXIV (n=0, Y=CH:CH, R=R′=Et, R″=$CHMe_2$, R^1=Me, X=I)	—		—	5350	5850	173
tetrazolo[a]quinoline	LXXVI(n=0, Y=CH:CH, R=R′=Et, X=I)	coppery flakes	244–246	—	—	—	172
tetrazole	LXXVII (n=0, Y=CH:CH, R=R′=Me, R^1=p-C_6H_4Me, X=I)	green needles	174	—	5550	5900	174
3,1,4-benzothiazine	LXXXVI (n=0, Y=CH:CH, R=R′=Et)	orange	212	4625	4900	5200	187
1,2,4-thiadiazole	CIV (Y=CH:CH, R=Et)	brown	225	—	4900	5100	137
Benzobisthiazole	CXIV (Y=CH:CH)	yellow-brown	—	—	5400	5600	219
Benzobisthiazole	CXXI (Y=CH:CH)	scarlet	—	— —	5400 ± 50	—	219

[a] Decomp. not recorded.

References

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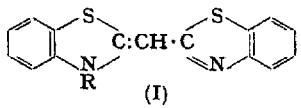
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CHAPTER XI

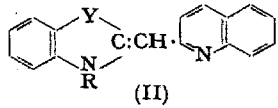
Bases, Including Some with Substituents on the Chain, of which Cyanines are the Quaternary Salts

1. General Survey

In work on the constitution of isocyanines in 1912, an ethiodide of this type was heated in a vacuum, whereby ethyl iodide was eliminated, leaving a base.[1] In 1922 the third stage in the four-stage synthesis of thiacyanines (see I-3-D) was the production of bases, I (R=Me or Et), which, by the action of alkyl iodide, were converted into the symmetrical *NN'*-dimethyl- or *NN'*-diethyl-thiacyanine iodides.[2] In 1936 condensation of 2-imino-3-methylbenzothiazoline with quinaldine (*cf.* II-5) gave rise to the base, II (Y=S, R=Me), of which it was noted that the hydrochloride was red, like thia-2'-cyanine, and the dihydrochloride nearly colourless.[3] In the previous year the important observation was recorded that bases, of which methincyanines and styryl compounds are the quaternary salts, comprise valuable photographic



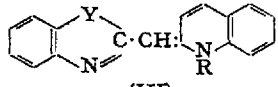
(I)



(II)

sensitisers.[4] Those of the former type were prepared by condensing a 2- or 4-methylquinoline with a quaternary salt having a 2-alkylthio-group (cf. II-4):[5] this led to bases, such as II, in which the *N*-alkyldihydro-structure was in the nucleus other than quinoline. Subsequently the method was extended to the use of 2-methylbenzothiazole and 2-methylbenzoselenazole, and thereby methincyanine bases, III, were made in which the *N*-alkyldihydro-structure was in the quinoline nucleus.[6] Alkotoluene-*p*-sulphonates had been used as the other re-

actant[5] and comparative experiments showed that, in the three instances studied, they gave a better yield than did alkiodides (section 2).[6] An alternative method of arriving at the bases of methincyanines was



(III)

to condense heterocyclic bases having a 2-alkylthio-group with quaternary salts having a reactive methyl group (section 3). The hydriodides or hydrochlorides of some of these bases were made, and their absorption maxima were compared with those of the corresponding ethiodides, which are methincyanines. On addition of acid to II (Y=S, R=Me or Et), the absorption maximum shifted 440 Å and 460 Å, respectively, towards the region of longer wavelength, whilst addition of methyl iodide or ethyl iodide involved shifts of 590 Å and 600 Å, respectively. Bases of type III (Y=S) differed from those of type II (Y=S) in that the position of the absorption maximum was affected by exposure to light. With special precautions in recording, it was noted that the absorption maxima of their solutions were unchanged by addition of acid and were almost the same as those of the corresponding alkiodides.[6] Through 3,3-dimethyl-2-methylthioindolenine, several types of base having a substituted indolenine nucleus were synthesised (section 3).[7] Some data about methincyanine bases are given in the table at the end of the chapter.

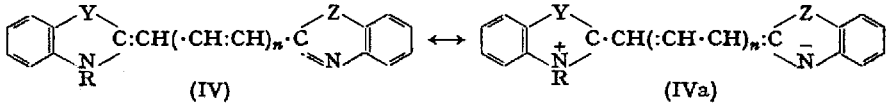
Another method of preparation consisted in condensing a heterocyclic base having a methyl sulphone group, SO_2Me, with a quaternary salt having a reactive methyl group (section 3).[8]

By condensation of a quinaldine with a quaternary salt having a 2-β-acetanilidovinyl group (cf. V-6-A), there were prepared bases of which trimethincyanines are the quaternary salts.[5] Salts with a 2-β-ethylthiovinyl group (cf. V-10) could be used similarly (section 4).[9]

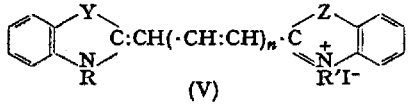
In 1935 there was patented a method of eliminating alkyl halide from methin- and trimethin-cyanines, and from styryl compounds (see XIII-1) by means of a high-boiling nitrogenous base, such as diethylaniline. It was noted that the resultant bases melt about 100° lower than their quaternary salts, are only slightly coloured, and with acid give salts of about the same colour as the quaternary salts.[10] With unsymmetrical dyes, such as thia-2'-cyanines, the product might be

either one of two isomeric bases, or it might be a mixture of the two.[6] The method was extended to the preparation of the base of a symmetrical thiadicarbocyanine (section 5).[11]

The absorptions of methanolic solutions of a set of three symmetrical cyanines having two benzothiazole nuclei and a methin-, trimethin-, or pentamethin-chain were compared with those of the corresponding three anhydronium bases. The bases absorbed at a shorter wavelength than did the corresponding quaternary salts. Increasing the length of the chain caused the absorption maximum to shift to a longer wavelength, but the shifts were smaller for the bases than for the salts, being 620 Å and 320 Å for the former, on passing from CH to



(IV) (IVa)



(V)

3CH and from 3CH to 5CH, respectively, but 1345 Å and 925 Å for the latter: thus difference in absorption between base and cyanine became greater as the chain was lengthened. The curves for the three bases, IV (Y=Z=S, n=0, 1, or 2, R=Et), and of four cyanine dyes, V (Y=Z=S, n=0, 1, 2, or 3, R=R′=Et), are given in Figure 1. The values of ε_{max} lay close together for the bases but were lower than those for the corresponding cyanines. Unlike their quaternary salts, the bases are not ionised, but the resonance scheme IV ⇌ IVa was suggested for them, though the former configuration was regarded as the more stable (See XVI-8).[11]

Since pyrroles and indoles having :*N*H usually yield potassium derivatives, and hence show a tendency to form negatively charged ions in which :$\bar{N}$ is stable, the base VI was prepared, by reaction of 2-methylbenzothiazole ethiodide with 3-formyl-2-methylindole in acetic anhydride. Its pyridine solution absorbed at a longer wavelength than did that of its methiodide, VII, which was obtained by addition of methyl iodide to VI (see X-5-A).[11] It had been observed as early as 1912 that the dimethin dyes obtained by condensing quinaldinium or lepidinium salts with 3-formyl-2-methylindole, and therefore having an :*N*H

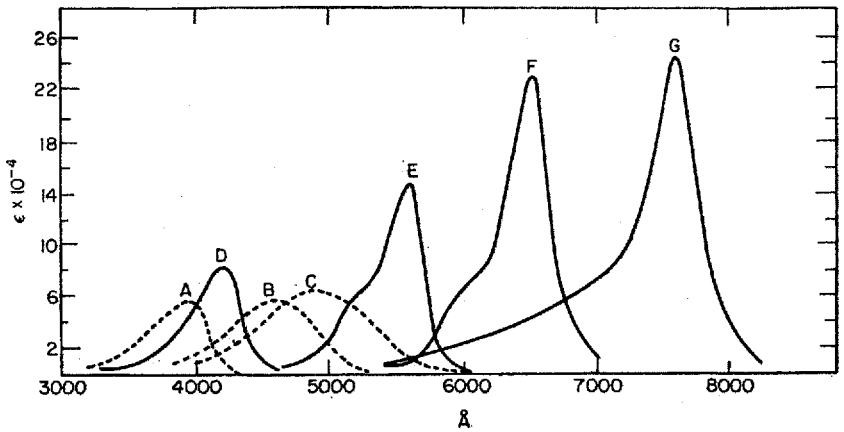
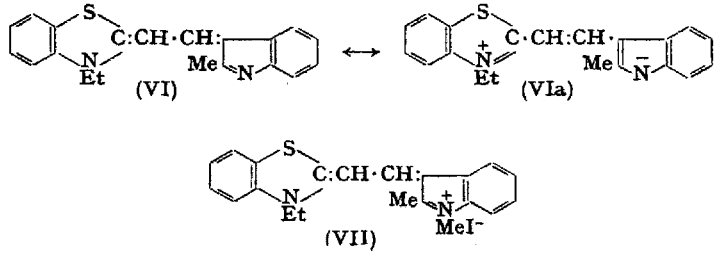


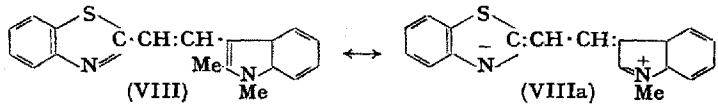
Fig. 1. Absorption curves in methyl alcohol. A, B, C=IV (Y=Z=S, R=Et, n=0, 1 or 2, respectively); D, E, F, G=V (Y=Z=S, R=R'=Et, n=0, 1, 2 or 3, respectively). [From Brooker, Sprague, Smyth and Lewis[11]. By courtesy of the authors and the American Chemical Society.]

group in the indole nucleus, were converted by alkali into very deeply coloured bases, thus showing a kind of reversed halochromism, but the blue dye obtained from a 9-methylacridinium salt behaved differently.[12] In 1940 it was suggested that the anomalous colour changes of the true dimethincyanines are attributable to two factors. One of them is that the tendency of indole to form an indolyl anion renders the configuration VIa relatively more stable than IVa, so that the base VI ⟷ VIa is more truly a resonance hybrid than is IV ⟷ IVa; the second factor is that the methiodide appears to absorb

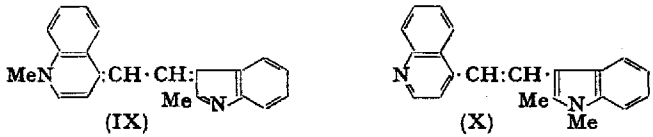


at an unusually short wavelength, owing to the weak basicity of the indole nitrogen atom. That the presence of an indole nucleus in an anhydronium base does not necessarily lead to absorption at an abnormally long wavelength was shown by the preparation of the

base, VIII, of a different type; it was obtained by reaction of 2-methylbenzothiazole with 3-formyl-1,2-dimethylindole in the presence of hydrochloric acid. With this compound, the second extreme resonance configuration, VIIIa, contains a negatively charged benzothiazole nitrogen and a quaternary indole nitrogen, both regarded as unstable,



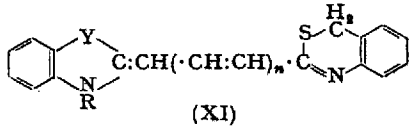
and resulting in a nearly colourless solution. The base was converted into the salt, VII, by the action of ethyl iodide. Another pair of bases, IX and X, was similarly synthesised and each of these isomers was



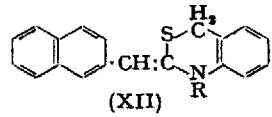
converted by methyl iodide into the same dimethincyanine (see X-5-A). Again the absorption maximum of the one type of base, IX, lay at a longer wavelength than that of the other type, X (see Table I[11] and section 6). The high melting points of some of these dimethincyanine bases are remarkable.

Certain complex thiazines were so weakly basic that their quaternary salts, which were required for cyanine dye formation, could not be made. In the instance of salts of 3-methyl-1,4,2-benzothiazine, this difficulty was ingeniously overcome by the direct synthesis of the salts themselves (see X-5-E).[13] Previously, the base 2-methyl-3,1,4-benzothiazine had been condensed with quaternary salts having a 2-β-acetanilidovinyl group (cf. section 4) to give five carbocyanine bases of type XI ($n=1$) (section 7-B); two of them were heated with ethyl toluene-p-sulphonate to give carbocyanines (see X-5-E).[14] 2-Methyl-3,1,4-benzothiazine was also used (cf. section 2) to give a methincyanine base of type XI ($n=0$), whilst others were prepared by condensing 2-alkylthio-3,1,4-benzothiazine (cf. section 3) with quaternary salts having a reactive methyl group. The base, XII, having the methyldihydro-structure in the benzothiazine nucleus, was prepared by condensing a quaternary salt of 2-methylthio-3,1,4-benzothiazine with quinaldine (cf. section 2)

Both this last base and its isomer were converted by heating with methyl sulphate, followed by potassium iodide, into the methincyanine (see X-5-E). The base of the symmetrical methincyanine, XIII, with two 3,1,4-benzothiazine nuclei was prepared (cf. section 2[15] and 7-A).

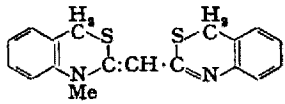


(XI)

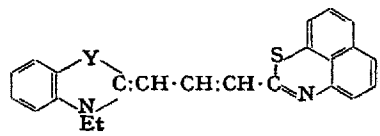


(XII)

By reaction of 2-methylperinaphtho-1,3-thiazine with a salt having a 2-β-acetanilidovinyl group (cf. section 4), there were prepared carbocyanine bases of the type XIV (section 7-C). One of these, by heating with methyl and ethyl iodide, respectively, was converted into the two corresponding carbocyanines (see X-5-E).[16]



(XIII)



(XIV)

Subsequently certain types of sensitising bases, having a 1,3,5-triazine, a tetrazolo[a]pyrimidine, or a s-triazolo-[2,3-a]pyrimidine nucleus were described (section 8).

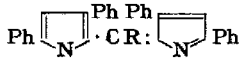
α-Cyano-bases of methincyanines were synthesised by condensation of a quaternary salt, having a reactive group ·SR, with a heterocyclic nitrogenous base having an α-cyanomethyl group;[17] their acid hydrolysis led to the bases of methincyanines with an unsubstituted chain.[18] Similarly α-cyano-bases of the tri-, penta-, and hepta-methincyanine series were synthesised[17] and hydrolysed to give the unsubstituted bases.[18] The α-cyano-bases were often stronger sensitisers than were the unsubstituted bases. Two α-cyanocarbocyanine bases were converted, by heating with an ester, into α-cyanocarbocyanines.[17] α-Cyano-bases of the tri- and penta-methincyanine series, comprising a 1,2,4-oxadiazole nucleus, were prepared from 5-cyanomethyl-1,2,4-oxadiazoles (section 9).[19] At a much later date, the absorption maxima of bases having a cyano-group in the α-position to a benzimidazole nucleus were compared with those of quaternary salts derived from them. The compounds were good sensitisers and, where the α-cyano-

group was the only substituent on the chain, the curve fell off sharply at the long wavelength end (section 9).[20]

Besides the cyano-group, other electronegative groups, such as ·COMe, ·CO_2Et, or ·CO·$C_6H_4NO_2$(-*p*) could be similarly introduced into the α-position of tri- and penta-methincyanine bases having a 1,2,4-oxadiazole nucleus; in one instance a 1-pyridinium chloride group was introduced.[19] Soon afterwards, a benzothiazole with a 2-CH_2CO_2Et group was caused to react with a 2-methylthiobenzothiazolium salt, to give a thiacyanine base with ·CO_2Et on the chain.[21] A thia-2'-cyanine base of this kind was prepared later.[22] Formulated generally, the group ·CH_2COR for the base gives ·COR on the chain of the cyanine and in these instances R=OEt. Other benzothiazoles with the group ·CH_2COR were described, where R was Me, Ph, NH_2, NHPh, or OCH_2Ph. Methincyanine dye bases prepared from them were photographic sensitisers;[21] so also were the bases of tri- or penta-methincyanines having an α-CONHR group.[23] Trimethincyanine bases with an α-CO_2Et group were described and one such was converted by ethyl iodide into a thiacarbocyanine iodide and was also hydrolysed to the unsubstituted carbocyanine base.[24] A *meso*-carbethoxythiacyanine base was converted by alkyl iodide into a *meso*-carbethoxythiacyanine iodide. The absorption maxima of some α-substituted methin- and trimethin-cyanine bases were recorded;[25] that of the thiacyanine base with an α-CO_2Et group lay at a longer wavelength by only 30 Å than that of the unsubstituted base,[25,26] but this close correspondence was regarded as accidental. A comparison of the infrared spectra of the unsubstituted thiacyanine base, its α-carbethoxy-derivative, ethyl acetate, and 2-carbethoxymethylene-3-methylbenzothiazoline showed that the last three have an absorption band which is lacking in the first. Hence strong conjugation of the ester group with the rest of the molecule was deduced. It was concluded that in the substituted thiacyanine base, the CO_2Et and benzothiazoline nucleus are co-planar, whilst the benzothiazole nucleus is in a different plane.[26] In an independent account of the preparation and sensitising action, especially towards chloride emulsions, of tri- and penta-methincyanine bases having an α-COR, or α-CSR, group, it was considered that this group enters into the resonance configuration. These dye bases were prepared by condensing heterocyclic bases having a ·CH_2COR group with quaternary salts having a reactive group, such as 2-β-acetanilidovinyl.[27] Some years later, heterocyclic bases having a ·CH_2COCO_2Et group were

condensed, not with quaternary salts, but with *N*-alkyldihydro-bases having a 2-*β*-aniloethylidene group: the yields of eleven α-$COCO_2Et$ bases varied from 33–89 %. Their intense colour was attributed to mesomerism, but in formulating the contributing structures, it was assumed that both heterocyclic nuclei, as well as the $COCO_2Et$ group, were involved.[28]

Dyes with *NN'*-diH structures in the nuclei (X-4-D) are not regarded as true cyanines, although bearing resemblance to them. So also certain bases, of which such dyes are the acid salts, resemble the bases considered in the present chapter. They are methin bases with two 5-linked pyrrole nuclei and were described in 1943 as prepared by heating a pyrrole with ethyl orthoformate in acetic acid, or with diphenylformamidine in acetic anhydride. Thus 2,4-diphenylpyrrole gave XV (R=H). By heating 2,4-diphenylpyrrole with benzotrichloride in acetic acid, it gave the *meso*-substituted base, XV (R=Ph). The base,



(XV)

XV (R=H), could also be prepared from 5-formyl-2,4-diphenylpyrrole and 2,4-diphenylpyrrole. The imido hydrogen atom is replaceable by metals.[29,30]

2. Bases of Methincyanines from Heterocyclic Bases Having a Reactive Methyl Group

A. Bases of 2,2'-Cyanines

In the 2,2'-cyanine series, the base, II (Y=CH:CH, R=Me), was prepared by fusing 2-methylthioquinoline and methyl toluene-*p*-sulphonate at 130–140° for 3·5 hours, boiling with quinaldine in pyridine for half an hour, pouring into water, and recrystallising from methanol;[5] it sensitised a chloride emulsion.[4] As thus prepared, the yield of base after recrystallisation from benzene was 25 %, but when it was prepared from 2-methylthioquinoline methiodide, the yield was only 8 %. The homologue, II (Y=CH:CH, R=Et), was prepared from 2-ethylthioquinoline ethotoluene-*p*-sulphonate and quinaldine and resulted in 36 % yield, after two recrystallisations from acetone.[6]

B. Bases of Thia-2'-, Oxa-2'-, and Selena-2'-cyanines

In the thia-2'-cyanine series, the base, II (Y=S, R=Me), was prepared by boiling 2-methylthio-(or methylseleno)benzothiazole methotoluene-*p*-sulphonate with quinaldine in pyridine; the oil precipitated by water solidified on treatment with spirit and ether, and was recrystallised from methanol. By use of substituted 2-methylthiobenzothiazolium salts, there were prepared derivatives with 4,5- or 6,7-benzo-, 5,6-methylenedioxy-, or 5,6-dimethoxy-groups. Use of substituted quinaldines gave bases with 6'-amino-, 3'-methyl, 4'-ethylthio-, or 4'-methylthio-groups. When both salt and quinaldine were substituted, derivatives with 6,7,5',6'-dibenzo- or 4,5-benzo-6'-methyl groups were obtained. The base, II (Y=S, R=Et), was prepared from 2-ethylthiobenzothiazole ethotoluene-*p*-sulphonate and quinaldine, and its 6,7-benzo-derivative was also made.[5] The sensitising properties towards silver chloride emulsions were described.[4] The yield of II (Y=S, R=Me), as prepared from 2-methylthiobenzothiazole methotoluene-*p*-sulphonate, was 44 % after two recrystallisations from acetone, whereas with the methiodide as starting point the result was negative; its hydrochloride was described. The isomer, III (Y=S, R=Me), was obtained in 57 % yield by heating 2-methylthioquinoline methotoluene-*p*-sulphonate with 2-methylbenzothiazole at 140–150° for 3 hours, liberating it with alkali, extracting with chloroform, and recrystallising from acetone; its hydriodide was prepared. The ethyl analogue, III (Y=S, R=Et), was obtained in 41 % yield and its hydriodide was made. 2-Alkylthioquinoline alkotoluene-*p*-sulphonates were used in the preparation of the 4,5-benzo-derivative of III (Y=S, R=Me) and of the 6,7-benzo-derivative of III (Y=S, R=Et).[6]

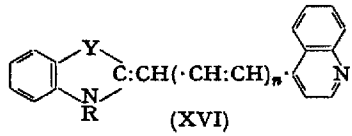
In the oxa-2'-cyanine series, the base, II (Y=O, R=Me), was prepared by boiling 2-methylthiobenzoxazole methotoluene-*p*-sulphonate with quinaldine and pyridine for 20 minutes;[5] its sensitising action was described.[4]

The 5,6-dimethoxy-derivative of the corresponding base, II (Y=Se, R=Me), of the selena-2'-cyanine series was similarly made[5] and its sensitising action was described.[4]

C. Base of Thia-4'-cyanine

The base, XVI (*n*=0, Y=S, R=Me), of a thia-4'-cyanine was made by heating 2-methylthiobenzothiazole methotoluene-*p*-sul-

phonate with lepidine and pyridine[5] and had its sensitising maximum at 5200 Å.[4] The hydriodide of XVI (n=0, Y=S, R=Et) was isolated by heating 2-ethylthiobenzothiazole ethotoluene-p-sulphonate with lepidine at 140–150° for 30 minutes, treating with alkali, extracting the



(XVI)

base with chloroform, dissolving it in acetic acid, and treating with potassium iodide: the salt was converted to the base by boiling and stirring with benzene and sodium hydroxide solution.[6]

D. Base of Quinazolinothiacyanine

The base of a quinazolinothiacyanine sensitised a silver chloride emulsion to 5500 Å.[4]

3. Bases of Methincyanines from Heterocyclic Bases Having a Reactive Alkylthio or Methyl Sulphone Group

A. Bases of Thia-2′- and Oxa-2′-cyanines

The base, II (Y=S, R=Et), of a thia-2′-cyanine was prepared by heating 2-methylbenzothiazole ethotoluene-p-sulphonate with 2-methylthioquinoline, liberating it with sodium hydroxide, extracting with chloroform, and twice recrystallising from acetone: it resulted in 19 % yield. Its acetic acid solution was treated with aqueous potassium iodide to give the hydriodide.[6] Its isomer, III (Y=S, R=Et), was obtained by boiling 2-benzothiazolyl methyl sulphone[31] with quinaldine ethiodide and triethylamine in ethanol for 30 minutes, and similarly for the 6,7-benzo-derivative of the sulphone.[8]

In the oxa-2′-cyanine series, the base, III (Y=O, R=Et), was prepared by heating 2-benzoxazolyl methyl sulphone and quinaldine ethiodide with triethylamine in ethanol.[8]

B. Bases of Thia- and Selenathia-cyanines

The thiacyanine base, I (R=Me), was made by heating 2-methylthiobenzothiazole with 2-methylbenzothiazole methotoluene-p-sul-

phonate at 165–175°, being liberated with aqueous sodium hydroxide solution, and extracted with chloroform; the residue from the extract was treated with acetone and the solid product twice recrystallised from acetone, giving a 13% yield. 2-Methylthiobenzothiazole failed to react with 2-methylbenzothiazole methiodide.[6]

Similarly 2-methylthiobenzothiazole and 2-methylbenzoselenazole ethotoluene-*p*-sulphonate gave the base, IV (n=0, Y=Se, Z=S, R=Et), of a selenathiacyanine; through its hydriodide, the pure base was obtained.[6]

C. Bases of Indo-, Indo-2′-, Indoselena-, Indothia-, Indoxa-, and Indothiazolocyanines

The base, IV (n=0, Y=Z=CMe_2, R=Me), of an indocyanine was prepared by fusing 3,3-dimethyl-2-methylthioindolenine and 2,3,3-trimethylindolenine methotoluene-*p*-sulphonate at 150° for 4 hours and treating a chloroform solution of the product with aqueous sodium hydroxide. Use of the corresponding salts of quinaldine, 2-methylbenzoselenazole, 2-methylbenzothiazole, and 2-methylbenzoxazole gave the bases of indo-2′-, indoselena-, indothia-, and indoxa-cyanines, IV (n=0, Y=CH:CH, Se, S or O, Z=CMe_2, R=Me), whilst the salt of 2-methyl-4-phenylthiazole gave the base of an indothiazolocyanine. In this last series and in the indothiacyanine series, a base with an *N*-ethyl group was also made. Some of the bases were sensitisers.[7]

4. Bases of Trimethincyanines from Heterocyclic Bases Having a Reactive Methyl Group

A. Base of 2,2′-Carbocyanine

To prepare the base, IV (n=1, Y=Z=CH:CH, R=Et), of the 2,2′-carbocyanine, quinaldine was heated with 2-β-ethylthiovinylquinoline ethotoluene-*p*-sulphonate, and the washed product was extracted with benzene and purified through its hydrochloride.[9]

B. Bases of Indo-2′- and Thia-2′-carbocyanines

The base, IV (n=1, Y=CMe_2, Z=CH:CH, R=Me), of the indo-2′-carbocyanine series, prepared by boiling quinaldine with 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide in pyridine for 40

minutes[5] was a powerful sensitiser.[4] Its 6'-ethoxy- and 6'-methyl derivatives were prepared by use of excess of the substituted quinaldines, which acted instead of pyridine as acid-binding agents.[5] The latter base was also prepared by heating 2-β-ethylthiovinyl-3,3-dimethylindolenine methotoluene-*p*-sulphonate with *p*-toluquinaldine.[9]

The base, IV (n=1, Y=S, Z=CH:CH, R=Me), of the thia-2'-carbocyanine group was prepared by boiling quinaldine with 2-β-acetanilidovinylbenzothiazole methiodide in pyridine[5] or, alternatively, with 2-β-ethylthiovinylbenzothiazole methotoluene-*p*-sulphonate in pyridine; the latter type of reactant was used in preparing the ethyl analogue, the salt being fused with excess of quinaldine.[9]

C. Base of Indo-4'-carbocyanine

The base, XVI (n=1, Y=CMe_2, R=Me), of the indo-4'-carbocyanine series was prepared by heating 2-β-ethylthiovinyl-3,3-dimethylindolenine methotoluene-*p*-sulphonate with lepidine, and was purified through its hydrochloride.[9]

D. Base of Thiacarbocyanine

The base, IV (n=1, Y=Z=S, R=Me), of a thiacarbocyanine was prepared by fusing 2-β-ethylthiovinylbenzothiazole methotoluene-*p*-sulphonate with 2-methylbenzothiazole, treating with ammonia, and extracting with benzene.[9]

5. Bases of Methin- and of Tri- and Penta-methin-cyanines by Boiling the Dyes with a Nitrogenous Base

A. Bases of Thia- and Thia-2'-cyanines

A sample of the base, I (R=Et), was prepared by boiling 3,3'-diethylthiacyanine iodide with 100 times its weight of diethylaniline for 1 hour; the residue after steam distillation was converted into hydriodide, which was decomposed by alkali.[10] Alternatively the residue was extracted with benzene; the product from that gave, on treatment with acetone, a 46% yield of base, which was recrystallised from acetone, giving a 29% yield.[6] Still better was extraction with methanol and two recrystallisations from methanol, which gave a 46% yield.[11]

When 3,1′-diethylthia-2′-cyanine iodide was boiled with diethylaniline, the product was a mixture of the bases, II and III (Y=S, R=Et). The 4,5-benzo-derivative of 3,1′-dimethylthia-2′-cyanine iodide gave the 4,5-benzo-derivative of III (Y=S, R=Me), but the 6,7-benzo-derivative of 3,1′-diethylthia-2′-cyanine iodide gave the 6,7-benzo-derivative of II (Y=S, R=Et), as was proved by comparison with synthetic products (section 2-B).[6]

B. Bases of 2,2′- and Thia-carbocyanines

By boiling 1,1′-diethyl-2,2′-carbocyanine iodide with 50 parts of quinoline and 50 of diethylaniline, the blue of pinacyanol changed to yellow; the original colour was regenerated by acid.[10]

3,3′-Diethylthiacarbocyanine iodide was boiled with diethylaniline for 1 hour or with dimethylaniline for 2 hours.[10] The residue after steam distillation, and recrystallisation from ethyl acetate, gave a 50 % yield of base.[6] Alternatively, part of the diethylaniline was distilled off, ether was added, and recrystallisation from ethanol gave a 65 % yield.[11] The 6,7,6′,7′-dibenzo-derivative of the thiacarbocyanine was converted to base by heating with diethylaniline and pyridine (10:90 parts) in a sealed tube at 200° for 2 hours.[10]

C. Base of Thiadicarbocyanine

The base, IV (n=2, Y=Z=S, R=Et), was prepared in 4 % yield by boiling 3,3′-diethylthiadicarbocyanine iodide with diethylaniline under carbon dioxide for 1 hour. The filtrate was concentrated *in vacuo* and the oil was extracted with methanol, caused to solidify with acetone, and recrystallised from acetone.[11]

6. Dimethincyanine Bases with a 3-Linked Indole Nucleus, Prepared through 3-Formylindoles

The hydriodide of the dimethincyanine base, VI, was prepared in 93 % yield by boiling equimolecular amounts of 2-methylbenzothiazole ethiodide and 3-formyl-2-methylindole in acetic anhydride for 2 minutes. By stirring the salt with sodium hydroxide in aqueous acetone, it gave a 91 % yield of base, which could be recrystallised from acetone. A 4-linked quinoline analogue, IX, was similarly prepared,

through its hydriodide, by use of lepidine methiodide. The other type of base, VIII, was prepared in 50 % yield by heating 2 mols. of 2-methylbenzothiazole, 1 mol. of 3-formyl-1,2-dimethylindole, and 2 mols. of concentrated hydrochloric acid at 100° for 16 hours, followed by dissolving in methanol and basification with triethylamine. The hydrochloride of its 4-linked quinoline analogue was recrystallised before basifying, and the base, X, was recrystallised from methanol and resulted in 43 % yield.[11]

7. Bases of Methin- and Trimethin-cyanines Comprising a Thiazine Nucleus

A. Bases of Methincyanines with a 3,1,4-Benzothiazine Nucleus

The base, XI (n=0, Y=S, R=Me), of an unsymmetrical methincyanine was prepared in 36 % yield (cf. section 3) by heating 2-methylbenzothiazole methotoluene-p-sulphonate with 2-methylthio-3,1,4-benzothiazine at 160° for 30 minutes, treating with sodium hydroxide, and recrystallising twice from acetone. Its N-ethyl analogue, and the derivative of that having a 4,5-benzobenzothiazole nucleus, were similarly made, the last being extracted with benzene and recrystallised from ethyl acetate.[15]

The unsymmetrical methincyanine base, XI (n=0, Y=O, R=Me), was prepared (cf. section 3), from 2-methylbenzoxazole methiodide and 2-methylthio-3,1,4-benzothiazine, in 17 % yield after recrystallisation from acetone. Its N-ethyl analogue was similarly made and was converted into hydriodide and hydrochloride.[15]

The base, XI (n=0, Y=CH:CH, R=Me), was prepared in 60 % yield by heating 2-methylthioquinoline methotoluene-p-sulphonate and 2-methyl-3,1-4-benzothiazine (cf. section 2) at 145° for 10 minutes, liberating with aqueous ammonia, and recrystallising from alcohol. The isomer, XII, was prepared in 14 % yield from 2-methylthio-3,1,4-benzothiazine methotoluene-p-sulphonate and quinaldine (cf. section 2).[15]

The base, XIII, of the symmetrical methincyanine resulted in 30 % yield from 2-methyl-3,1,4-benzothiazine with 2-methylthio-3,1,4-benzothiazine methotoluene-p-sulphonate (cf. section 2), but with the methiodide the yield was only 17 %.[15]

B. Bases of Trimethincyanines with a 3,1,4-Benzothiazine Nucleus

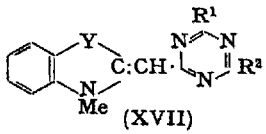
The base, XI (n=1, Y=O, R=Et), of an unsymmetrical carbocyamine was prepared in 37% yield (cf. section 4) by boiling 2-methyl-3,1,4-benzothiazine and 2-β-acetanilidovinylbenzoxazole ethiodide in pyridine for 5 minutes, treating with aqueous ammonia, washing with water and then acetone, and recrystallising from ethyl acetate; its analogue with a 6,7-benzobenzoxazole nucleus was made similarly. So also were XI (n=1, Y=S, R=Et), and the 4,5-benzo-derivative of that, and XI (n=1, Y=Se, R=Et).[14]

C. Bases of Trimethincyanines with a Perinaphtho-1,3-thiazine Nucleus

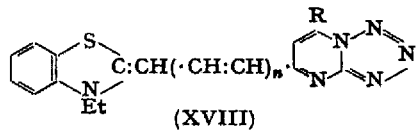
The base, XIV (Y=O, R=Et), of a carbocyanine was prepared by fusing together at 125° 2-methylperinaphtho-1,3-thiazine and 2-β-acetanilidovinylbenzoxazole ethiodide for 30 minutes, liberating with sodium hydroxide, extracting with chloroform, and recrystallising from ethyl acetate: its hydrochloride was made. The sulphur analogue, XIV (Y=S, R=Et), was prepared similarly, also, by use of substituted benzoxazolium and benzothiazolium salts, the 4,5- and 6,7-benzo-derivatives of each of the two bases; the hydrochloride of the last was prepared.[16]

8. Various Cyanine Bases, Having a 1,3,5-Triazine, a Tetrazolo-[2]pyrimidine, or a s-Triazolo[2,3-a]pyrimidine Nucleus

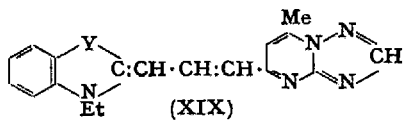
Methincyanine bases having a 2,4-dichloro-1,3,5-triazine nucleus were made by heating a heterocyclic methylene base with cyanuric acid in benzene or toluene, examples being XVII (Y=CH:CH or



(XVII)



(XVIII)



(XIX)

CMe_2, R^1=R^2=Cl) and the 5-methoxy-derivative of the latter:[32] the first of these had its sensitising maximum at 4800 Å and the third at

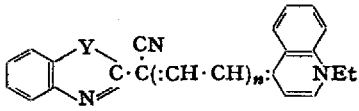
4550 Å.[33] By heating a dye of this kind with ammonia, or with a primary or secondary amine, in an inert solvent, its 4-chloro-substituent was replaced by 4-NR^1R^2, but prolonged boiling with potassium hydroxide in methanol resulted in replacement of both chlorine atoms by OMe groups.[34] The sensitising maxima of XVII (Y=CMe_2, R^1=Cl, R^2=NH_2 and Y=CMe_2, R^1=R^2=OMe) were at 4300 Å and 4350 Å, respectively. The sensitising maxima of a trinuclear and a tetranuclear dye base, in which two and three heterocyclic nuclei, respectively, were linked to a central 1,3,5-triazine nucleus, were also given.[33]

5-Methyltetrazolo[a]pyrimidine was used to give the two bases, XVIII (n=1 or 2, R=H), which sensitised to 6850 Å and 7300 Å, respectively. The benzoxazole analogue of the former sensitised to 6300 Å and the *N*-methyl analogue of XVIII (n=0, R=H) to 5150 Å. The base, XVIII (n=1, R=Me), was prepared through 5,7-dimethyltetrazolo[a]pyrimidine. From 5,7-dimethyl-s-triazolo[2,3-a]pyrimidine there were obtained the bases, XIX (Y=O or S), with sensitising maxima at 5200 Å and 5700 Å, respectively.[35]

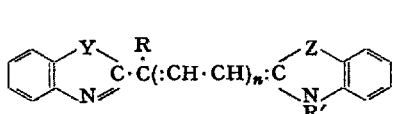
9. α-Cyano-Bases of Methincyanines and of Tri-, Penta-, and Hepta-methincyanines, and their Hydrolysis to Bases with Unsubstituted Chains

A. Bases of the Methincyanine Series

The α-cyano-base, XX (n=0, Y=CH:CH), of the 2,4'-cyanine group was prepared by reaction of 2-quinolylacetonitrile[36] and 4-phenylthioquinoline ethiodide (cf. II-4) with triethylamine in ethanol, followed by sodium hydroxide, and was purified through its hydrochloride. The base itself sensitised weakly but the hydrochloride



(XX)



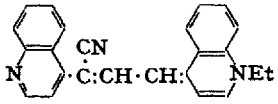
(XXI)

did not. By hydrolysis of the hydrochloride by boiling with 60 % sulphuric acid, and basifying with ammonia, the unsubstituted base resulted in 97 % yield. The α-cyano-base, XXI (n=0, Y=Z=S, R=CN, R'=Et), of the thiacyanine series was prepared from 2-benzothiazolyl-

acetonitrile,[37] 2-ethylthiobenzothiazole ethiodide, and triethylamine in ethanol.[17,18] The base of an α-cyanobenzimidazolo-2′-cyanine, prepared through 2-cyanomethylbenzimidazole[38] had its absorption maximum at 4400 Å, whilst a quaternary salt absorbed at 4550 Å.[20]

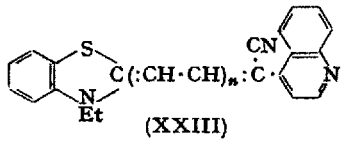
B. Bases of the Trimethincyanine Series

The α-cyano-base, XXII, of the 4,4′-carbocyanine series was prepared from 4-quinolylacetonitrile,[39], 4-β-acetanilidovinylquinoline ethiodide, and triethylamine in ethanol, by boiling for 5 minutes, and was purified by acetone, and recrystallised from methanol, resulting in 67 % yield.[17]



(XXII)

In the thia-2′-carbocyanine series, the α-cyano-base, XXI (n=1, Y=CH:CH, Z=S, R=CN, R′=Et), was prepared by heating 2-quinolylacetonitrile and 2-β-acetanilidovinylbenzothiazole ethiodide in pyridine. It sensitised weakly, and the unsubstituted base, prepared by its acid hydrolysis, sensitised very weakly. In making the α′-cyano-base of the oxa-2′-carbocyanine class, XXI (n=1, Y=CH:CH, Z=O, R=CN, R′=Et), the condensing agent was triethylamine in ethanol. An analogous base of the thiazolino-2′-carbocyanine type was similarly prepared from 2-quinolylacetonitrile and 2-β-acetanilidovinylthiazoline methiodide. An α-cyano-base, XX (n=1, Y=S), of the thia-4′-carbocyanine group was obtained by use of 2-benzothiazolylacetonitrile, whilst its isomer, XXIII (n=1), was obtained through 4-quinolylacetonitrile. By heating XXIII (n=1) with methyl toluene-p-sulphonate,

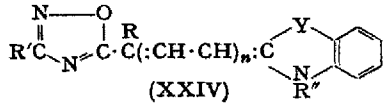


(XXIII)

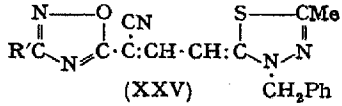
followed by potassium bromide, it was converted to an α-cyanothia-4′-carbocyanine bromide. An α-cyano-base, XXI (n=1, Y=Z=S, R=CN, R′=Et), of the thiacarbocyanine series was prepared and was

converted, by heating with ethyl toluene-*p*-sulphonate, followed by sodium iodide, to the corresponding thiacarbocyanine iodide.[17,18]

Examples of α-cyano-bases with a 1,2,4-oxadiazole nucleus were XXIV (n=1, Y=S, R=CN, R′=*p*-$CH_2 \cdot C_6H_4 \cdot CO_2Et$, R″=Et) and XXV (R′=*p*-$C_6H_4 \cdot Me$), with sensitising maxima at 5100 Å and 4900 Å, respectively.[19]

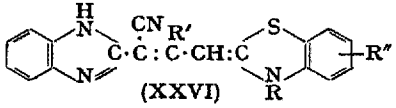


(XXIV)

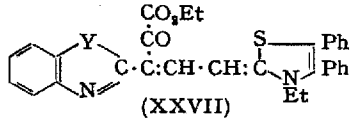


(XXV)

The base of an α-cyanobenzimidazolo-2′-carbocyanine absorbed at 5150 Å and one of its quaternary salts at 5250 Å. The base of an α-cyanobenzimidazolothiacarbocyanine absorbed at 4650 Å and its salt at 5000 Å; bases of this series with substituted benzothiazole nuclei, one of them having also a β-phenyl group, were compared with their salts as regards absorption maxima. An α-cyanobenzimidazoloselenacarbocyanine base was prepared by warming α-cyanomethylbenzimidazole with 3-ethyl-2-aniloethylidenebenzoselenazoline and benzoyl chloride for 1 minute; its absorption maximum lay at 4700 Å and that of a quaternary salt at 5050 Å. The absorption of the base of an α-cyano-β-phenylbenzimidazolothiazolocarbocyanine, in which the thiazole



(XXVI)



(XXVII)

nucleus had 4,5-diphenyl groups, was compared with that of a salt.[20] Absorption and sensitising data were given for twenty bases of type XXVI (R′=Me or Ph). For some of the *meso*-methyl compounds, the sensitising maximum lay at a longer wavelength than the absorption maximum by > 600 Å, whence aggregation was inferred (cf. XVII-2).[40]

C. Bases of the Pentamethincyanine Series

The α-cyano-base, XXI (n=2, Y=S, Z=CH:CH, R=CN, R′=Et), of the thia-2′-dicarbocyanine series was prepared from 2-benzothiazolylacetonitrile and 2-(4-acetanilido-1,3-butadienyl)quinoline ethiodide (cf. VII-1) with triethylamine in ethanol, by boiling for 5

minutes. It was hydrolysed to the unsubstituted base. In the thia-4'-dicarbocyanine series, the α-cyano-base, XXI (n=2, Y=S), was prepared through 2-benzothiazolylacetonitrile, and the α'-cyano-isomer, XXIII (n=2), was prepared through 4-quinolylacetonitrile. Both sensitised, but the latter only weakly; it was hydrolysed to the unsubstituted base, which did not sensitise. In the thiadicarbocyanine series, through 2-benzothiazolylacetonitrile, there were prepared the α-cyano-base, XXI (n=2, Y=Z=S, R=CN, R'=Et), and its 4,5-benzo-derivative.[17,18]

The α-cyano-dye base, XXIV (n=2, Y=S, R=CN, R'=p-C_6H_4·Me, R''=Et), with a 1,2,4-oxadiazole nucleus, had a broad sensitising maximum at 6100 Å.[19]

The absorption maximum of an α-cyanobenzimidazolothiadicarbocyanine base lay at 5400 Å and that of a quaternary salt at 5700 Å.[20]

D. Bases of the Heptamethincyanine Series

The α-cyano-base, XXI (n=3, Y=Z=S, R=CN, R'=Et), of the thiatricarbocyanine series was prepared from 2-benzothiazolylacetonitrile, 2-[6-acetanilido(1,3,5-hexatrienyl)]benzothiazole ethiodide (cf. VIII-2), and triethylamine in ethanol, by boiling for 5 minutes. It sensitised strongly, but the unsubstituted base, obtained by its hydrolysis, did not sensitise.[17,18]

10. Bases of Methincyanines, and of Tri- and Penta-methincyanines, Having an α-·CRO Group, Through Heterocyclic Nitrogenous Bases Having a ·CH_2·CRO Group: Their Hydrolysis to Unsubstituted Bases

A. Bases of the Methincyanine Series

Ethyl 2-benzothiazolylacetate was prepared by condensation of o-aminothiophenol with malonic acid ester chloride.[21] The group ·CH_2COOEt was converted by aniline, ammonia, and hydrazine, respectively, into the groups ·CH_2CONHPh, ·CH_2CONH_2, and ·$CH_2CONHNH_2$, and the last was converted by benzaldehyde into ·CH_2CONH·N:CHPh.[25] By boiling ethyl 2-benzothiazolylacetate with 2-methylthiobenzothiazole methomethylsulphate and triethylamine in ethanol for 30 minutes, it gave the α-carbethoxy-base, XXI (n=0,

Y=Z=S, R=CO_2Et, R'=Me), of the thiacyanine series; the analogue with an α-$CONH_2$ group was also described[21, 25] and others with an α-CONHPh or α-CO·NH·N:CHPh.[25] By boiling the first base with 60% sulphuric acid for 10 minutes, and making alkaline with ammonia, the α-CO_2Et group was replaced by hydrogen, and similarly with the base having an α-CONH·N:CHPh group.[24] The α-carbethoxy-bases, XXI (n=0, Y=S, Z=S or CH:CH, R=CO_2Et, R'=Et), of the thiacyanine and thia-2'-cyanine series were purified through their hydroperchlorates.[22]

B. Bases of the Trimethincyanine Series

In the 1,2,4-oxadiazole series, the dye base, XXIV (n=1, Y=S, R=Ac, R'=p-C_6H_4Me, R"=Et), was not only prepared from an oxadiazole having a 5-CH_2Ac group by reaction with 2-β-anilinovinylbenzothiazole ethiodide, but also from an oxadiazole with a 5-CAc:CH·NHPh group (prepared from the other base by use of diphenylformamidine), by reaction with a 2-methylbenzothiazolium salt. The bases, XXIV (n=1, Y=O, R=Ac, R'=p-C_6H_4Me, R"=p-$CH_2 \cdot C_6H_4 \cdot CO_2Et$; n=1, Y=S, R=Ac, R'=o-C_6H_4OMe, R"=Et; and n=1, Y=S, R=CO_2Et, R'=p-C_6H_4Me, R"=Et), were all prepared by a method analogous to the former procedure.[19]

The sensitising action of an α-phenylcarbamyl-base, XXI (n=1, Y=Z=S, R=CONHPh, R'=Me), of the thiacarbocyanine series was patented: it was prepared through 2-benzothiazolylacetanilide and a 2-β-anilinovinylbenzothiazolium salt.[23] Similar bases of this type were XXI (n=1, Y=Z=S, R=COOEt, CONHPh, or CONH·N:CHPh, R'=Et).[24, 25] The first of these was converted by ethyl iodide into the corresponding α-carbethoxythiacarbocyanine iodide, and was also hydrolysed to the dye with an unsubstituted chain.[24] At about the same date, various heterocyclic bases having a CH_2COR group were condensed, by means of triethylamine in pyridine, with quaternary salts having a 2-β-acetanilidovinyl group to give the α-substituted bases, XXI (n=1, Y=Z=S, R=COOEt, $COCO_2Et$, COMe, COPh, CO·C_6H_4OMe(-p), or CO·$C_6H_3O_2CH_2$(-m,p), R'=Et), including derivatives in which one nucleus was substituted; a thiacarbocyanine base with an α-CSMe group was also made.[27] Subsequently, from ethyl 2-benzothiazolylpyruvate, and its 4,5-benzo- and 5,6-dimethyl derivvatives, by heating in pyridine containing acetic anhydride with 2-aniloethylidene-3-ethylbenzothiazoline, there were prepared XXI

(n=1, Y=Z=S, R=$COCO_2Et$, R'=Et), and the corresponding two derivatives, in yields of 75, 58, and 56%. The α-$COCO_2Et$ base, XXI (n=1, Y=Z=Se, R=$COCO_2Et$, R'=Et), of the selenacarbocyanine group was similarly made.[28]

The sensitising action of the α'-phenylcarbamyl base, XXI (n=1, Y=S, Z=O, R=CONHPh, R'=Me), of the oxathiacarbocyanine series was described[23] and the 5,6-dimethyl derivative of XXI (n=1, Y=S, Z=O, R=Ac, R'=Et) was prepared; a base, XXI (n=1, Y=O, Z=S, R=Ac, R'=Et), with the substituent in the α-position to the benzoxazole nucleus, was also made.[27] In the selenathiacarbocyanine series, there were prepared the bases, XXI (n=1, Y=S, Z=Se, R=COOEt, R'=Et), and the 5-ethoxy-derivative of XXI (n=1, Y=S, Z=Se, R=Ac, R'=Et.)[27] The two bases, XXI (n=1, Y=S, Z=S or Se, R=COOEt, R'=Et), were hydrolysed by sulphuric acid to the corresponding bases with unsubstituted chains.[24] With an α-$COCO_2Et$ group there were prepared the isomers, XXI (n=1, Y=Se, Z=S, R=$COCO_2Et$, R'=Et; and n=1, Y=S, Z=Se, R=$COCO_2Et$, R'=Et), also two derivatives o. the latter in which the benzothiazole nucleus had 4,5-benzo- or 5,6-dimethyl substituents.[28] The 5-methyl derivative of the base, XXI (n=1, Y=S, Z=CMe_2, R=Ac, R'=Et), of the indothiacarbocyanine series was described.[27]

In the thiathiazolocarbocyanine class, a base, XXVII (Y=S), with an α-$COCO_2Et$ group was prepared, also its 4,5-benzo-derivative. In the selenathiazolocarbocyanine class, an analogue, XXVII (Y=Se), of the former base was also described.[28]

C. Base of the Pentamethincyanine Series

One base, XXI (n=2, Y=Z=S, R=COMe, R'=Et), of the thiadicarbocyanine type was described.[27]

TABLE I. Some Properties of Cyanine Bases

Formula of base	Type of its ethiodide	Appearance of crystals	M.p. (°C)	Absorption maximum (Å)	Absorption maximum (Å) of its ethiodide	Bathochromic shift (Å) base → ethiodide	Ref.
Methincyanine Group							
II (Y=CH:CH, R=Et)	2,2′-cyanine	bright red	140[a]	4750[b]	5220	470	6
I (R=Et)	thiacyanine	pale yellow	163	3960	4230	270	2, 11
II (Y=S, R=Et)	thia-2′-cyanine	lemon yellow	151	4260[b]	4860	600	6
III (Y=S, R=Et)	thia-2′-cyanine	orange	160	4820[b]	4860	40	6
XVI (*n*=0, Y=S, R=Et)	thia-4′-cyanine	orange yellow	131	4320	5030	710	6, 41
XXI (*n*=0, Y=Z=S, R=CO_2Et, R′=Et)	thiacyanine	pale yellow	127	3430	4370	940	22
XXI (*n*=0, Y=S, Z=CH:CH, R=CO_2Et, R′=Et)	thia-2′-cyanine	almost black	179[c]	5170	4780	—390	22
Dimethincyanine Group							
VI	indolothia-	reddish brown prisms; green reflex	286–288[c]	5060[d]	4970[d,e]	—90	11
VIII	indolothia-	canary yellow	150–151[c]	3920[d]	4970[d]	1050	11
IX	indolo-4′-	dark blue needles	249–251[c]	5710[d,f] 6160[d]	5390[d,e]	—320	11
X	indolo-4′-	yellow needles	192–193[c]	3940[d]	5390[d,e]	1450	11
Trimethincyanine Group							
IV (*n*=1, Y=Z=S, R=Et)	thiacarbocyanine	red	136–137	4580	5575	995	6, 11
XXI (*n*=1, Y=Z=S, R=CO_2Et, R′=Et)	α-CO_2Et-thia-carbocyanine	—	162–162·5	4891	5040	149	24, 25

[a] With previous softening. [b] Also secondary maximum. [c] With decomposition.
[d] Absorption in pyridine, whereas the rest are in methanol. [e] Salt is methiodide of base. [f] Stronger band.

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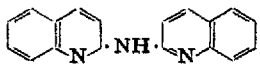
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CHAPTER XII

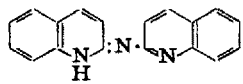
Azacyanines, Including Dyes Substituted on the Chain, and Bases of which the Quaternary Salts are Azacyanines

1. General Survey

The possibility of preparing azacyanines, having two heterocyclic nuclei linked by nitrogen instead of by a methin group, was first discussed in 1924, when it was recorded that a 2,4′-azacyanine could not be prepared simply by replacing quinaldine methiodide in a 4′-cyanine condensation (II-1-C) by 2-aminoquinoline methiodide.[1] 2-Aminoquinoline, however, unlike quinaldine, showed greater reactivity than its methiodide, so that it could be condensed with 2-chloroquinoline to give the hydrochloride of 2,2′-diquinolylamine.[1,2] The base existed in two modifications, for which formulae I and II were

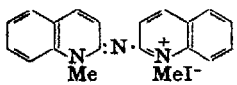


(I)

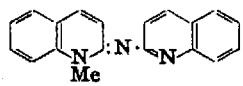


(II)

proposed. On heating it with methyl iodide, it gave a mixture of its hydriodide and the azacyanine, III, in equimolecular proportions. The latter was synthesised by converting the acetyl derivative of 2,2′-diquinolylamine into its methomethylsulphate and into its methiodide,



(III)

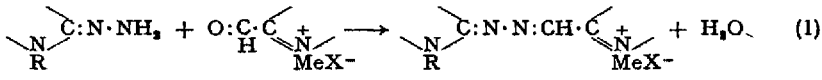


(IV)

either of which with sodium hydroxide gave the base, IV, which combined with methyl iodide to give III. A solution of the iodide was pale yellow with a blue fluorescence and showed very narrow absorption

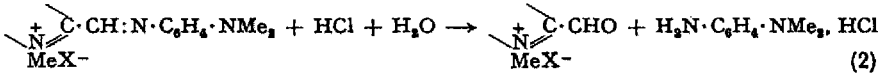
bands, of which the principal one lay at a shorter wavelength, by 990 Å, than that of the corresponding 2,2′-cyanine.[1] Several years later, a simplified process for obtaining other diheterocyclic amines consisted in condensing 2-iodoquinoline alkiodide with 2-aminopyridine or 2-aminothiazole, and 1-iodoisoquinoline ethiodide with 2-aminopyridine, and hence three other types of azamethincyanines were prepared. Replacement of :CH· by :N· in a 2-pyrido-2′- and a thiazolo-2′-cyanine, respectively, led to hypsochromic shifts of 1020 Å and 700 Å,[3] but in the thiacyanine series it was only 540 Å (section 2-A).[4]

Historically, $\alpha\beta$-diazatrimethincyanines follow next, for in 1928 they were synthesised by condensing the quaternary salt of a heterocyclic aldehyde with the hydrazone of a heterocyclic ketone (equation 1).



(1)

The aldehyde component was not isolated but was liberated from an anil (see XIII-2) by the action of hydrochloric acid (equation 2) and then presented with the hydrazone.[5] A later and simpler method for



(2)

obtaining a β-anilino-β-azavinyl quaternary salt was by condensation of one having a reactive methyl group with diazoaminobenzene.[4] Five $\alpha\beta$-diazatrimethincyanines all possessed powerful desensitising properties (section 5-A).[5] Subsequently it was noted that, with each of three types of $\alpha\beta$-diazatrimethincyanines, the principal absorption maximum lay at a shorter wavelength than did a second ill-defined band, whereas with trimethincyanines possessing a secondary absorption band the reverse was usual. The three compounds with the chain :N·N:CH· had their absorption maximum at a shorter wavelength by 770–820 Å than had the corresponding dyes with the chain :CH·CH:CH· (see also section 5-B).[3]

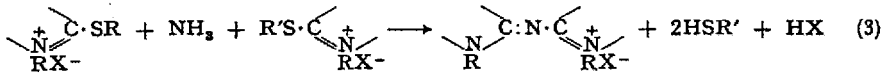
It was recorded in 1934 that various types of azacyanines exhibit photographic sensitising properties, and that their preparation could be effected by an extension of certain general methods, applicable to

compounds having a reactive methyl group, to other compounds having an amino group.[6] Thus azamethincyanines, in which the nuclei were linked by :N·, were prepared by condensation of a quaternary salt having an amino-group with one having an alkylthio-group (cf. II-4), or, in one example, an iodo-substituent (cf. II-2) (section 2-B), and bases of azamethincyanines were also made[6] (section 9) (cf. XI-2). The names cyazine and cyadiazine were proposed for certain salts of the azacyanine group.[6]

α-Azatrimethincyanines, with the chain :N·CH:CH·, were formulated as obtainable by reaction of a quaternary salt having an amino-group with one having the group ·CH:CH·NRR′ (section 3) (cf. V-6) and the base of one such compound was described (section 9).[6] Absorption maxima of three α-azatrimethincyanines lay at a shorter wavelength by 90–300 Å than those of the corresponding αβ-diazatrimethincyanines. In three series, each of ten members, of α-azatrimethincyanines, the absorption maxima lay at a shorter wavelength than those of the corresponding trimethincyanines.[4] According to a patent of 1943, a quaternary salt having the group ·CH:CH·CH:CH·SEt could be condensed, not only with salts having a reactive methyl group (see VII-3), but also with those having an amino-group, and an α-azapentamethincyanine, having the chain :N·CH:CH·CH:CH·, was thus prepared (section 3).[7]

In 1934, again, symmetrical αγ-diazatrimethincyanines, with the chain :N·CR:N·, were formulated. Examples with the unsubstituted chain :N·CH:N· were prepared by condensation of salts having an amino group with ethyl orthoformate (section 6-C) (cf. IV-6). Alternatively, bases having an amino-group could be condensed with ethyl orthoformate to give diheterocyclic bases, with the chain ·NH·CH:N·, and one of these, by fusion with an ester, was converted into an αγ-diazatrimethincyanine (section 6-A).[6]

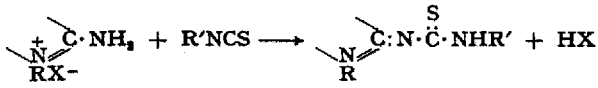
In 1935 various types of symmetrical azamethincyanines were prepared by the action of ammonia, or of an ammonium salt in the presence of a base, on quaternary salts having an alkylthio-group (equation 3) (section 2-C).[8]



(3)

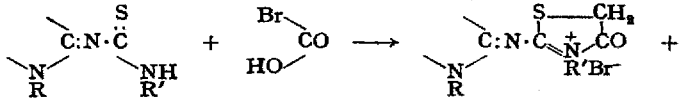
Special unsymmetrical azamethincyanines in which a benzothiazole or thiazole nucleus, on the one hand, was linked through

:N· to a 4-oxothiazoline nucleus on the other, were synthesised in 1951. The method consisted in converting a 2-amino-benzothiazolium or -thiazolium salt into an *N*-alkylbenzothiazoline or -thiazoline having a substituted thiocarbimido-group (equation 4).



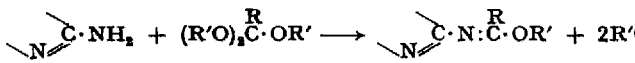
(4)

This compound was then brought into reaction with halogenoacetic acid (equation 5) (section 2-D).[9] Dyes of this kind were used in the preparation of trinuclear dyes (see XV-5-E and F).



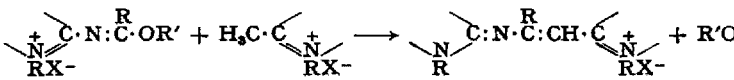
(5)

In 1940 a two-stage synthesis of *meso*-substituted α-azatrimethincyanines was patented. The first stage consisted in the reaction of an ortho-ester with a heterocyclic base having an amino-group (and there is no counterpart to this with one having a methyl group), to give a base with the group ·N:CR(OR') (equation 6). The resultant base,



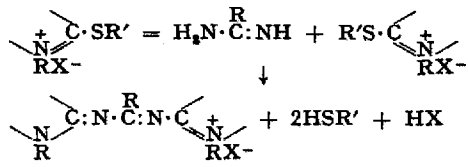
(6)

together with another having a methyl group, was heated with alkyl toluene-*p*-sulphonate, followed by pyridine, and the salts gave the dye (equation 7) (section 4).[10]



(7)

One *meso*-substituted αγ-diazatrimethincyanine was prepared by a modification of the above method, in which the base used at the second stage had an amino, instead of a methyl group (section 6-B).[10] Another procedure was the preparation of symmetrical αγ-diazatrimethincyanines, all of them, with one exception, *meso*-substituted, by reaction of amidines with salts having an amino-group (equation 8) (section 6-D).[8]



(8)

In Figure 1, from a publication of 1951, the absorption curves of an α-azathiacarbocyanine and an αγ-diazathiacarbocyanine are compared with that of the corresponding thiacarbocyanine, to illustrate that the effect of dividing a long resonating chain into shorter fragments is to shift the absorption to shorter wavelengths and to reduce its intensity.[11]

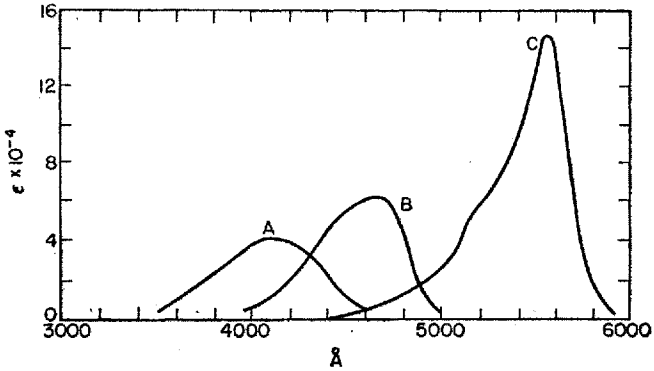
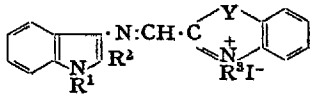


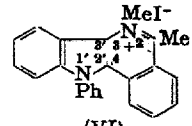
Fig. 1. Absorption spectra. A=3,3′-diethyl-αγ-diazathiacarbocyanine iodide, XXXVIII (Y=Z=S, R=Et, R′=H, X=I), in ethylene chloride; B=3,3′-diethyl-α-azathiacarbocyanine iodide, XXXII (Y=Z=S, n=1, R=H, R′=Et), in methanol; C=3,3′-diethylthiacarbocyanine iodide in methanol. [From Brooker, White and Sprague[11] (Fig. 4). By courtesy of the authors and the American Chemical Society].

In 1944 a series of azadimethincyanines was prepared (section 7) by condensation of 1,2-disubstituted-3-nitroso-indoles with numerous types of quaternary salts having a reactive methyl group. Thus substances of the types V (Y=CH:CH, CMe_2, S, or Se) were described, and other quaternary salts that were used were of the α- and γ-picolinium and lepidinium types. The catalyst was piperidine in ethanol and formation of a heterocyclic methylene base and of piperidine hydriodide as intermediate products was postulated. A dye, V (Y=CMe_2), was obtained without a catalyst by use of the appropriate methiodide, but that salt is known to lose hydriodic acid readily, giving

the methylene base; the pure methylene base would not condense with the nitroso-compound.[12,13] Many of the dyes were desensitisers, which was to be expected,[14] since both heterocyclic nitrogen atoms are separated from the nitrogen atom of the chain by an even number of carbon atoms.[12,13] In 1949 the azadimethincyanine, V (R^1=R^2=Ph, R^3=Me), was prepared by the action of methyl iodide on the anhydronium base (section 9-C).[15]



(V)

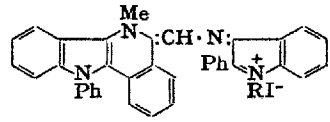


(VI)

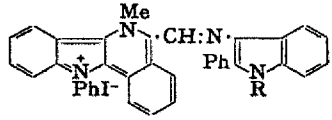
In the same year, indolo(3′,2′-3,4)isoquinolines were synthesised and the methiodide, VI, was condensed with 1-ethyl-3-nitroso-2-phenylindole to give an azadimethincyanine. Unlike typical cyanines, which are formulated as resonance hybrids of two canonical forms, this compound was represented by the three forms, VIIa, b, and c. Condensation of VI with 3-nitroso-1,2-diphenylindole gave a compound like



(VIIa)



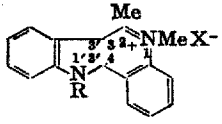
(VIIb)



(VIIc)

the preceding one but without methyl iodide. It was considered that loss of methyl iodide occurred after dye formation: the methylindoloisoquinoline would not condense with the nitrosodiphenylindole.[16] In 1956 the synthesis of 2-methylindolo(3′,2′-3,4)quinoline and its 1,2-dimethyl homologue was described and these bases were converted into their quaternary salts, VIII (R=H or Me). The salts were condensed with 1-ethyl-3-nitroso-2-phenylindole to give azadimethincyanines, IX, for which again three canonical forms were postulated. For making such a dye from VIII (R=Me), the condensing agent was

piperidine in ethanol, but it was ineffective with VIII (R=H) and triethylamine in acetic anhydride was used with that (section 7). On boiling the nitroso-compound and VIII (R=H) with sodium methoxide

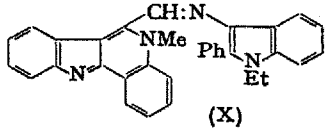


(VIII)



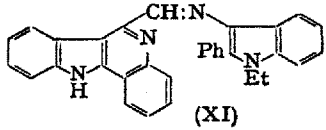
(IX)

in methanol for 50 hours, two products of almost identical composition were formed. The minor component showed no band in the 2·9 μ region corresponding to an :NH group and was almost certainly X, formed



(X)

by loss of toluene-*p*-sulphonic acid from the salt, VIII (R=H, X= *p*-$SO_3 \cdot C_6H_4Me$). The infrared spectrum of the second compound showed a band at 2·95 μ characteristic of an :NH group, and the compound was formulated as the base, XI, formed by loss of methyl toluene-*p*-sulphonate (section 9-C). The salts, VIII (R=H or Me), were also used for preparing a trimethincyanine (see X-5-B), styryl compounds (see XIII-1-M.2), and anils (see XIII-2-B.2).[17]

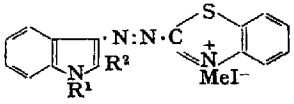


(XI)

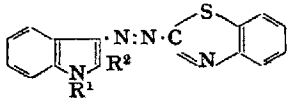
Four nitroso-derivatives of pyrrocoline[18] were, like the nitrosoindoles, condensed with heterocyclic methiodides to give azadimethincyanines. In eleven out of twelve instances, there was a hypsochromic shift on passing from a dye with a 2-substituted 3-linked pyrrocoline nucleus to one with a 2-substituted 3-acetyl-1-linked pyrrocoline nucleus.[19]

Four diazadimethincyanines of type XII (see section 8) were pre-

pared from bases of type XIII (see section 9-D). They all desensitised strongly and, with one, weak sensitisation was also observed. In these salts, one nitrogen atom of the chain is separated by an even, and the other by an odd, number of atoms from both the heterocyclic nitrogen atoms, whence, according to theory,[14] the compounds should both desensitise and sensitise.[20]



(XII)



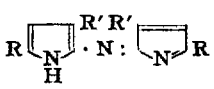
(XIII)

The first base of which an azacyanine is the quaternary salt was IV, which was synthesised in 1924 as the penultimate stage in arriving at III.[1] The sensitising action of bases of which azamethincyanines and α-azatrimethincyanines are the quaternary salts, was patented in 1935.[21] They were all derived from 2-aminobenzothiazole, by its reaction with a quaternary salt having a 2-methylthio- or a 2-β-acetanilidovinyl group, respectively[6, 21] (see sections 9-A and B). Subsequently 2-amino-3,1,4-benzothiazine was used in the preparation of an α-azatrimethincyanine base[22] (section 9-B). 2-Aminobenzothiazole had been condensed with ethyl orthoformate to give dibenzothiazolylformamidine, with the chain ·NH·CH:N·, and other bases of this type had also been prepared;[6] they sensitised chloride emulsions,[21] although they do not possess the conjugated chain of alternate double and single bonds which is characteristic of cyanines. Other diheterocyclic bases which sensitised, without being of the cyanine type, were prepared by condensing salts having a 2-alkylthio-group with diamines, such as hydrazine, phenylenediamine, or benzidine: they had chains such as :N·N:, :N·C_6H_4N:, and :N·C_6H_4·C_6H_4·N:.[23] Salts having a 2-β-acetanilidovinyl group[23] or a 2-β-ethylthiovinyl group[24] were similarly condensed with diamines.

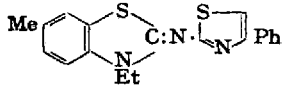
Methin dyes with an *NN'*-diH structure (X-4-D) are not regarded as true cyanines, nor are certain bases, XIV, of which azamethin analogues would be the salts, yet they do bear some resemblance to cyanine bases. These 2,2',4,4'-tetra-aryl-5,5'-azadipyrromethins were described in 1943 as intensely blue, high melting solids, which were sparingly soluble in most organic solvents. They could be prepared by various methods, such as heating a 2,4-diaryl-5-nitrosopyrrole with a

2,4-diarylpyrrole, or by heating a 5-amino-2,4-diarylpyrrole (or substance adapted to yield it *in situ*) with an oxidising agent. Thus 1,3-diaryl-1-nitromethyl-3-propanone could be melted with an agent yielding ammonia, or 1-cyano-1,3-diaryl-3-propanone, $CN \cdot CHR' \cdot CH_2 \cdot CRO$, could be heated with such an agent, together with an oxidising agent.[25,26] Subsequently it was found that a cyano-compound $CNCH_2 \cdot CH_2 \cdot CRO$ could be heated with a hydroxylamine salt to give azamethin dyes, XIV (R=aryl, 2-thienyl, 2-furyl, 2-thiazolyl, carbazyl, or tetralinyl, R'=H), which were sometimes isolated as hydrochlorides or dihydrochlorides.[27]

In 1953 an *N*-alkyl-2-iminobenzothiazoline, useful as a starting point for methincyanines (II-5), was also condensed with 2-amino-4-phenylthiazole to give the azamethincyanine base, XV (section 9-A).[28]

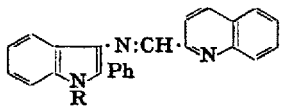


(XIV)

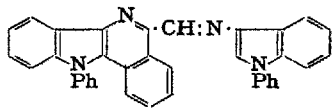


(XV)

Bases, XVI (R=Et or Ph), of azadimethincyanines (section 9-C) were prepared by condensing 3-aminoindoles with 2-formylquinoline and the latter product was converted into quaternary salts (section 7).[15] When the methiodide, VI, was condensed with 3-nitroso-1,2-diphenylindole, instead of giving an azadimethincyanine (like VII) (cf. section 7), loss of methyl iodide occurred, leading to the base XVII.[16]



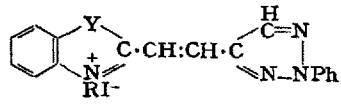
(XVI)



(XVII)

A triazole nucleus (cf. X-5-C) was first introduced into cyanine dyes in 1950, when there were described azacyanines of a special type, having a 2,1,3-triazole nucleus: they are dimethincyanines in which an extra part of the chain joining the nitrogen atoms is cyclic, and the chain itself includes a nitrogen atom. These dyes, XVIII, were prepared by use of 4-formyl-2-phenyl-2,1,3-triazole, which, like 1-alkyl-3-formyl-2,5-dimethylpyrrole (see X-5-A), condensed with quaternary salts

having a reactive methyl group. Besides dyes of type XVIII, analogues with a 3-linked isoquinoline (cf. X-5-A), 2-linked pyridine, or 4-linked quinoline nucleus were also made (section 10).[29]

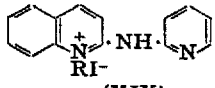


(XVIII)

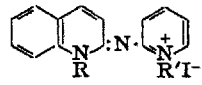
2. Azamethincyanines

A. Synthesis through Diheterocyclic Amines

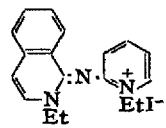
The original synthesis of the 2,2′-azacyanine, III, from 2-chloro- and 2-amino-quinoline, through 2,2′-diquinolylamine, I → its acetyl derivative → quaternary salt → IV → III[1] was simplified in later analogous preparations where 2-iodoquinoline alkiodide was condensed with 2-aminopyridine to give 2,2′-pyridylaminoquinoline alkiodide, XIX (R=Me or Et). Removal of hydriodic acid gave bases analogous with IV and these were forthwith treated with alkyl iodide to give the 2-pyrido-2′-azacyanines, XX (R=R′=Me or Et and R=Et, R′=Me), which were obtained from XIX in yields of 52–61 %; they sensitised weakly. By heating 1-iodoisoquinoline ethiodide with 2-aminopyridine



(XIX)

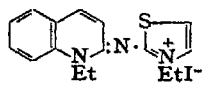


(XX)



(XXI)

in ethanol, liberating the diheterocyclic base by means of sodium carbonate, and heating it with ethyl iodide, there resulted the azamethincyanine, XXI, which was recrystallised from methanol (14 %



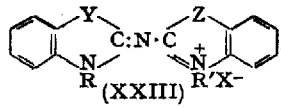
(XXII)

yield): like other dyes containing an isoquinoline nucleus (see X-5-A), it did not sensitise. The thiazolo-2′-azacyanine, XXI, was similarly prepared, in 16 % yield, from the condensation product of 2-iodoquinoline ethiodide and 2-aminothiazole.[3]

B. Azamethincyanines from a Quaternary Salt Having an Amino Group and One Having an Alkylthio-Group

The sensitising action of the 2,2′-azacyanine, III, towards a chloride emulsion extended to 4600 Å, with maxima at 4150 Å and 4400 Å. The corresponding 2,4′-azacyanine was prepared from 2-methylthioquinoline methotoluene-*p*-sulphonate and 4-aminoquinoline methiodide by the action of sodium ethoxide; it sensitised to 4800 Å, with maxima at 4250 Å and 4550 Å. The 4,4′-azacyanine was prepared by the action of sodium ethoxide on 1-methyl-4-thiodihydroquinoline methotoluene-*p*-sulphonate and 4-aminoquinoline methiodide; it sensitised to 5000 Å, with maxima at 4550 Å and 4825 Å.[6]

The thia-2′-azacyanine, XXIII (Y=S, Z=CH:CH, R=R′=Me, X=I), was prepared by heating together 2-aminobenzothiazole, 2-methylthioquinoline, and methyl toluene-*p*-sulphonate, and treating with pyridine and aqueous potassium iodide. Its homologue, XXIII



(XXIII)

(Y=S, Z=CH:CH, R=Me, R′=Et, X=I), was prepared by heating 2-aminobenzothiazole methobromide and 2-iodoquinoline ethiodide with sodium ethoxide in ethanol. A thia-4′-azacyanine was prepared by heating together 1-alkyl-4-thiodihydroquinoline, 2-aminobenzothiazole, and methyl toluene-*p*-sulphonate, followed by pyridine and potassium iodide.[6]

The thia-azacyanine, XXIII (Y=Z=S, R=R′=Me, X=*p*-$SO_3 \cdot C_6H_4Me$), was prepared by heating 2-amino- and 2-methylthiobenzothiazole with methyl toluene-*p*-sulphonate, followed by pyridine, and it was converted into the corresponding iodide. The 4,5-benzo-derivative of the former salt, and the 6,7-benzo-derivative of the latter, were similarly prepared, by use of suitable amino-compounds. XXIII (Y=Z=S, R=Me, R′=Et, X=I) was prepared from 2-methylthio-

benzothiazole methotoluene-*p*-sulphonate and 2-aminobenzothiazole ethobromide, followed by pyridine and potassium iodide. The oxa-azacyanine, XXIII (Y=Z=O, R=R′=Me, X=I), was prepared similarly.[6]

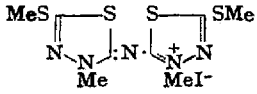
The oxathia-azacyanine, XXIII (Y=O, Z=S, R=R′=Me, X=I), was prepared through 2-aminobenzothiazole.[6]

C. Symmetrical Azamethincyanines from Quaternary Salts, Having an Alkylthio-Group, with Ammonia

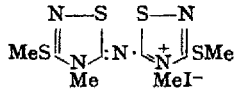
A 2,2′-azacyanine was prepared by passing ammonia into an alcoholic solution of 2-ethylthioquinoline methotoluene-*p*-sulphonate, treating with sodium ethoxide in ethanol, and converting the product into perchlorate.[8]

The thia-azacyanine, XXIII (Y=Z=S, R=R′=Me, X=I), was prepared by heating 2-methylthiobenzothiazole methotoluene-*p*-sulphonate with ammonium nitrate in pyridine, and treating with potassium iodide.[8]

By boiling each of two di(methylthio)thiadiazolium salts with ammonium nitrate in pyridine for 30 minutes, followed by aqueous potassium iodide, there resulted the thiadiazoloazacyanines, XXIV and XXV.[8]



(XXIV)

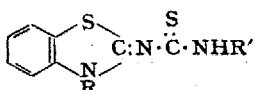


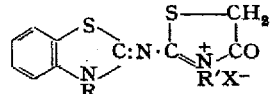
(XXV)

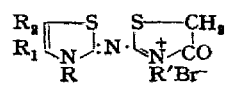
D. Synthesis of Azamethincyanines, Having one Benzothiazole or Thiazole Nucleus, and One 4-Oxothiazoline Nucleus, by Reaction of a 2-Thiocarbimidobenzothiazoline or -thiazoline with Halogenoacetic Acid

The compound, XXVI (R=Et, R′=Ph), m.p. 158°, was prepared by heating 2-aminobenzothiazole ethiodide with phenyl isothiocyanate in pyridine; its *N*-methyl analogue and its 6-ethoxy-derivative were made similarly; so were analogues from 2-amino-4-methylthiazole methiodide and from 2-amino-5-methyl-4-phenylthiazole ethiodide; the 6-ethoxy-derivative of XXVI (R=Et, R′=CH_2·CH:CH_2) was also made. By reaction of XXVI (R=Me or Et, R′=Ph) with halogenoacetic acid in acetic acid, there were prepared XXVII (R=Me or Et,

R′=Ph, X=Br); the 6-ethoxy-derivative of the latter was made, also XXVII (R=Et, R′=Ph, X=Cl); from the 6-ethoxy-derivative of XXVI (R=Et, R′=CH_2·CH:CH_2) there resulted the 6-ethoxy-derivative of XXVII (R=Et, R′=CH_2·CH:CH_2, X=Br). The compounds, XXVIII (R=Et, R′=R^1=Ph, R^2=Me, and R=R^1=Me, R′=Ph, R^2=H), were made similarly.[9]

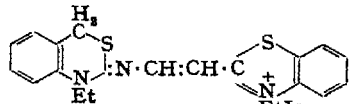

(XXVI)


(XXVII)


(XXVIII)

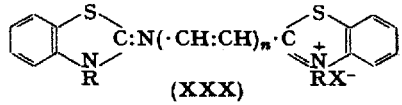
3. α-Azatri- and α-Azapenta-methincyanines by Reaction of a Quaternary Salt Having an Amino Group with Another Having the Group ·CH:CH·NAcPh or ·CH:CH·CH:CH·SR. α-Azatrimethincyanine from an Anhydronium Base with an Ester

The sensitising action of α-azatrimethincyanines was patented in 1934[6] but apparently the first salt of this kind, XXIX, was not described until 1942. It was obtained in 74% yield by boiling 2-β-acetanilidovinylbenzothiazole ethiodide and 2-amino-3,1,4-benzothiazine ethiodide with anhydrous potassium carbonate in ethanol for 7 minutes,


(XXIX)

and recrystallising from methanol. The corresponding dye base was also prepared (see section 9-B).[22] In 1951, three series of α-azatrimethincyanines were described, consisting of ethiodides or perchlorates having a benzothiazole, a 2-linked quinoline, or a 4-methylthiazole nucleus, respectively, linked to one of ten different heterocyclic nuclei. The method consisted in condensing a quaternary salt having an amino- with one having a β-acetanilidovinyl group, by heating with triethylamine in ethanol.[4] The dye base of the α-azathiacarbocyanine series (see section 9-B) was converted into its ethoethylsulphate, XXX (n=1, R=Et, X=SO_4Et) (85% yield), and that into the ethiodide, XXX (n=1, R=Et, X=I). The ethiodide was also prepared by boiling

2-aminobenzothiazole ethiodide with 2-β-acetanilidovinylbenzothiazole ethiodide in pyridine for 5 minutes: after three recrystallisations from methanol, the yield was 22%.[11]

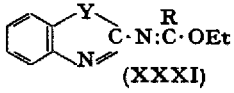


(XXX)

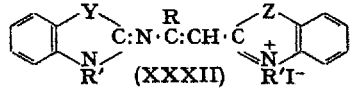
The α-azathiadicarbocyanine, XXX (n=2, R=Me, X=I), was prepared by heating a benzothiazole methiodide having the group ·CH:CH·CH:CH·SEt with 2-aminobenzothiazole methotoluene-p-sulphonate in pyridine at 100° for 15 minutes.[7]

4. *Meso*-Substituted α-Azatrimethincyanines from a Base with a Methyl Group, One with the Group ·N:CR(OR'), and an Ester

By boiling 2-aminobenzothiazole with excess of ethyl orthoacetate for 15 minutes, the base, XXXI (Y=S, R=Me), was obtained as an oil, b.p. 198°/29 mm. Its 6-ethoxy- and 4,5-benzo-derivatives were similarly made, also the benzoxazole, XXXI (Y=O, R=Me). By reaction of 2-aminobenzothiazole with ethyl orthopropionate or orthobenzoate, there resulted XXXI (Y=S, R=Et or Ph). By heating XXXI (Y=S, R=Me) and quinaldine with methyl toluene-p-sulphonate at 130–140° for 3 hours, boiling with pyridine for 30 minutes, and



(XXXI)



(XXXII)

converting into iodide, there was obtained the β-methyl-α-azathia-2'-carbocyanine, XXXII (Y=S, Z=CH:CH, R=R'=Me). The 4,5-benzo-derivative of XXXI (Y=S, R=Me) was used to prepare the 4,5-benzo-derivative of the dye.[10]

By heating XXXI (Y=S, R=Me) and 2-methylbenzothiazole with methyl, or ethyl, toluene-p-sulphonate, followed by pyridine and potassium iodide, there resulted the β-methyl-α-azathiacarbocyanines, XXXII (Y=Z=S, R=Me, R'=Me or Et). Through the 6-ethoxy- or 4,5-benzo-derivatives of XXXI (Y=S, R=Me), derivatives of the former dye were made, whilst use of XXXI (Y=S, R=Et) gave

XXXII (Y=Z=S, R=Et, R′=Me). Reaction of XXXI (Y=S, R=Ph) with 2-ethylbenzothiazole (cf. VI-17) and methyl toluene-*p*-sulphonate, followed by pyridine and iodide, gave a *γ*-methyl-*β*-phenyl-*α*-azathiacarbocyanine.[10]

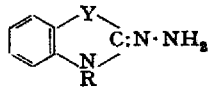
The *β*-methyl-*α*-azaoxathiacarbocyanine, XXXII (Y=O, Z=S, R=R′=Me), was prepared from XXXI (Y=O, R=Me), 2-methylbenzothiazole, and methyl toluene-*p*-sulphonate; the isomeric *γ*-azacompound, XXXII (Y=S, Z=O, R=R′=Me), was prepared from XXXI (Y=S, R=Me), 2-methylbenzoxazole, and methyl toluene-*p*-sulphonate.[10]

The *β*-methyl-*γ*-azaselenathiacarbocyanine, XXXII (Y=S, Z=Se, R=Me, R′=Et), was prepared from XXXI (Y=S, R=Me), 2-methylbenzoselenazole, and ethyl toluene-*p*-sulphonate.[10]

5. *αβ*-Diazatrimethincyanines

A. From the Quaternary Salt of a Heterocyclic Aldehyde with the Hydrazone of a Heterocyclic Ketone

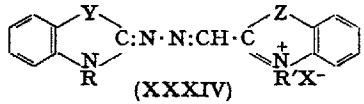
In the quinoline series, the hydrochloride of the hydrazone, XXXIII (Y=CH:CH, R=Me), was obtained by condensing 2-iodoquinoline methiodide with hydrazine methyl carboxylate and hydrolysing the ester with hydrochloric acid. In the benzothiazole series, the hydrazone, XXXIII (Y=S, R=Et), was synthesised from *N*-ethyl-2-iminobenzothiazoline, through the nitrosoimino-compound, which was reduced by



(XXXIII)

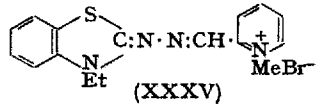
zinc and acetic acid. To prepare the *αβ*-diaza-2,2′-carbocyanine, XXXIV (Y=Z=CH:CH, R=R′=Me, X=ClO_4), an acid reaction mixture containing the hydrochloride of XXXIII (Y=CH:CH, R=Me) was added to one containing the anil prepared from quinaldine methoperchlorate and *p*-nitrosodimethylaniline in dilute perchloric acid, and the mixture was boiled for 30 minutes. The same hydrazone hydrochloride was similarly used to give the *βγ*-diazathia-2′-carbocyanine, XXXIV (Y=CH:CH, Z=S, R=R′=Me, X=ClO_4). The *αβ*-diazathia-2′-carbocyanine, XXXIV (Y=S, Z=CH:CH, R=Et, R′=Me, X=

ClO_4), on the other hand, was prepared by boiling a hot aqueous solution of the hydrochloride or perchlorate of XXXIII (Y=S, R=Et) with the *p*-dimethylaminoanil of quinaldinaldehyde methoperchlorate in dilute perchloric acid.[5] Subsequently a dye, XXXIV (Y=S, Z=CH:CH, R=R'=Et, X=Br), of the latter type was prepared in 62 %



(XXXIV)

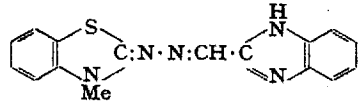
yield by treating the *p*-dimethylaminoanil of quinaldinaldehyde ethobromide with cold dilute hydrochloric acid, adding XXXIII (Y=S, R=Et), boiling for 1 minute, treating with sodium bromide, and recrystallising the washed dye from dilute methanol.[3] An $\alpha\beta$-diazathiacarbocyanine, XXXIV (Y=Z=S, R=Et, R'=Me, X=ClO_4), was prepared through XXXIII (Y=S, R=Et)[5]; subsequently XXXIV (Y=Z=S, R=R'=Et, X=Br) was prepared in 59 % yield through the same hydrazone with acid and the *p*-dimethylaminoanil of benzothiazole-2-aldehyde ethochloride, being recrystallised from dilute methanol. The $\beta\gamma$-diazaselenathiacarbocyanine, XXXIV (Y=S, Z=Se, R=R'=Et, X=Br), resulted in 30% yield by use of the same hydrazone with acid and the *p*-dimethylaminoanil of benzoselenazole-2-aldehyde ethobromide.[3] The hydrazone, XXXIII (Y=S, R=Et), was used to prepare the $\beta\gamma$-diaza-2-pyridothiacarbocyanine, XXXV.[5]



(XXXV)

B. From a Heterocyclic Aldehyde and the Hydrazone of a Heterocyclic Ketone, followed by Quaternary Salt Formation

The hydrazone, XXXIII (Y=S, R=Me), was condensed with a 2-formyl- or 2-dichloromethyl-benzimidazole to give a base, XXXVI,



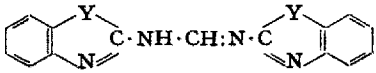
(XXXVI)

which could be converted by methyl sulphate into the yellow salt, XXXIV (Y=S, Z=NMe, R=R'=Me, X=SO_4Me). Alternatively by means of magnesium oxide and benzyl chloride there could be prepared a chloride having an *NN'*-dibenzylbenzimidazole nucleus.[30]

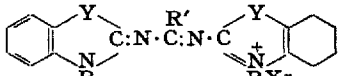
6. αγ-Diazatrimethincyanines, Including *Meso*-Substituted Dyes

A. Symmetrical Dye by Reaction of a Heterocyclic Base, Having an Amino Group, with Ethyl Orthoformate, and Treatment of the Diheterocyclic Product with an Ester

The bases, XXXVII (Y=O or S), were prepared by boiling 2-amino-benzoxazole or -benzothiazole with excess of ethyl orthoformate for a few minutes. On fusing the latter base with methyl toluene-*p*-sulphonate, there resulted the αγ-diazathiacarbocyanine, XXXVIII (Y=S, R=Me, R'=H, X=*p*-$SO_3 \cdot C_6H_4Me$). Other analogous di-heterocyclic bases were described.[6]



(XXXVII)



(XXXVIII)

B. *Meso*-Substituted αγ-Diazatrimethincyanine from a Base with an Amino Group, One with the Group ·N:CR(OR'), and an Ester

By heating XXXI (Y=S, R=Me) and 2-aminobenzothiazole with methyl toluene-*p*-sulphonate at 140–150° for 3 hours, boiling with pyridine for 30 minutes, and pouring into potassium iodide solution, there resulted the *meso*-methyl-αγ-diazathiacarbocyanine, XXXVIII (Y=S, R=R'=Me, X=I).[10]

C. Symmetrical αγ-Diazatrimethincyanines from a Quaternary Salt, Having an Amino Group, with an Ortho-ester

By heating 2-aminoquinoline alkiodide with excess of ethyl ortho-formate in pyridine for 1 hour, the αγ-diaza-2,2'-carbocyanines, XXXVIII (Y=CH:CH, R=Me or Et, R'=H, X=I), resulted, but the yields of recrystallised products, 17 % and 25 %, were considerably less than those of the comparable 2,2'-carbocyanines. The former diazacarbocyanine was photographically inert, whilst the latter weakly sensitised a chloride emulsion. The absorption maximum of the latter lay

at a shorter wavelength by 2620 Å than that of the 2,2′-carbocyanine.[3]

A sample of *meso*-methyl-αγ-diazathiacarbocyanine, XXXVIII (Y=S, R=R′=Me, X=I), was prepared by heating 2-aminobenzothiazole methotoluene-*p*-sulphonate with ethyl orthoacetate in pyridine and converting into iodide.[6] Subsequently the unsubstituted αγ-diazathiacarbocyanine was prepared in 53 % yield by boiling 2-aminobenzothiazole ethiodide with ethyl orthoformate in pyridine for 5 minutes: the dye was unstable in methanol.[11]

D. Meso-Substituted αγ-Diazatrimethincyanines from a Quaternary Salt, Having an Alkylthio-Group, and an Amidine

The *meso*-methyl-αγ-diaza-2,2′-carbocyanine, XXXVIII (Y=CH:CH, R=R′=Me, X=ClO_4), resulted on fusing 2-ethylthioquinoline with methyl toluene-*p*-sulphonate, warming the salt with acetamidine hydrochloride in ethanol, boiling with sodium methoxide in methanol, and treating with potassium perchlorate.[8]

The one example of an unsubstituted αγ-diazathiacarbocyanine, XXXVIII (Y=S, R=Me, R′=H, X=*p*-$SO_3 \cdot C_6H_4Me$), was prepared from 2-methylthiobenzothiazole methotoluene-*p*-sulphonate and formamidine hydrochloride in pyridine. Acetamidine in pyridine was used for preparing the *meso*-methyl-αγ-diazathiacarbocyanines, XXXVIII (Y=S, R=Me or Et, R′=Me, X=I), and also for the 4,5- or 6,7-benzo-, 5,6-methylenedioxy-, and 5,6-dimethoxy-derivatives of XXXVIII (Y=S, R=R′=Me, X=*p*-$SO_3 \cdot C_6H_4Me$). Propionamidine hydrochloride and pyridine were used in the preparation of XXXVIII (Y=S, R=Me, R′=Et, X=*p*-$SO_3 \cdot C_6H_4Me$) and its 4,5- and 6,7-benzo-derivatives.[8]

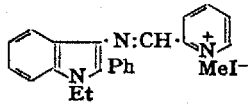
The *meso*-methyl- and -ethyl-αγ-diazaoxacarbocyanines, XXXVIII (Y=O, R=Me, R′=Me or Et, X=*p*-$SO_3 \cdot C_6H_4Me$), were similarly prepared.[8]

A *meso*-methyl-αγ-diazaquinazolinocarbocyanine (cf. X-5-B) was also made.[8]

7. Azadimethincyanines from a Quaternary Salt Having a Reactive Methyl Group and a 1,2-Disubstituted-3-nitroso-indole or a Substituted Nitrosopyrrocoline

The azadimethin dye, XXXIX, was prepared by boiling 1-ethyl-3-nitroso-2-phenylindole and 2-picoline methiodide with piperidine in

ethanol for 5 hours, and recrystallising the washed product (46% yield) from ethanol. Its analogue from γ-picoline methiodide was made similarly. 2-*p*-Chlorophenyl-1-ethyl-3-nitroso-indole and 3-nitroso-1,2-diphenylindole were likewise condensed with α- and γ-picoline methiodide.[12]



(XXXIX)

By reaction of 1-ethyl-3-nitroso-2-phenylindole with quinaldine methiodide and piperidine in ethanol, there was prepared V (Y=CH:CH, R^1=Et, R^2=Ph, R^3=Me); the 4-linked quinoline analogue was similarly made from lepidine methiodide. This latter salt was also condensed with 2-*p*-chlorophenyl-1-ethyl-3-nitroso-indole and with 3-nitroso-1,2-diphenylindole.[12] A similar method was applied to the preparation of V (Y=CH:CH, R^1=R^2=Ph, R^3=Me), which was also prepared by boiling the corresponding base (see section 9-C) with methyl iodide for 76 hours; alternatively, quaternary salt formation could be effected by boiling the base with methyl toluene-*p*-sulphonate in xylene for 4.5 hours.[15]

2-Methylbenzothiazole ethiodide and 2 methylbenzoselenazole ethiodide reacted with 1-ethyl-3-nitroso-2-phenylindole on boiling in ethanol, without a catalyst, giving V (Y=S or Se, R^1=R^3=Et, R^2=Ph); the tetrahydro-derivative of the former was also made. 2-Methylbenzothiazole ethiodide was also condensed with 2-*p*-chlorophenyl-1-ethyl-3-nitroso-indole, 3-nitroso-1,2-diphenylindole, and 1-methyl-3-nitroso-2-oximinomethylindole: with the last compound, it was assumed from analogy that condensation had occurred in the 3-position.[12] Subsequently V (Y=S, R^1=Et, R^2=*p*-C_6H_4Cl, R^3=Me; and Y=S, R^1=R^2=Ph, R^3=Me) were prepared for comparison with the corresponding diazadimethincyanines.[20]

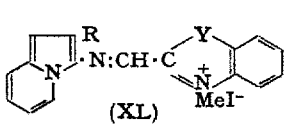
The preparation of V (Y=CMe_2, R^1=R^2=Ph, R^3=Me) was carried out without a catalyst.[12]

1-Methyl-1′-phenylindolo(3′,2′-3,4)isoquinoline methiodide, VI, was condensed with 1-ethyl-3-nitroso-2-phenylindole by boiling in alcohol with a trace of piperidine for 20 hours, giving rise to VII (cf. section 9).[18]

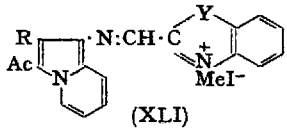
2-Methylindolo(3′,2′-3,4)quinoline methotoluene-*p*-sulphonate, VIII (R=H, X=$SO_3C_6H_4Me$), on boiling for 15 minutes with 1-ethyl-

3-nitroso-2-phenylindole and triethylamine in acetic anhydride gave IX (R=H, X=$SO_3C_6H_4Me$), obtained in 62 % yield as scarlet needles, which were recrystallised from dimethylformamide. The salt, VIII (R=Me, X=*p*-$SO_3C_6H_4Me$), was boiled with the nitroso-compound and piperidine in ethanol for 5 hours to give IX (R=Me, X=*p*-$SO_3C_6H_4Me$), obtained in 61 % yield and recrystallised from ethanol.[17]

The 3-nitroso-2-phenyl(or methyl)- and the 3-acetyl-2-methyl(or phenyl)-1-nitroso-derivatives of pyrrocoline[18] were condensed with the methiodides of 2-picoline, quinaldine, and 2,3,3-trimethylindolenine to give twelve azadimethincyanines, e.g., of types XL and XLI (Y=CH:CH or CMe_2, R=Me or Ph). In general, sodium hydroxide in aqueous ethanol was a better condensing agent than piperidine.[19]



(XL)



(XLI)

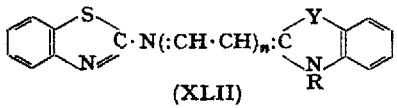
8. Diazadimethincyanines

The four diazadimethincyanine iodides, XII ($R^1=R^2=$Me or Ph; R^1=Me, R^2=Ph; and R^1=Et, $R^2=p$-C_6H_4Cl) were prepared by heating the bases with methyl toluene-*p*-sulphonate, followed by treatment with sodium iodide.[20]

9. Bases of which Azacyanines are the Quaternary Salts

A. Bases of Azamethincyanines

In the thia-2'-, oxathia-, and thia-azacyanine series, the bases, XLII (*n*=0, Y=CH:CH, O, or S, R=Me), were all prepared from



(XLII)

2-aminobenzothiazole by heating in pyridine with the methotoluene-*p*-sulphonate of the appropriate base having a 2-methylthio-group; 2-aminobenzothiazole was also used to give a 6,7-benzo-derivative of

XLII (n=0, Y=S, R=Et), whilst 2-amino-6,7-benzobenzothiazole was used to give a 6,7-benzo-derivative of XLII (Y=S, R=Me)[6,21].

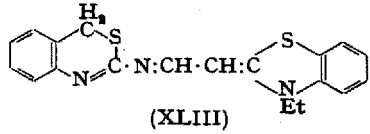
The base, XV, of the thiathiazoloazacyanine type, was prepared in 56 % yield by heating 3-ethyl-2-imino-6-methylbenzothiazoline with 2-amino-4-phenylthiazole at 165–170° in a vacuum, until evolution of ammonia ceased; it was twice recrystallised from ethanol.[28]

B. Bases of α-Azatrimethincyanines

A base, XLII (n=1, Y=CMe_2, R=Me), of the γ-azaindothiacarbocyanine series was prepared by heating 2-aminobenzothiazole with 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide in pyridine[6] and was found to sensitise.[21]

In the α-azathiacarbocyanine series, a base, XLII (n=1, Y=S, R=Et), was prepared in 40 % yield by boiling 2-aminobenzothiazole with 2-β-acetanilidovinylbenzothiazole ethiodide in pyridine for 5 minutes, precipitating with water, and recrystallising from methanol: quaternary salts were made from it (see section 3).[11]

The base, XLIII, was prepared in 20 % yield by boiling 2-amino-3,1,4-benzothiazine and 2-β-acetanilidovinylbenzothiazole ethiodide in



(XLIII)

pyridine for 5 minutes, treating with aqueous ammonia, and recrystallising the washed product from benzene and light petroleum (cf. section 3).[22]

C. Bases of Azadimethincyanines

By heating 3-amino-1-ethyl-2-phenylindole with 2-formylquinoline under nitrogen at 150–160° for 2 hours, and boiling the resultant black syrup with ethanol, there were obtained yellow crystals of the base, XVI (R=Et), which was recrystallised from ethanol. The analogue, XVI (R=Ph) was similarly prepared by use of 3-amino-1,2-diphenylindole, being obtained crystalline from xylene, and was recrystallised from acetone.[15]

When the methiodide, VI, and 3-nitroso-1,2-diphenylindole were

boiled for 5 hours in ethanol containing a trace of piperidine, crystals of the base, XVII, were deposited on cooling and were recrystallised from ethanol.[16]

The salt, VIII (R=H, X=$SO_3C_6H_4Me$), condensed with 1-ethyl-3-nitroso-2-phenylindole on boiling with sodium methoxide in methanol for 50 hours, and a mixture of bases was deposited on cooling. Extraction with boiling methanol, and recrystallisation of the residue from dimethylformamide gave X, m.p. 295–297° (decomp.). By working up the methanolic extract and recrystallising from methanol, there was obtained XI, m.p. 261–264°.[17]

D. Bases of Diazadimethincyanines

The four bases, XIII (R^1=R^2=Me or Ph; R^1=Me, R^2=Ph; and R^1=Et, R^2=*p*-C_6H_4Cl), were prepared by coupling diazotised 2-aminobenzothiazole with the appropriate 1,2-disubstituted indole.[20]

10. Dimethincyanines Having a 2,1,3-Triazole Nucleus

The dye iodide, XVIII (Y=CMe_2, R=Et), was obtained in 59 % yield, after recrystallisation, by boiling 4-formyl-2-phenyl-2,1,3-triazole and 2,3,3-trimethylindolenine ethiodide in acetic anhydride for 10 minutes. Other types of dimethincyanines with a 2,1,3-triazole nucleus were XVIII (Y=S or CH:CH), besides analogues with a 3-isoquinoline, 2-pyridine, or 4-quinoline nucleus.[29]

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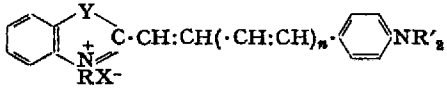
CHAPTER XIII

Certain Classes of Dyes Related to Cyanines

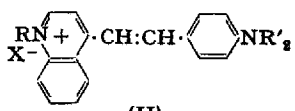
1. Styryl Compounds and their Higher Vinylene Homologues

A. General Survey

Certain substituted styryl compounds resemble cyanines in having two nitrogen atoms connected by a chain of conjugated double bonds, but differ from them in that one nitrogen atom is not part of a heterocyclic nucleus. The first salts of this kind were described in 1920, when alkiodides of 6-dimethylamino-quinaldine or -lepidine were condensed with *p*-dimethylaminobenzaldehyde, by heating with piperidine in ethanol, to give derivatives of I (n=0, Y=CH:CH) and II, respectively. All proved of interest as sensitisers[1] and one was used commercially as Pantochrome.[2] In 1921 an unsubstituted dye of type I (n=0, Y=CH:CH) was made and also its higher vinylene homologue, I (n=1, Y=CH:CH), the latter being prepared in a medium of acetic anhydride;



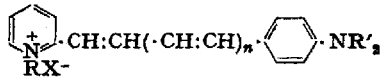
(I)



(II)

analogues with an *o*-dimethylamino-group were also prepared and the colours were discussed in connection with the open-chain formulae for cyanine and isocyanine (see I-2). *p*-Dimethylaminostyryl compounds with a 4-linked quinoline, a benzothiazole, or a pyridine nucleus were also described. They were all decolorised by mineral acid, but less readily than were the isocyanines, and they were not observed to show useful sensitising properties.[3] In 1922, however, the styryl salt, III (n=0, R=R'=Me, X=I), was prepared from α-picoline methiodide

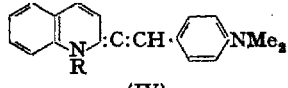
and *p*-dimethylaminobenzaldehyde and proved the most powerful known sensitiser for green light.[4] The commercial dye Pinaflavol,[5] which sensitised to green and yellow light[6] is identical, and exemplifies the early commercial value of certain styryl compounds. It was claimed in



(III)

1926 that sensitisation for the whole visible spectrum was procured by means of a dye-bath containing water, pyridine, pinacyanol, and pinaflavol, the effect of the latter dye being to eliminate the gap in the green.[7,8]

In 1925 it was suggested that the mechanism of formation of the styryl salt, I (n=0, Y=CH:CH, R=Et, R′=Me, X=I), consisted in liberation of a reactive methylene base from quinaldine ethiodide by the piperidine used as catalyst, and that this base condensed with *p*-dimethylaminobenzaldehyde. The methylene base could be condensed with *p*-dimethylaminobenzaldehyde in the absence of a catalyst but the product, IV (R=Et), was too unstable to isolate; it was

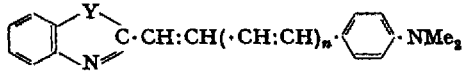


(IV)

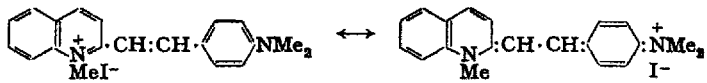
converted, either by hydriodic acid or by piperidine hydriodide, into the styryl salt, I (n=0, Y=CH:CH, R=Et, R′=Me, X=I). The bases of the 5,6-benzo-derivatives of IV (R=Me or Et) were stable enough to be isolated; they likewise were converted into styryl salts by hydriodic acid; these salts were also prepared directly from α-naphthoquinaldine alkiodide.[9] Twenty years later, the observation that dihydro-β-quinindene methiodide, which cannot form an intermediate compound analogous to IV, is nevertheless capable of condensation with *p*-dimethylaminobenzaldehyde (see Sect. 1-O)[10] indicated that the proposed mechanism must be modified. Even when the base and aldehyde reacted in the absence of a catalyst, several intermediate steps must be inserted. When piperidine was present, a sequence which was an application of the modern general theory of base-catalysed carbonyl condensations was postulated.[11]

In 1930 absorption and sensitising curves of a series of twelve styryl compounds having various heterocyclic nuclei were published, the data being compared with those for methincyanines (see Chapter II) and anils (see section 2) having the same nuclei.[12] In 1927 preparations of ten pairs of styryl compounds, I (n=0), and their higher vinylene homologues, I (n=1), with the same heterocyclic nucleus, were recorded, and sensitising maxima were compared.[13,14] The absorption maximum of III (n=0, R=R′=Me, X=I), with a 2-linked pyridine nucleus, was compared with that of its analogue with a 4-linked pyridine nucleus and with that of a 2,4-bis-styryl dye.[15]

It was recorded in 1935 that the styryl base, V (n=0, Y=CH:CH), gave two mono-methiodides, one of which was red, the other almost colourless. As the red one was obtained by condensing quinaldine methiodide with p-dimethylaminobenzaldehyde, it was identified as I (n=0, Y=CH:CH, R=R′=Me, X=I),[16] for which the resonance scheme VIa ⟷ VIb was subsequently given.[17] The colourless meth-

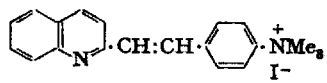


(V)



(VIa) (VIb)

iodide, VII, was prepared by condensing quinaldine with the methiodide of p-dimethylaminobenzaldehyde[16] and for it no plausible second formula could be devised.[17] The styryl compound, I (n=0, Y=CH:CH, R=R′=Me, X=I), is an unsymmetrical compound, which may be



(VII)

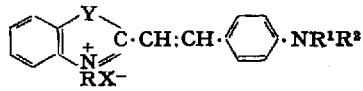
regarded as a cross between two symmetrical compounds. Its absorption maximum lies at a shorter wavelength than the harmonic mean of the maxima of the two symmetrical dyes, the difference between the observed and calculated values being called the deviation.[17] Similar comparisons were made for the styryl compound, I (n=0, Y=S,

R=Et, R′=Me, X=I), of the benzothiazole series.[17,18] In 1942 a series of the *p*-dimethylaminostyryl derivatives of thirty-six different quaternary heterocyclic salts of various types were arranged in order of increasing deviation of λ_{max}, and this was regarded as the order of increasing basicity of the heterocyclic nuclei. Preparative details were given for those twenty-two of the styryl compounds which were described for the first time.[19]

After an aldehyde group had been introduced into (halogenoalkyl)arylamines by means of the formyl derivative of a secondary amine and a halogenide of sulphur or phosphorus (e.g., equation 1),

$$\mathrm{PhN^{Me}\cdot CH_2\cdot CH_2Cl} + \mathrm{PhN^{Me}\cdot CHO} \xrightarrow{POCl_3} \mathrm{\textit{p}\text{-}OCH\cdot C_6H_4\cdot N^{Me}\cdot CH_2CH_2Cl} \qquad (1)$$

the resultant halogenated aldehydes were condensed with 2-methyleneindolines to give styryl dyes of type VIII (Y=CMe_2), in which one or



(VIII)

both of the alkyl groups, R^1 and R^2, were alkylated.[20] A 2-methyleneindoline was similarly used to give a styryl dye having an *N*-*β*-cyanoethyl group. The latter compound was also prepared, as were others of the same type, by condensing a 2-(formylmethylene)indoline with an arylamine having a *β*-cyanoethyl group (equation 2).[21] At a later date,

$$\mathrm{\overset{N}{\underset{Me}{}}C{:}CH\cdot CHO} + \mathrm{PhN^{R'}_{CH_2CH_2CN}} + HCl \xrightarrow{POCl_3} \mathrm{\overset{+}{N}C\cdot CH{:}CH\cdot C_6H_4N^{R'}\cdot CH_2CH_2CN\ MeCl^-} + H_2O \qquad (2)$$

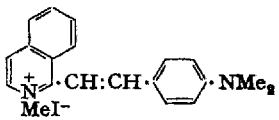
halogenated aldehydes were condensed with a variety of types of heterocyclic quaternary salts.[22]

m-Dimethylaminobenzaldehyde was condensed with various quaternary salts (see section 1-B, E, I, and K) but only two of the styryl compounds showed the slightest sensitising power. The lack of sensitisation was attributed to the absence of a fully conjugated system.[23,24]

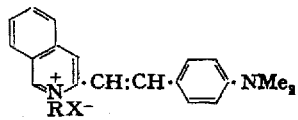
When, in the patent literature, special substituents or special nuclei are claimed to give cyanines with valuable properties, *p*-dimethylaminostyryl compounds are frequently included. In the present

chapter the styryl compounds have been arranged according to the heterocyclic nuclei involved. Variations in the group attached to the nitrogen atoms of cyanines included dyes made from betaines (see X-4-A), and such a betaine was also used to give a styryl compound of the benzothiazole series (section 1-E). Just as *N*-aryl groups have been introduced into cyanines (see X-4-C), so have they into styryl compounds of the 2-linked quinoline, benzothiazole, and thiazole series (see section 1-B, E, K, and P). Again, in some cyanine dyes the heterocyclic nitrogen atom is linked by a chain to the second ring (see X-4-E), and this also occurs with styryl compounds of the benzothiazole series (section 1-E and P). Cleavage of the $\alpha\beta$-linking of the chain of a carbocyanine by a quaternary salt (see V-12) has its parallel in the cleavage of the $\alpha\beta$-linking of a thiatricarbocyanine by means of *p*-dimethylaminobenzaldehyde to give a styryl salt of the benzothiazole series (see section 1-E).

Unusual nuclei which enter into cyanine molecules (see X-5) have, when they also occur in the molecules of styryl compounds, been dealt with in the same order as before (section 1-M). Amongst nuclei having nitrogen as the one hetero-atom (X-5-A), the reactivity of 1-methylisoquinoline methiodide was shown in 1922 by its condensation with *p*-dimethylaminobenzaldehyde to give IX and a negative result with 3-methylisoquinoline methiodide was attributed to the absence of a double bond in the 2,3-position.[25] A compound of type X was, however,



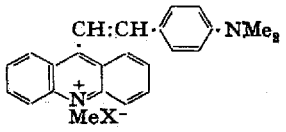
(IX)



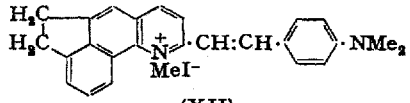
(X)

successfully prepared nearly thirty years later, when it was pointed out that, in the light of the resonance theory, reactivity of 3-methylisoquinoline methiodide was to be expected.[26] The exceptionally high basicity of the *N*-ethyl-3-isoquinoline nucleus, expected from a comparison of the uncharged and positively charged forms of the ring, was confirmed by the high deviation of λ_{max} shown by X (R=Et, X=I).[27] The high reactivity of a 3-methylisoquinolinium salt may also be explained by regarding it as a 4,5-benzo-α-picoline.[28] Claims in the literature that styryl compounds have been prepared from β-picolinium

salts[29,30] fall into a different category from the work on 3-methylisoquinolinium salts. Highly purified β-picoline methiodide does not show the reactivity which has been claimed.[28] Styryl dyes, XI, containing a 9-linked acridine nucleus were prepared only from a styryl base (section 1-Q.2)[31] but the compound, XII, could be directly prepared from 2-methylacenaphthenopyridine methiodide.[32]

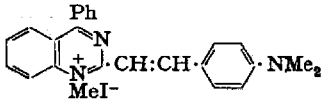


(XI)

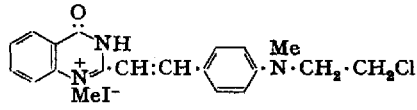


(XII)

Amongst nuclei having two nitrogen atoms as the only heteroatoms (X-5-B), a quinazoline nucleus figured in styryl compounds such as XIII.[33] A styryl compound, XIV, with a 4-oxo-3,4-dihydroquinazoline nucleus was described in 1944,[22] and, in 1958, one with a 4-oxo-

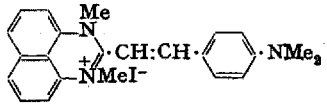


(XIII)

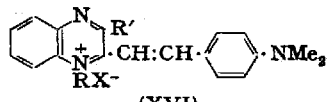


(XIV)

3,4,5,6,7,8-hexahydroquinazoline nucleus (section 1-M.2). A styryl salt, XV, with a perimidine nucleus was described in 1954.[34,35] Salts of 2,3-dimethylquinoxaline were prepared in 1942 and were condensed with *p*-dimethylaminobenzaldehyde to give styryl dyes of type XVI



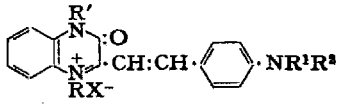
(XV)



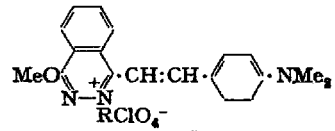
(XVI)

(R′=Me); under special conditions, others of type XVI (R′=Ph) were prepared through methylene bases and the aldehyde.[36] Alkoalkyl sulphates of 3-methyl-2-oxodihydroquinoxaline, or of its *N*-substituted derivatives, gave styryl compounds of type XVII (R^1=R^2=Me).[37,38] Chlorine-containing aldehydes were used to give salts of type XVII (where R^1, or both R^1 and R^2=CH_2CH_2Cl).[22,38] The phthalazine nucleus

was one which was introduced into styryl dyes of type XVIII, as well as into cyanines, but methylene bases having this nucleus were less reactive than that derived from quinaldine methiodide, so that more

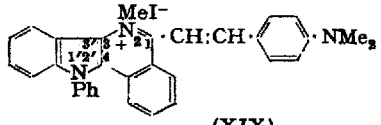


(XVII)



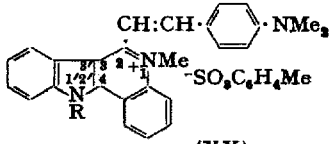
(XVIII)

drastic conditions than piperidine in ethanol were necessary.[39] The indolo(3′,2′-3,4)isoquinoline nucleus, which was introduced into aza-dimethincyanines (see XII-7) was also used in the styryl dye, XIX.[40]

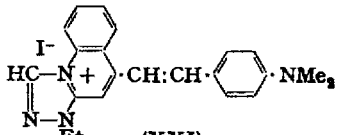


(XIX)

The indolo(3′,2′-3,4)quinoline nucleus is found not only in cyanine molecules but also in the styryl salts, XX (R=H or Me).[41]

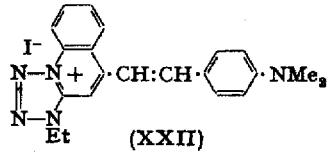


(XX)

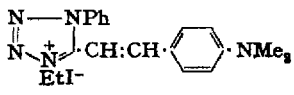


(XXI)

Styryl dyes such as XXI, having a triazolo[4,3-a]quinoline nucleus (cf. X-5-C) or XXII, having a tetrazolo[a]quinoline nucleus (cf. X-5-D) were useful for filter layers.[42] The salt, XXIII, with a simple tetrazole nucleus was a sensitiser.[43]



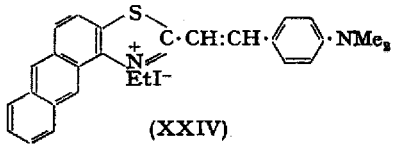
(XXII)



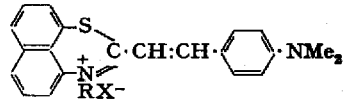
(XXIII)

Amongst cyanines having nuclei with one nitrogen and one sulphur as hetero-atoms (see X-5-E), those with complex benzothiazole

nuclei were included; a styryl dye, XXIV, of this nature was also described.[44] The perinaphtho-1,3-thiazine nucleus was introduced into the styryl compound, XXV (section 1-M.5; cf. section 1-Q.2).[45] Quaternary salts having a 1,4,2-benzothiazine nucleus were used not only for

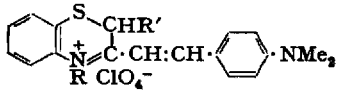


(XXIV)

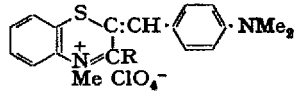


(XXV)

making cyanines, but also for styryl compounds of type XXVI. In the absence of a reactive methyl group, *p*-dimethylaminobenzaldehyde condensed with the 2-methylene group of the thiazinium salt to give benzylidene derivatives of type XXVII.[46] A styryl compound having a 4,5-trimethylenethiazole nucleus was described (see section 1-M.5).

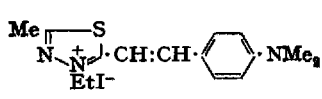


(XXVI)

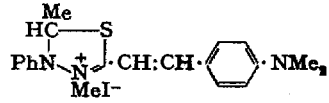


(XXVII)

Of nuclei with two nitrogen atoms and one sulphur as hetero-atoms, the 1,3,4-thiadiazole nucleus appeared in cyanines (see X-5-G) and in the styryl compound, XXVIII,[47] and the dihydro-1,3,4-thiadiazole nucleus similarly entered into the styryl compound, XXIX.[48]

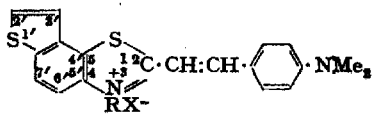


(XXVIII)



(XXIX)

Of complex heterocyclic nuclei with one nitrogen and two sulphur atoms, the thianaphtheno[4',5'-5,4]thiazole nucleus was introduced into cyanines (see X-5-I) and a styryl dye, XXX, of this type was also mentioned.[49]

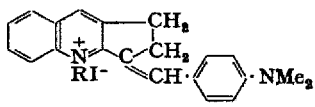


(XXX)

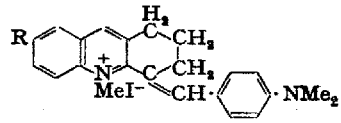
Absorption data as to heterocyclic ethiodides, etc., having a 2-*p*-dimethylaminophenyl group, are considered elsewhere (XVI-7), but higher vinylene analogues are included here. Whereas, starting from a methincyanine, analogues with one, two, three, four, or even five vinylene increments in the chain may be synthesised (see VIII-7 and 8), so far, in the present series, the only higher vinylene analogues of styryl salts are those prepared from *p*-dimethylaminocinnamaldehyde, having one extra vinylene group (section 1-N). Absorption spectra of three further aldehydes of this kind, having methin chains of six, eight, and ten members, were published in 1928, but the highest yield, that for the aldehyde with the eight-membered methin chain, was only 6 %.[50] Higher vinylene analogues of the styryl compounds were first prepared in 1921 by reaction of *p*-dimethylaminocinnamaldehyde with a quinaldinium or 2-methylbenzothiazolium salt.[3] In 1930 absorption and sensitising curves for a dye of the latter series and for one with a 2-linked pyridine nucleus were published.[12] It was observed in 1935 that, in the indolenine series, a dye of type I (n=1, Y=CMe_2) was more strongly adsorbed chromatographically than was its lower vinylene analogue.[51] In 1937 eleven pairs of styryl and phenylbutadienyl salts were compared; it was observed that the absorption and sensitising maxima of the former lay at a shorter wavelength than those of the latter.[13,14] In 1941 absorption maxima in methanol were recorded for I (n=1, Y=CH:CH, R=R′=Me, X=I) of the 2-linked quinoline series and I (n=1, Y=S, R=Et, R′=Me, X=I) of the benzothiazole series. The former lay at a longer wavelength by 360 Å than that of the corresponding styryl compound.[17] In the following year, absorption maxima in nitromethane were given for three more phenylbutadienyl salts of the benzothiazole series, in which the basicity of the nucleus was reduced by the introduction of negative substituents. Each was compared with the corresponding styryl salt as well as with the related pair of symmetrical dyes.[18,52]

Just as there are cyanines in which the odd-numbered carbon chain, which links the nuclei, or part of it, is cyclic (see Chapter IX), so, similarly, reaction of *p*-dimethylaminobenzaldehyde with methiodides having a homocyclic methylene group, gave rise to styryl analogues in which part of the chain was cyclic, so that the products were in fact benzylidene compounds. These have been grouped together (section 1-O). They include XXXI, with a dihydro-*β*-quinindene nucleus,[10] which nucleus was subsequently introduced into the molecules of methin- and

dimethin-cyanines (see IX-7), and compounds such as XXXII, with a tetrahydroacridine nucleus. For effecting these condensations, the method was to heat the methiodide with *p*-dimethylaminobenzaldehyde

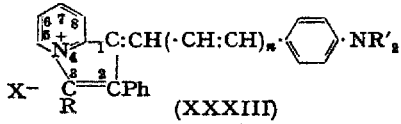


(XXXI)

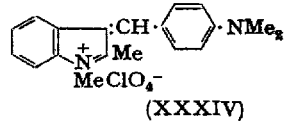


(XXXII)

in acetic anhydride, but piperidine in ethanol gave a negative result and the same was observed with 6-methylphenanthridine methiodide (section 1-B).[10] Another *p*-dimethylaminobenzylidene compound had the dihydropyrindine nucleus. Analogous to cyanines with a pyrrocoline nucleus (X-5-A) are compounds of type XXXIII (n=0 or 1), obtained by condensing certain pyrrocoline derivatives with *p*-dimethylaminobenzaldehyde, or *p*-dimethylaminocinnamaldehyde, in the presence of acid, and described as useful for filter layers.[53] Although cyanine dyes

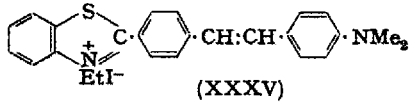


(XXXIII)



(XXXIV)

having a 3-linked indole nucleus were included with those having unusual nuclei (X-5-A), they also come in the category of cyanines in which part of the chain is cyclic. In the styryl analogue, XXXIV,[17] not only is part of the chain cyclic, but it carries a methyl group as substituent. Comparable with pentamethincyanines in which four units of the chain are part of a benzene ring (see IX-6), is the salt, XXXV,

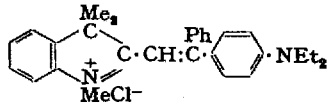


(XXXV)

which was prepared through 2-*p*-tolylbenzothiazole ethiodide; although it is to be regarded as the analogue of the unknown I (n=2, Y=S, R=Et, R′=Me, X=I), its absorption curve was almost identical with that of the styryl compound.[54]

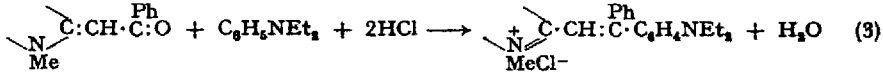
As with cyanines, so also with *p*-dimethylaminostyryl, and *p*-dimethylaminophenylbutadienyl salts, derivatives having substituents

on the chain have been synthesised (section 1-P). The earliest record of such a derivative is in a patent of 1937, on *meso*-substituted carbocyanines, where the β-substituted styryl salt, XXXVI, was prepared



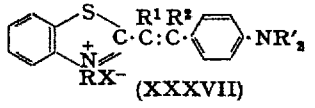
(XXXVI)

by reaction of 2-benzoylmethylene-1,3,3-trimethylindoline with diethylaniline and phosphorus oxychloride[55] as indicated in equation 3. It is



(3)

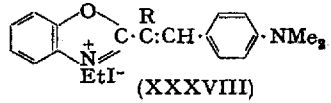
an isolated instance, both as regards the method employed and as regards the heterocyclic nucleus. 2-Ethyl- and 2-benzyl-pyridine methiodide do not condense with *p*-dimethylaminobenzaldehyde, under the influence of piperidine in ethanol, to give α-substituted styryl salts, and this has been attributed to steric factors.[11] The second chain-substituted styryl compound, belonging to the benzothiazole series, was XXXVII (R=R′=Me, R^1=CONHPh, R^2=H, X=I), and it was arrived at by



(XXXVII)

addition of methyl iodide to the corresponding base[56] (see section 1-Q). In the following year, 1948, another was described, XXXVII (R=R′=Me, R^1=CO_2H, R^2=H, X=I): it was prepared through 2-carboxymethylbenzothiazole methiodide and was said to be unstable.[57] In 1950 the use of salts, having a 2-CH_2OR group, to give styryl salts with an α-OR group on the chain was recorded.[58,59] It was noted in that year that substitution of the α-hydrogen atom of the dimethin chain in I (*n*=0, Y=S, R=R′=Me) by methyl or isopropyl caused a hypsochromic shift of the absorption maximum, and this was attributed to steric disturbance of the planarity of the molecule.[60] Absorption data were given for two sets of four *p*-dimethylaminostyrylbenzothiazolium salts, each set having H, Me, Et, or Ph in the α-position, and one series

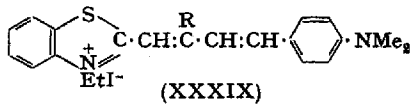
having *N*-Et, the other *N*-Ph. The hypsochromic shifts induced by α-substitution were accompanied by reduction in intensity; the shift for α-phenyl was less than for α-alkyl. Three dyes with a β-substituent were prepared: that also gave a hypsochromic shift but less than for an α-substituent. It was remarked that, in the styryl dyes, the principal resonance structures are not energetically equivalent; it was considered that the steric effects are reinforced by electronic influences.[61] Subsequently absorption data were compared for a set of five *p*-dimethylaminostyryl salts, each having a 6-methyl and an *N*-*p*-tolyl group in the benzothiazole nucleus, but with various α-substituents on the chain,[62] also for a set of five, each with an *N*-cyclohexyl group, but with various α-substituents.[63] A styryl salt with a 3,4-trimethylenebenzothiazolium nucleus (section 1-E) was compared with four others having α-substituents.[64] In the *p*-dimethylaminostyrylbenzothiazole series, ethiodides with five different α-substituents were prepared, one being a 2-benzothiazolyl group, which is interesting because of its size. In preparing XXXVII (R=Et, R′=Me, R^1=Me or *p*-$C_6H_4NO_2$, R^2=H, X=I), and the *p*-diethylamino-analogue of the former, basic by-products (see section 1-Q.3) were formed. In the benzoxazole series, the



(XXXVIII)

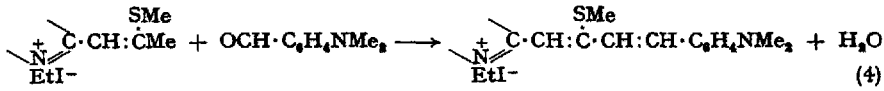
parent dye, XXXVIII (R=H), was compared with two α-substituted derivatives, XXXVIII (R=Me or Ph).[65] The hypsochromic shifts caused by substitution on the chain of some styryl dyes are given in Table I.

Three chain-substituted salts of the 4-*p*-dimethylaminophenyl-1,3-butadienyl type, belonging to the benzothiazole series, were prepared independently by various processes. The one dye, XXXIX

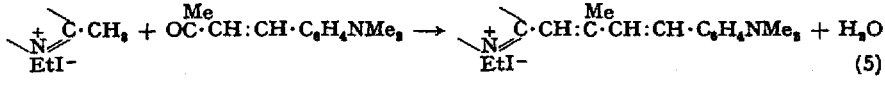


(XXXIX)

(R=SMe), with a β-methylthio-group, was prepared according to equation 4.[66] another with a β-methyl group was prepared by use of *p*-dimethylaminostyryl methyl ketone (equation 5).[67]

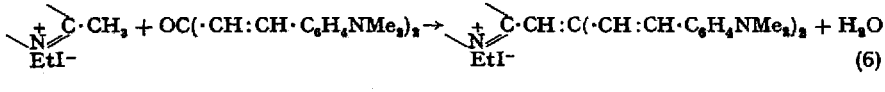


(4)



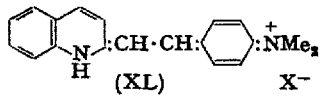
(5)

The third, with a β-(*p*-dimethylaminostyryl) group, was prepared by use of di-(*p*-dimethylaminostyryl) ketone.[67] (equation 6) (section 1-P-2).



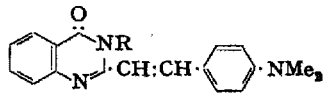
(6)

Bases (see Chapter XI) of which cyanine dyes are the quaternary salts, have their parallel in *p*-dimethylaminostyryl bases and their higher vinylene analogues (section 1-Q). As early as 1923 it was noted that the acid salt of the styryl base, V (n=0, Y=CH:CH), formed with nitrous acid a colourless nitrosoamine, stable to alkali, for which reason the



(XL)

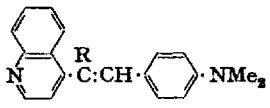
salt was formulated as XL.[68] In the following year, 2-methyldihydroquinazolones were condensed with *p*-dimethylaminobenzaldehyde to give styryl bases, XLI (R=H, Me, or Et), of which *cis*- and *trans*-



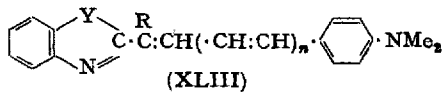
(XLI)

isomers were described.[69] Like cyanine bases, those of the *p*-dimethylaminostyryl series sensitised.[70] The base, V (n=1, Y=CH:CH), with a tetramethin chain was described in 1941 (section 1-Q).[17] The method of eliminating alkyl halide from cyanines by heating with a high-boiling base (see XI-5) was also applied to *p*-dimethylaminostyryl salts (section 1-Q.1).[71] Of unusual nuclei which were introduced into *p*-dimethylaminostyryl salts (see section 1-M), a few appear also into the bases (section 1-Q.2).

In patents on α-cyano-substituted bases of cyanines, synthesised by use of heterocyclylacetonitrile (see XI-9), there is one example of a *p*-dimethylaminostyryl- and another of a 4-*p*-dimethylaminophenyl-1,3-butadienyl-base, XLII and XLIII ($n=1$), respectively, each with



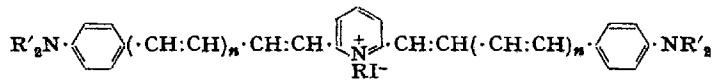
(XLII)



(XLIII)

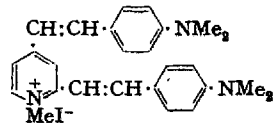
a cyano-group in the α-position to the heterocyclic nucleus (section 1.-Q.3).[72] A study of cyanine bases having a cyano-group in the α-position to a benzimidazole nucleus included one styryl base.[73] Like the bases of methincyanines having an α-COR group (see XI-10-A), bases of the *p*-dimethylaminostyryl series, with a COR substituent in the α-position to the heterocyclic nucleus, were described as sensitisers.[56] In the benzothiazole series, three such bases with an α-COR group had almost the same absorption maximum as the unsubstituted base.[57]

Bis-(*p*-dialkylaminostyryl) salts (section 1-R) bear some analogy to trinuclear cyanine dyes and the first such salt was described in 1923 (see XV-2-E). In the pyridine series, two mols. of *p*-dialkylaminobenzaldehyde were condensed with one of 2,6-dimethylpyridine alkiodide to



(XLIV)

give dyes of type XLIV ($n=0$)[74] and subsequently 2,4-dimethylpyridine methiodide was used to give XLV.[15] A higher vinylene analogue, XLIV ($n=1$, R=Et, R′=Me), of a bis-styryl salt was also de-

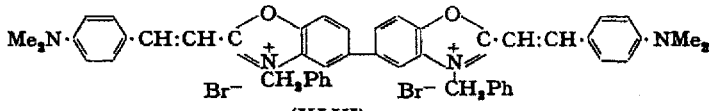


(XLV)

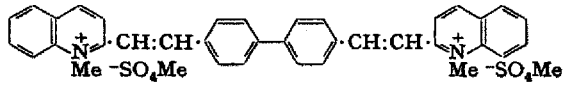
scribed.[74] In the quinoline series a 2,4-bis-(*p*-dimethylaminostyryl) salt was described.[12]

From a bis-[5-(2-methylbenzoxazolium)] salt there was prepared

the bis-styryl salt, XLVI, which was a sensitiser.[75] A bis-styryl salt, lacking the *p*-dimethylamino-groups, was prepared by condensation of



(XLVI)



(XLVII)

a quinaldinium salt with diphenyl-4,4′-dialdehyde: this salt, XLVII, was useful for anti-halation.[76]

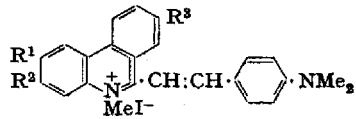
Some styryl compounds without a *p*-dimethylamino-group have been included in the sections that follow. Quinoline bases of this nature were prepared in 1920 by condensing aldehydes such as benzaldehyde, its *o*- and *p*-hydroxy-, or its *p*-hydroxy-*m*-methoxy-derivatives with quinaldine by heating with zinc chloride; furfural was also used, whilst *m*,*p*-dioxymethylenebenzaldehyde was condensed with α-picoline. By the action of methyl iodide, these bases were converted into quaternary salts. When a hydroxy-substituent was present in the styryl group, the salts gave a blood-red colour with sodium hydroxide, whence the possibility of using them as indicators was suggested.[77] In 1930 anti-halation layers, which were irreversibly decolorised by the developing solution, were patented, and comprised styryl compounds obtained by condensing an aromatic aldehyde with a quaternary salt having a reactive methyl group. Whereas the cyanine-like dye, I (n=0, Y=CH:CH, R=Et, R′=Me, X=Br), gave a red solution, an analogue of I (n=0, Y=CH:CH, R=Me, X=SO_4Me), in which a *m*-MeO-group took the place of the *p*-NR'_2-group, was yellow.[78] In 1940 *o*- and *p*-hydroxybenzaldehyde were condensed with quinaldine ethiodide, 2-methylbenzothiazole ethiodide, 2-methyl-4-phenylthiazole ethiodide, and 2,4-dimethylthiazole ethiodide in the presence of pyridine. By aqueous potash these were converted into quinonoid dyes, for which absorption maxima in various solvents were recorded: the colours varied greatly according to the nature of the solvent (see XIV-12).[79] In 1947 α-picoline methiodide was condensed with benzaldehyde and, besides the parent styryl salt, nineteen derivatives were made, for nine

of which absorption data were given (Table II). The *p*-dialkylamino-derivatives were a bright purple-red, the rest yellow. An *o*-hydroxystyryl compound was pale yellow, becoming deep red with alkali. The presence of a large atom adjacent to the *p*-dimethylamino-group exerted steric hindrance and inhibited resonance.[80] The anhydronium bases, produced by the action of alkali on hydroxystyryl salts are dimethinmerocyanines (see XIV-12) and were used to indicate the polarity of solvents.[81] Styryl salts prepared by condensing heterocyclic quaternary salts, having a reactive methyl group, with certain halogenohydroxybenzaldehydes, were described as good sensitisers.[82]

B. Styryl Salts with a 2-Linked Quinoline Nucleus

Styryl compounds having a 2-linked quinoline nucleus were amongst the first to be described: the 6-dimethylamino-derivatives of I (n=0, Y=CH:CH, R=Et or Me, R′=Me, X=I) were prepared by heating 6-dimethylaminoquinaldine alkiodide and *p*-dimethylaminobenzaldehyde with piperidine in ethanol. They were useful sensitisers,[1] the ethiodide being used as Pantachrome.[2] The unsubstituted perchlorate, I (n=0, Y=CH:CH, R=R′=Me, X=ClO_4), and its *o*-dimethylamino-analogue, were made.[3] The preparation of styryl compounds from methylene bases[9] has been referred to (section 1-A). In 1926 a series of thirty-six styryl compounds of type I (n=0, Y=CH:CH) were prepared, with the object of studying their antiseptic properties: various substituents were introduced, including fused-on rings or sulphonic groups, also the acid radical was varied (X=Cl, I, or SO_4Me), as was the substituted amino-group (R′=H, Me, or Et); in addition, a salt with an unsubstituted styryl group was made, and five with a *p*-acetylamino-group, whilst two had *m*,*p*-diOH or *m*,*p*-O_2CH_2 substituents.[83] Another fifty styryl compounds, with acylamino-, formylamino-, *etc.*, in various positions in the quinoline nucleus were later studied from the same angle.[84] A further series of eight had a group such as amino-, acetylamino-, lactylamino-, or glycerylamino- in the 6-position, whilst the *p*-dimethylamino-group might be replaced by an amino-, acetylamino-, lactylamino-, or acetyl-lactylamino-group.[85] Subsequently seven *p*-dimethylamino- or *p*-diethylamino-compounds of type I (n=0, Y=CH:CH, R=Me, R′=Me or Et, X=Cl) were examined, in which an amino- or substituted amino-group was present in position 4.[86] The 6-phenyl derivative of I (n=0, Y=CH:CH, R=R′=Me, X=

SO_4Me) was prepared for use as an anti-halation dye, which was decolorised by the developer.[76] In 1930 the absorption and sensitising curves of I (n=0, Y=CH:CH, R=Et, R′=Me, X=I) and of its 5,6-benzo-derivative were published;[12] its sensitising action was also described later,[13,87] the maximum being compared with that of its higher vinylene homologue.[13,14] Its 4-phenyl derivatives sensitised less strongly than the parent dye, and the corresponding methiodide desensitised.[33] The absorption spectra of I (n=0, Y=CH:CH, R=Et, R′=Me, X=I) in methanol and in nitromethane were published,[17] also absorption maxima in the latter solvent for this dye and its 5,6-benzo-derivative.[19] With piperidine in ethanol as condensing agent, only a moderate yield of the 3-methyl derivative of I (n=0, Y=CH:CH, R=R′=Me, X=I) was obtained from 2,3-dimethylquinoline methiodide, but with boiling acetic anhydride as medium, the yield was excellent. The piperidine in ethanol method failed with 6-methylphenanthridine methiodide and the aldehyde, but with acetic anhydride there resulted a good yield of the 3,4-benzo-derivative of I (n=0, Y=CH:CH, R=R′=Me, X=I). Other phenanthridine methiodides were prepared and were condensed with *p*-dimethylaminobenzaldehyde similarly to give XLVIII (R′=NHAc, R^2=R^3=H; R^1=R^3=H, R^2=Me; and R^1=R^2=H, R^3=NHAc); the first of these was hydrolysed to the corresponding amino-derivative, which was isolated as methochloride hydrochloride.[10] The absorption maximum of I (n=0, Y=CH:CH, R=Et, R′=Me, X=I) and of other such dyes was included in a study of colour and constitution.[88] A series of four styryl compounds, I (n=0, Y=CH:CH, R=Me, Et, Pr, or Bu, R′=Et, X=I), with different *N*-alkyl groups was



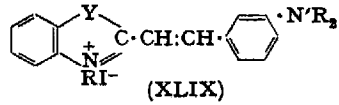
(XLVIII)

prepared, in pyridine as medium; they sensitised weakly, the ethiodide being the best. Its 6-methyl derivative was a strong sensitiser, but its 6-ethoxy-derivative a weak one.[89] The 5,6-benzo-derivative of the diethylamino-compound, I (n=0, Y=CH:CH, R=R′=Et, X=I), sensitised further into the red than did the corresponding derivative of the dimethylamino-analogue.[90] The 6-amino-, 6-chloro-, 6-bromo-, and 6-iodo-derivatives of I (n=0, Y=CH:CH, R=R′=Et, X=I) were made,

but none of them was a useful sensitiser,[91] though the 6-formamido- and 6-acetamido-derivatives were good.[92] The condensation of *p*-(*β*-chloroethyl)methylaminobenzaldehyde with quinaldine methiodide, by heating them in acetic anhydride, gave VIII (Y=CH:CH, R=R¹=Me, R²=CH_2CH_2Cl, X=I).[22]

The styryl compound, I (*n*=0, Y=CH:CH, R=Ph, R′=Me, X=ClO_4), with an *N*-phenyl group, was prepared in 1951.[93] The 5,6-benzo-derivative of an *N*-*p*-tolyl salt, I (*n*=0, Y=CH:CH, R=*p*-C_6H_4Me, R′=Me, X=I), was made by use of pyridine as condensing agent.[94] The same medium gave a 30 % yield of the 7,8-benzo-derivative of I (*n*=0, Y=CH:CH, R=*β*-$C_{10}H_7$, R′=Me, X=I), whilst use of pyridine containing some acetic anhydride gave a 32 % yield of the 6-hydroxy-derivative of I (*n*=0, Y=CH:CH, R=Ph, R′=Me, X=I) and a 27 % yield of the 8-methyl derivative of I (*n*=0, Y=CH:CH, R=*o*-C_6H_4Me, R′=Me, X=ClO_4).[95]

m-Dimethylaminobenzaldehyde was condensed with quinaldine methiodide by heating them with piperidine in ethanol to give XLIX

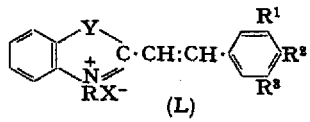


(XLIX)

(Y=CH:CH, R=R′=Me, X=I).[23] Its 6-bromo- and 6-methyl derivatives were prepared later. Whereas its 6-methoxy-derivative was only made with difficulty, the 6-methoxy-derivative of XLIX (Y=CH:CH, R=Me, R′=Et, X=I) was easily obtained. Neither of the two isomeric methiodides prepared by the action of methyl iodide on 6-dimethylaminoquinaldine methiodide would condense with *m*-dimethylaminobenzaldehyde. From these negative results it was concluded that *m*-dimethylaminobenzaldehyde develops an anti-catalyst on keeping.[24]

Styryl compounds with a hydroxy-substituent instead of a dialkylamino-group were proposed as indicators,[77] and both types were suggested for anti-halation layers.[78] Whereas the 4-phenyl derivatives of I (*n*=0, Y=CH:CH, R=Me or Et, R′=Me, X=I) both absorbed at 5300 Å, the corresponding *p*-hydroxy-4-phenyl compounds absorbed at 4300 Å. A *p*-methoxy-4-phenyl compound was also made.[33] By means of piperidine in ethanol, quinaldine ethiodide was condensed with *o*- and *p*-hydroxybenzaldehyde.[79] The styryl dye, L (Y=CH:CH,

R=Et, $R^1=R^3=Br$, $R^2=OH$, X=I), was prepared with pyridine as medium.[82]



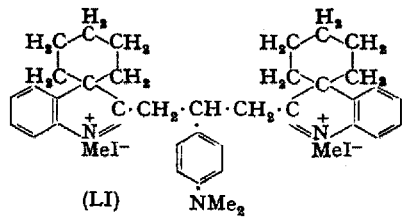
(L)

C. Styryl Salts with a 4-Linked Quinoline Nucleus

The preparation of sensitising dyes by condensing *p*-dimethylaminobenzaldehyde with 6-dimethylaminolepidine alkiodide was recorded in 1920, when the 6-dimethylamino-derivatives of II (R=Me or Et, R′=Me, X=I) were prepared.[1] In the following year II (R=R′=Me, $X=ClO_4$) was described.[3] In 1926 a study of the antiseptic properties of styryl dyes included those of the 6-methyl derivative of II (R=R′=Me, X=Cl).[83] A comparison in 1930 of the absorption and sensitising maxima of certain methincyanines, styryl compounds and anils, included data for II (R=Et, R′=Me, X=I),[12] and its sensitising maximum was also recorded elsewhere,[13,14,87] as was its absorption maximum in nitromethane[19,52] and in methanol.[88] For the diethylamino-analogue, II (R=R′=Et, X=I), lack of sensitising capacity was noted.[89]

D. Styryl Salts with an Indolenine Nucleus

The purple styryl compound, I (*n*=0, $Y=CMe_2$, R=R′=Me, X=I), was described in 1923.[96] Its absorption curve was published in 1930; only a tail of extra-sensitivity was shown[12] but sensitising action was recorded elsewhere.[87] In 1937 the sensitising maximum was compared with that of the higher vinylene homologue.[13,14] The perchlorate of the styryl dye was prepared in 20% yield and its absorption maximum in nitromethane solution was recorded.[19,52] From an aqueous pyridine solution the corresponding methochloride was less strongly adsorbed by alumina than was its higher vinylene homologue.[51] Absorption maxima in methanol were given for I (*n*=0, $Y=CMe_2$, R=Ph, R′=Me, $X=ClO_4$) and for the corresponding ethiodide.[88] By condensing equimolecular proportions of 3-cyclohexanespiran-2-methylindolenine methiodide and *p*-dimethylaminobenzaldehyde, there was obtained the spiran methiodide, I (*n*=0, $Y=C_6H_{10}$, R=R′=Me, R=I), but, with different proportions, the dimethiodide, LI, resulted.[97] By condensing 1,3,3-trimethyl-2-methyleneindoline with halogen-containing aldehydes,



(LI)

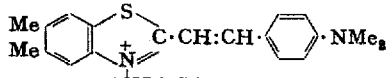
there were prepared the styryl compounds, I (n=0, Y=CMe_2, R=Me, R′=CH_2CH_2Cl, X=Cl), VIII (Y=CMe_2, R=R′=Me, R^2=$CH_2CHClMe$, X=OAc), and the *o*-methyl derivative of VIII (Y=CMe_2, R=Me, R^1=Et, R^2=CH_2CH_2Cl, X=OAc); there was also prepared a benzo-derivative of VIII (Y=CMe_2, R=Et, R^1=Me, R^2=*p*-C_6H_4OEt), which was salted out with sodium phosphate.[20] Similarly a 2-methyleneindoline was condensed with an aldehyde having an *N*-*β*-cyanoethyl group to give the 5-methoxy-derivative of VIII (Y=CMe_2, R=R^1=Me, R^2=CH_2CH_2CN, X=Cl). The same dye was prepared by the alternative method (equation 2) from 2-formylmethylene-5-methoxy-1,3,3-trimethylindoline and (*β*-cyanoethyl)methylaniline with phosphorus oxychloride in benzene. This latter method was applied to the preparation of VIII (Y=CMe_2, R=Me, R^1=Et, R^2=CH_2CH_2CN, X=Cl) and the 5-methoxy-derivative of VIII (Y=CMe_2, R=Me, R^1=CH_2Ph, R^2=CH_2CH_2CN, X=Cl).[21] Subsequently, from 2,3,3,-trimethylindolenine methiodide and halogen-containing aldehydes, by use of piperidine in ethanol, there were prepared I (n=0, Y=CMe_2, R′=CH_2CH_2Cl, X=I) and VIII (Y=CMe_2, R=Me, R′=CH_2CH_2Cl, X=I).[22]

The styryl compound, L (Y=CMe_2, R=Me, R^1=R^3=Me, R^2=OH, X=ClO_4), was prepared by heating together the quaternary salt and the aldehyde at 110°; it had its sensitising maximum at 5550 Å.[82]

E. Styryl Salts with a Benzothiazole Nucleus

A styryl compound, I (n=0, Y=S, R=R′=Me, X=ClO_4), with a benzothiazole nucleus was described in 1921, also its *o*-dimethylamino-analogue.[3] In 1923 the corresponding iodide was made, as were also its 4,5- and 6,7-benzo-derivatives, and sensitising maxima were recorded.[96] The 6-chloro- and 6-methoxy-derivatives of I (n=0, Y=S, R=R′=Me, X=Br), and the 6-chloro-4-methyl- and chloro-6-methoxy-derivatives of I (n=0, Y=S, R=R′=Me, X=I), were described later, and absorption maxima were given.[98] An early patent on anti-halation

layers included I (n=0, Y=S, R=R'=Me, X=Cl).[78] In 1932 a study of the trypanocidal properties of styryl compounds included those of the 6-lactylamino-derivative of I (n=0, Y=S, R=Me, R'=H, X=Cl) and of the 6-amino-derivative of VIII (Y=S, R=Me, R^1=Ac, R^2=lactyl, X=Cl).[85] The 4,5- and 6,7-benzo-derivatives of I (n=0, Y=S, R=Et, R'=Me, X=I) were prepared in 46 % and 67 % yields, respectively: the former sensitised more strongly than the latter.[99] Absorption and sensitising curves for these two benzo-derivatives, and for the parent dye, were published.[12] The sensitising maxima of I (n=0, Y=S, R=Et, R'=Me, X=I) and of the 6,7-benzo-derivative of I (n=0, Y=S, R=R'=Me, X=I) were compared with those of their higher vinylene analogues.[13,14] The absorption curves of I (n=0, Y=S, R=Et, R'=Me, X=I) in methanol and in nitromethane were compared.[17] In the latter solvent, maxima were given for I (n=0, Y=S, R=Ph or *o*-$C_6H_4NO_2$, R'=Me, X=ClO_4) and the 6-nitro-derivative of I (n=0, Y=S, R=Et, R'=Me, X=Cl),[18,52] together with preparative details.[18] These data were also recorded for the 4,5,6,7-dibenzo- and -tetrahydro-, and the 5-nitro-, 6-chloro-, 6-methyl, and 6-ethoxy-derivatives of the iodide and the 5-ethoxy-derivative of the toluene-*p*-sulphonate; also for an iodide having a 3,4-trimethylene group, and for I (n=0, Y=S, R=*p*-$C_6H_4NO_2$, CH_2CO_2Et, CH_2COPh, or CH_2Ph, R'=Me, X=I); absorption maxima in nitromethane were given for the 4,5-, 5,6-, and 6,7-benzo-derivatives of I (n=0, Y=S, R=Et, R'=Me, X=I).[19] Absorption maxima in methanol were given for I (n=0, Y=S, R=Et, R'=Me, X=I), its 4,5-benzo-, and 4,5,6,7-tetrahydro-derivatives, also for the hexahydro-derivatives of the corresponding toluene-*p*-sulphonate, which was prepared in 48 % yield.[88] Patents on cyanine dyes having a 5,6-benzobenzothiazole[100] or a tetrahydrobenzothiazole nucleus[101] included the 5,6-benzo- and tetrahydro-derivatives of I (n=0, Y=S, R=Et, R'=Me, X=I). A patent on cyanines prepared from betaines included the styryl compound LII.[102] When cyanines having a 3,4-trimethylenebenzothiazole nucleus were described, the patent included



(LII)

2-*p*-dimethylaminostyryl-3,4-trimethylenebenzothiazolium bromide;[103] the iodide was described later.[19,64] A styryl dye was described as

prepared from a supposed 2,3-trimethylenebenzothiazolium salt[104] but the salt was in fact diquaternary with an *NN'*-dimethylene linkage (see IX-1, X-4-B). The 6-fluoro-derivative of I (n=0, Y=S, R=Et, R'=Me, X=I) was described in 1950,[105] and, subsequently, the 5-trifluoromethyl[106] and 6-trifluoromethylthio-[107] derivatives of the corresponding methiodide, the 5-trifluoromethyl derivative of the etho-perchlorate,[108] and the 5- and 6-trifluoromethoxy-derivatives of the ethiodide.[109] By boiling the appropriate salt and aldehyde in acetic anhydride, there was prepared the 6-methyl derivative of the *p*-toliodide, I (n=0, Y=S, R=*p*-C_6H_4Me, R'=Me, X=I),[62] and just as the *N*-cyclohexyl group was introduced into cyanines, so, with acetic anhydride as condensing agent, there was prepared a 75 % yield of the styryl compound, I (n=0, Y=S, R=C_6H_{11}, R'=Me, X=I).[63] The styryl salt, I (n=0, Y=S, R=Et, R'=Me, X=I), resulted on cleavage of the $\alpha\beta$-linking of 3,3'-diethylthiatricarbocyanine iodide, by heating it with *p*-dimethylaminobenzaldehyde in acetic anhydride at 120° for 40 minutes.[110]

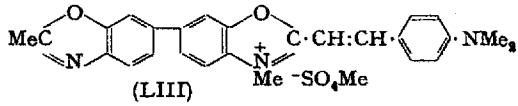
p-Diethylaminobenzaldehyde, in boiling acetic anhydride, was used in the preparation of I (n=0, Y=S, R=R'=Et, X=I) and a 62 % yield of thrice-recrystallised product was obtained.[65] With piperidine in ethanol as catalyst, *p*-diethylaminobenzaldehyde was used in the preparation of I (n=0, Y=S, R=Me, R'=Et, X=I), and of its 4,5- and 6,7-benzo-derivatives.[111] The 4,6-dimethyl and 6-methyl derivatives of the styryl salt were also made,[112] also its 6-bromo-, 6-chloro-, 6-ethoxy-, and 6-methoxy-derivatives, which showed little or no sensitising action.[113] From halogen-containing aldehydes, in acetic anhydride, there were prepared VIII (Y=S, R=Me, R^1=Me or Et, R^2=CH_2CH_2Cl, X=I).[22]

m-Dialkylaminobenzaldehyde was condensed with 2-methylbenzothiazole ethiodide, by heating with piperidine in ethanol, to give XLIX (Y=S, R=Me, R'=Me or Et).[23]

2-Methylbenzothiazole ethiodide was condensed with *o*- or *p*-hydroxybenzaldehyde in the presence of pyridine.[79] The same salt was condensed with aldehydes in pyridine to give the *o*-hydroxy-derivatives of L (Y=S, R=Et, R^1=R^3=Br, R^2=H or OH, X=I); there were also prepared L (Y=S, R=$CH_2CH_2CO_2H$, R^1=Br, R^2=OH, R^3=OEt, X=Br), the *o*-methyl derivative of L (Y=S, R^1=R^3=Br, R^2=OH, X=Br), and the 6,7-benzo-derivative of L (Y=S, R=Et, R^1=R^3=Br, R^2=OH, X=I).[82]

F. Styryl Salts with a Benzoxazole Nucleus

The sensitising maximum of a styryl compound, I (n=0, Y=O, R=Et, R′=Me, X=I), of the benzoxazole series was given,[12] also the absorption maxima of its solution in aqueous ethanol,[12] in methanol,[88] and in nitromethane.[19,52] It was prepared in 30 % yield by use of triethylamine in ethanol, with 3 hours' boiling.[65] The sensitising maximum of I (n=0, Y=O, R=R′=Me, X=I) was recorded.[13,14] A quaternary salt of a bis(methylbenzoxazole) reacted with p-dimethylaminobenzaldehyde in acetic anhydride to give a dye, which was probably LIII,



(LIII)

and which was suitable for anti-halation.[76] With various types of cyanine molecules having a 5,6-benzobenzoxazole nucleus, there was included the 5,6-benzo-derivative of I (n=0, Y=O, R=R^1=Me, X=I).[114] Improved sensitising was claimed for cyanines in which a benzoxazole nucleus carried a substituted 5-phenyl group and the examples included the 5-β-naphthyl derivative of I (n=0, Y=O, R=Et, R′=Me, X=SO_4Et), which was prepared in acetic anhydride.[115] With cyanines and merocyanines prepared from a 2-methyl-4,5,6,7-tetrahydrobenzoxazolium salt, there was also a styryl salt.[116]

Styryl dyes prepared from halogenohydroxybenzaldehydes were good sensitisers; they included one prepared from 2-methylbenzoxazole ethiodide and m,m′-dibromo-p-hydroxybenzaldehyde, also the 5-chloro- and 5-phenyl derivatives of the corresponding ethoethylsulphate.[82]

G. Styryl Salts with a Benzoselenazole Nucleus

A styryl compound, I (n=0, Y=Se, R=Et, R′=Me, X=I), having a benzoselenazole nucleus, was prepared in 70 % yield by boiling 2-methylbenzoselenazole ethiodide and p-dimethylaminobenzaldehyde with piperidine in ethanol, and recrystallising.[19] Its absorption maximum in nitromethane[19,52] and that in methanol[88] were compared with those of analogues.

The 5,6-dimethyl derivative of L (Y=Se, R=Et, R^1=H, R^2=OH, R^3=Br, X=I) was prepared by boiling the appropriate ethiodide and aldehyde in pyridine.[82]

H. Styryl Salts with a Benzimidazole Nucleus

A styryl compound, I (n=0, Y=NMe, R=R′=Me, X=I), with a benzimidazole nucleus was prepared as early as 1923 and its sensitising action was described.[96] This was also described later.[13,14] The analogue, I (n=0, Y=NEt, R=Et, R′=Me, X=I), was obtained in 31 % yield by boiling the reactants in pyridine, with piperidine as catalyst; its absorption in nitromethane was recorded,[19] also that in methanol.[88]

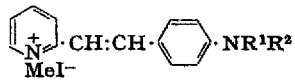
A styryl dye, L (Y=NPh, R=Me, R^1=R^3=Br, R^2=OH, X=SO_4Me), was prepared by heating the benzimidazolium salt with the sodium salt of 3,5-dibromo-4-hydroxybenzaldehyde, in pyridine containing piperidine, at 110° for 6 hours: it proved to be a sensitiser.[82]

I. Styryl Salts with a 2-Linked Pyridine Nucleus

In 1921 the 6-phenyl derivative of III (n=0, R=R′=Me, X=ClO_4), with a 2-linked pyridine nucleus, was prepared, but did not show useful sensitising properties.[3] In the same year, the commercial dye Pinaflavol was described as a sensitiser for green and yellow light.[6] In the following year the styryl compound, III (n=0, R=R′=Me, X=I), prepared by heating 2-picoline methiodide and *p*-dimethylaminobenzaldehyde with piperidine in ethanol, was described as the most powerful known sensitiser to green light.[4] This compound was included in a study of the antiseptic properties of styryl compounds and anils, most of which had a 2-linked quinoline nucleus.[83] Its absorption and sensitising curves were depicted in 1930;[12] its sensitising maximum was compared with that of its higher vinylene homologue,[13,14] and its sensitising action was described elsewhere,[29,87] also that of III (n=0, R=Et, R′=Me, X=I).[29] Its absorption was compared with that of its 4-linked analogue,[15] and subsequently the absorption spectra and fluorescence of the various salts, III (n=0, R=R′=Me, X=Cl, Br, or I), were described,[117] as well as their sensitising action.[118] As regards sensitising power, the members of the *p*-dimethylamino-series, III (n=0, R=Me, Et, Pr, or Bu, R′=Me, X=I)[119] were in general less good than those of the *p*-diethylamino-series, III (n=0, R=Me, Et, Pr, or Bu, R′=Et, X=I).[120] The absorption maxima of III (n=0, R=Et, R′=Me, X=I) in nitromethane[19,52] and in methanol[88] were compared with those of styryl dyes having other heterocyclic nuclei.

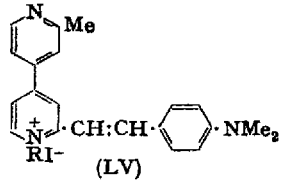
The absorption spectra of styryl compounds, III (n=0, R=$CHMe_2$,

$CHMeEt$, CH_2CHMe_2, or $CH_2CH_2CHMe_2$, R′=Me, X=I), in which the *N*-alkyl group of the pyridinium nucleus had a branched chain, resembled those in which the chain was straight.[121] Through suitable aldehydes and 2-picoline ethiodide, with piperidine in ethanol, there were prepared LIV ($R^1=CH_2CH_2Cl$, $R^2=Et$ or CH_2CH_2Cl).[21] Certain



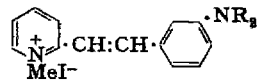
(LIV)

4,6-diaryl-2-*p*-dimethylaminostyrylpyridinium salts were obtained by the action of bases on the corresponding pyrylium salts (see sections 6-A and B). A styryl compound with, supposedly, an α-*N*-methylene group[122] must be discounted, as the salt used as starting point was in fact diquaternary with an *NN′*-methylene linkage (see IX-1 and X-4-B). From 2,2′-dimethyl-4,4′-bipyridine alkiodide there were prepared LV (R=Me or Et), both of which were desensitisers; the former was converted into methochloride. By addition of methyl iodide to LV (R=Me), a dimethiodide was formed but the methiodide would not add on ethyl iodide.[123]



(LV)

By use of *m*-dialkylaminobenzaldehyde, the dyes LVI (R=Me, Et, or Pr) were prepared.[23]



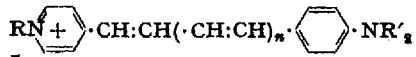
(LVI)

By dissolving 2-picoline methiodide in a little alcohol at room temperature and treating with an aldehyde in the presence of piperidine, styryl derivatives with substituents such as *m*-nitro-, *p*-hydroxy-, or *p*-methoxy-, were formed; the methiodide was also condensed with furfural. By heating the products at 250° under reduced pressure, methyl iodide was eliminated.[124] Excess of aldehyde was used in the

preparation of the salts in Table II, as it could easily be eliminated, and heating in methanol with piperidine (½ mol. per mol. of quaternary salt) was applied for 1–4 hours.[80]

J. Styryl Salts with a 4-Linked Pyridine Nucleus

The sensitising maximum of LVII (n=0, R=R′=Me) was in 1937 compared with that of its higher vinylene homologues.[13,14] Its absorption maximum lay at a longer wavelength by 200 Å than that of the



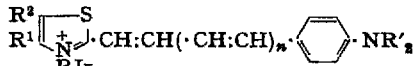
(LVII)

2-linked pyridine analogue.[15] To prepare LVII (n=0, R=Me or Et, R′=Me), the aldehyde and alkiodide were boiled in ethanol, with piperidine as catalyst, for 5 hours.[30] The absorption maxima of the latter, in nitromethane[19,52] and in methanol,[88] were compared with those of styryl compounds having other heterocyclic nuclei. The preparation of the salt, in 53 % yield, was described.[19]

A series of twenty-one 4-styrylpyridine methiodides was prepared. There was the same general relationship between colour, yield, and resonance possibilities as with the 2-styrylpyridine compounds. Unlike the o- and p-hydroxy-salts, the m-hydroxy-analogue gave little colour change with alkali. Some aldehydes gave better yields with 4- than with 2-picoline methiodide (Table II).[125]

K. Styryl Salts with a Thiazole Nucleus

As the sensitising action of the styryl compound, LVIII (n=0, R=R′=Me, R¹=Ph, R²=H), with a thiazole nucleus, was described in 1922,[25] and that of LVIII (n=0, R=R′=Me, R¹=R²=H; and n=0, R=R′=Me, R¹=Ph, R²=Me or Ph) in 1923,[96] it is surprising to

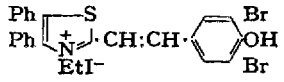


(LVIII)

find it patented in 1931.[126] Absorption and sensitising curves of LVIII (n=0, R=Et, R′=R¹=Me, R²=H) were published in 1930,[12] and in 1937 the sensitising maxima of the two styryl dyes, LVIII (n=0,

R=R′=Me, R¹=H or Me, R²=H), were compared with those of their higher vinylene homologues.[13,14] The preparation of LVIII (*n*=0, R=Et, R¹=R′=Me, R²=H) was described.[79] The absorption maximum in methanol was given for LVIII (*n*=0, R=Et, R′=R¹=Me, R²=H)[88] and in nitromethane for LVIII (*n*=0, R=Et, R′=Me, R¹=H, Me, or Ph, R²=H; and *n*=0, R=Ph or *p*-C_6H_4Ph, R′=R¹=Me, R²=H), with preparative details for the last three.[19] Sensitising by cyanines having an *N*-*m*- or *N*-*p*-carboxyaralkyl group included the styryl dye, LVIII (*n*=0, R=*p*-$CH_2 \cdot C_6H_4CO_2H$, R′=R¹=Me, R²=H, X=Br).[127] Amongst cyanines and merocyanines having a 4-aminothiazole nucleus, there was also a styryl dye.[128] Patents on the preparation and sensitising action of thiazolocyanines having an *N*-phenyl group (cf. X-4-C) included the styryl dye, LVIII (*n*=0, R=Ph, R′=R¹=Me, R²=H).[129] By use of *p*-diethylaminobenzaldehyde, there were prepared LVIII (*n*=0, R=Me, R′=Et, R¹=Me or Ph, R²=H), the former by use of acetic anhydride, the latter by piperidine in ethanol.[111] The latter method was also applied to the preparation of LVIII (*n*=0, R=R²=Me, R′=Et, R¹=H or Me).[112] Four styryl dyes having a *p*-substituted 4-phenyl group in the thiazole nucleus were prepared, *viz.* LVIII (*n*=0, R=R′=Me, R¹=*p*-C_6H_4Me, *p*-C_6H_4Cl, *p*-C_6H_4Br, or *p*-C_6H_4I, R²=H), of which the last was the weakest sensitiser.[130] By use of *m*-dimethylaminobenzaldehyde there was prepared the *m*-analogue corresponding with LVIII (*n*=0, R=R′=Me, R¹=R²=H).[23]

2-Methyl-4-phenylthiazole ethiodide and 2,4-dimethylthiazole ethiodide were condensed with *o*- and *p*-hydroxybenzaldehyde in the presence of pyridine.[79] Styryl dyes, which were obtained by condensing



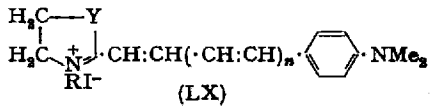
(LIX)

3(or 5)-halogeno-2(or 4)-hydroxybenzaldehyde with quaternary salts and which were useful for sensitising, and also for dyeing acetate silk, included LIX.[82]

L. Styryl Salts with a Thiazoline Nucleus

When cyanine dyes containing a thiazoline nucleus were first described, the styryl salts, LX (*n*=0, Y=S, R′=Et or Me), were pre-

pared by boiling 2-methylthiazoline alkiodide and *p*-dimethylaminobenzaldehyde with piperidine in methanol for 16 hours and recrystallising; the former was obtained in 51 % yield.[131,132] The absorption and



(LX)

sensitising maxima of the latter were compared with those of its higher vinylene analogue.[14] Its absorption maximum was also compared with those of two salts having an open chain instead of a heterocyclic nucleus (see section 5-A).[133] Besides the absorption maximum of LX (*n*=0, Y=S, R=Et) in methanolic solution,[88,131] the value for its solution in nitromethane was also recorded.[19,52]

2-Methylthiazoline methiodide was condensed with 4-hydroxy-3,5-di-iodobenzaldehyde by heating them in pyridine.[82]

M. Styryl Salts with Unusual Nuclei

(*I*) *Nuclei with Nitrogen as the One Hetero-Atom*

In 1922 1-methylisoquinoline methiodide was condensed with *p*-dimethylaminobenzaldehyde, by heating with piperidine in ethanol, to give IX.[25] In 1951 similar conditions with 3-methylisoquinoline methiodide gave a 7 % yield of X (R=Me, X=I), but fusion with piperidine at 135° gave a 67 % yield, and by use of a 100 % excess of aldehyde the yield was increased to 79 %. The dye, X (R=Et, X=ClO_4), was obtained in a crude yield of 34 %. Styryl compounds with a 3-linked isoquinoline nucleus were also prepared by reaction with benzaldehyde and with *m*-nitrobenzaldehyde.[26]

Although 9-methylacridine methiodide could not be condensed with *p*-dimethylaminobenzaldehyde,[32] styryl compounds such as XI (X=Cl, I, or *p*-$SO_3 \cdot C_6H_4Me$) were prepared from the styryl base (see section 1-Q.2).[31]

By boiling 2-methylacenaphthenopyridine methiodide with *p*-dimethylaminobenzaldehyde and piperidine in ethanol, the salt XII, which sensitised weakly, was obtained.[32] Absorption and sensitising curves were published.[12]

On heating 5-methyl-2*H*-pyrroline ethiodide with *p*-dimethyl-

aminobenzaldehyde in pyridine containing acetic anhydride, it gave LX (n=0, Y=CH_2, R=Et), which was converted into perchlorate.[134] Perchlorates of the 5-methyl, 5-phenyl, and 4,5-diphenyl derivatives were also made.[135]

(2) *Nuclei, Including Complex Nuclei, with Two Nitrogen Atoms as the Only Hetero-Atoms*

From 2-methyl-4-phenylquinazoline methiodide, the styryl compound, XIII, was prepared by reaction with *p*-dimethylaminobenzaldehyde; the salt was also condensed with *o*-hydroxybenzaldehyde.[33] Reaction of 4-methylquinazoline methiodide with *p*-dimethylaminobenzaldehyde was also recorded.[136] The styryl salt, XIV, was prepared by boiling 2-methyl-4-oxo-3,4-dihydroquinazoline methiodide with the aldehyde in acetic anhydride.[22] 2,3-Dimethyl-4-oxo-3,4,5,6,7,8-hexahydroquinazoline methiodide was condensed with *p*-dimethylaminobenzaldehyde by heating with acetic anhydride in pyridine, giving orange crystals.[137]

The styryl dye, XV, with a perimidine nucleus was prepared by boiling 1,2,3-trimethylperimidinium toluene-*p*-sulphonate and *p*-dimethylaminobenzaldehyde in pyridine, with piperidine as catalyst, for 2 hours, then treating with iodide.[34, 35]

An early attempt to condense 2,3-dimethylquinoxaline methiodide with aldehydes led to black insoluble products.[138] In 1942 quaternary salts of 2,3-dimethylquinoxaline were prepared by means of alkyl sulphates or toluene-*p*-sulphonates. They were condensed with *p*-dimethylaminobenzaldehyde by heating in a mixture of pyridine and acetic anhydride to give styryl salts, XVI (R=R′=Me, X=I or SO_4Me; and R=Et, R′=Me, X=SO_4Et). The condensation of 3-methyl-2-methylene-1-phenyl-1,2-dihydroquinoxaline with the aldehyde was catalysed by boron fluoride or methyl orthoborate, especially in the presence of pyridine, giving XVI (R=Ph, R′=Me, X=Cl). That method failed with 2-methylene-1,3-diphenyl-1,2-dihydroquinoxaline, but XVI (R=R′=Ph, X=I) was prepared from it by use of phosphorus oxychloride or acetyl chloride. The styryl salt, XVI (R=Ph, R′=H, X=I), was also prepared from the appropriate methylene base and the aldehyde by use of one of these chlorides, preferably acetyl chloride, but not by use of boron fluoride.[36] The methomethylsulphate of 1,3-dimethyl-2-oxodihydroquinoxaline condensed with *p*-dimethylamino-

benzaldehyde in acetic anhydride, followed by pyridine, to give XVII ($R=R'=R^1=R^2=Me$, $X=SO_4Me$). Similarly there were prepared, from alkoalkylsulphates, by heating just to boiling with the aldehyde in acetic anhydride, XVII ($R=Me$ or Et, $R'=Ph$, $R^1=R^2=Me$, $X=Cl$). Condensation of the crude methomethylsulphate of 3-methyl-2-oxodihydroquinoxaline with the aldehyde in boiling acetic anhydride gave XVII ($R=R^1=R^2=Me$, $R'=H$, $X=SO_4Me$), which could be converted into the iodide: no appreciable *N*-alkylation had occurred.[37,38] Other chlorine-containing aldehydes were used in acetic anhydride containing pyridine to give XVII ($R=R^1=Me$, $R'=H$, $R^2=CH_2CH_2Cl$, $X=I$; and $R=Me$, $R'=H$, $R^1=R^2=CH_2CH_2Cl$, $X=SO_4Me$), the latter being accompanied by another product. There were also prepared XVII ($R=R'=R^1=Me$, $R^2=CH_2CH_2Cl$, $X=Cl$ or I; $R=R^1=Me$, $R'=Ph$, $R^2=CH_2CH_2Cl$, $X=SO_4Me$; and $R=Me$, $R'=Ph$, $R^1=R^2=CH_2CH_2Cl$, $X=SO_4Me$).[22,38]

The styryl dyes, XVIII ($R=p$-$C_6H_4NO_2$, *o,o'*-diCl-*p*-$NO_2C_6H_2$, or *m*-$C_6H_4NO_2$), having a phthalazine nucleus, were prepared by heating the appropriate methylene base with *p*-dimethylaminobenzaldehyde in acetic anhydride containing acetic acid at 100° for 5 hours.[39]

By heating 1-methyl-1'-phenylindolo(3',2'-3,4)isoquinoline with 50 % excess of *p*-dimethylaminobenzaldehyde in ethanol for 33 hours, concentrating in a vacuum, and twice recrystallising from methanol, the styryl salt, XIX, was obtained as dimethanolate.[40]

After boiling 2-methylindolo(3',2'-3,4)quinoline methotoluene-*p*-sulphonate and 50 % excess of *p*-dimethylaminobenzaldehyde with triethylamine in acetic anhydride for 1 hour, the styryl salt, XX (R=H), was precipitated by water in low yield, which was not improved by varying the conditions. Use of piperidine in ethanol gave a base (see section 1-Q.2). Yet an 88 % yield of styryl salt, XX (R=Me), was prepared by boiling 2,1'-dimethylindolo(3',2'-3,4)quinoline methotoluene-*p*-sulphonate and *p*-dimethylaminobenzaldehyde with piperidine in ethanol for 30 hours.[41]

(*3*) *Nuclei with Three Nitrogen Atoms as Hetero-Atoms*

The styryl compound, XXI, was prepared by boiling 5-methyl-s-triazolo[4,3-a]quinoline ethotoluene-*p*-sulphonate and *p*-dimethylaminobenzaldehyde in piperidine for 5 minutes, and treating with iodide, resulting in 17 % yield after two recrystallisations from methanol.[42]

(4) *Nuclei with Four Nitrogen Atoms as Hetero-Atoms*

The styryl compound, XXII, was prepared from 5-methyltetrazolo[a]quinoline ethotoluene-*p*-sulphonate, by use of piperidine in ethanol, and the yield of recrystallised iodide was 50 %.[42]

A styryl salt, XXIII, with a simple tetrazole nucleus, was prepared by means of pyridine containing triethylamine and acetic acid.[43]

(5) *Nuclei with One Nitrogen and One Sulphur as Hetero-Atoms*

Of remarkable nuclei containing one nitrogen and one sulphur as hetero-atoms (X-5-E), the perinaphtho-1,3-thiazine nucleus was introduced into the styryl compound, XXV (R=Me, X=I): the method was to boil 2-methylperinaphtho-1,3-thiazine methiodide and the aldehyde with ethanol or with acetic anhydride for 10 minutes, but piperidine inhibited the condensation. Although the absorption maximum of the methiodide was given as 4700 Å,[45] for a methanolic solution of the methomethylsulphate, XXV (R=Me, X=SO_4Me), the value 5520 Å was recorded elsewhere. The salt gave practically no sensitising and depressed the sensitivity to blue light.[139]

Quaternary salts of 3-methyl-1,4,2-benzothiazines on boiling with *p*-dimethylaminobenzaldehyde in acetic anhydride for 5–10 minutes gave the styryl perchlorates, XXVI (R=Me, R'=H, Et, or CO_2Et; and R=Ph, R'=CO_2Et) in yields of 23–52 % after recrystallisation. In the absence of a reactive methyl group, the aldehyde condensed with the 2-methylene group of the 1,4,2-benzothiazine. Thus 3-phenyl-1,4,2-benzothiazine methoperchlorate gave a 67 % yield of XXVII (R=Ph) on boiling with the aldehyde in acetic anhydride for 5 minutes and recrystallising twice from ethanol; 1,4,2-benzothiazine methoperchlorate gave XXVII (R=H) on boiling with the aldehyde in acetic acid, but use of acetic anhydride containing pyridine gave the benzothiazolium compound, I (*n*=0, Y=S, R=R'=Me, X=ClO_4).[46]

2-Methyl-4,5-trimethylenethiazole[140] was converted into its methiodide, which was condensed with *p*-dimethylaminobenzaldehyde, to give a 29 % crude yield of styryl salt.[141] Through the reactive methyl group in quaternary salts of various special thiazoles and benzothiazoles, including types with spirocyclic groups, there were prepared styryl salts, as well as cyanines and dimethinmerocyanines[142–146] (cf. X-5-E; XIV-10-C.1e).

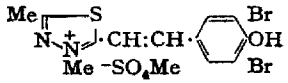
(6) *Nuclei with a Nitrogen, an Oxygen, and a Sulphur as Hetero-Atoms*

Quaternary salts of two types of dihydropyranothiazole, with a reactive methyl group, were converted into *p*-dimethylaminostyryl salts, as well as into cyanines and dimethinmerocyanines (cf. X-5-F and XIV-10-C.1f).[147–149]

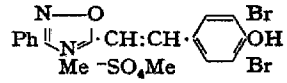
(7) *Nuclei with Two Nitrogen Atoms and One Sulphur or One Oxygen as Hetero-Atoms*

The 1,3,4-thiadiazole nucleus was introduced into the molecule of the styryl compound, XXVIII, which had its sensitising maximum at 5500 Å.[47] It was prepared in 54% yield, with acetic anhydride as medium, and its absorption maximum in nitromethane was recorded.[19] The compound, XXIX, with a dihydro-1,3,4-thiadiazole nucleus was prepared from 2,5-dimethyl-4-phenyldihydro-1,3,4-thiadiazole methiodide and the aldehyde, by use of piperidine in ethanol.[48]

2,5-Dimethyl-1,3,4-thiadiazole methomethylsulphate was fused with 3,5-dibromo-4-hydroxybenzaldehyde to give LXI, which sensitised at 5450 Å. The same aldehyde with 5-methyl-3-phenyl-1,2,4-oxadiazole methomethylsulphate gave LXII, with its absorption and sensitising maxima at 5000 Å and 5200 Å, respectively.[82]



(LXI)



(LXII)

A styryl dye, XXX, with a thionaphtheno(4',5'-5,4)-thiazole nucleus sensitised for green, yellow, and bright red light, but with no decided maximum.[49]

(8) *Nuclei with One Nitrogen and Two Sulphur Atoms as Hetero-Atoms*

Two types of dihydrothiopyranothiazole nucleus were introduced into styryl salts, as well as into cyanines and dimethinmerocyanines[147,150,151] (cf. X-5-I, XIV-10-C.1i).

N. Phenylbutadienyl Salts

In 1921 the butadienyl perchlorate of the 2-linked quinoline series, I (n=1, Y=CH:CH, R=R'=Me, X=ClO_4), was prepared in 35%

yield, after washing, by boiling quinaldine methoperchlorate with *p*-dimethylaminocinnamaldehyde in acetic anhydride, and similarly for I (n=1, Y=S, R=R′=Me, X=ClO_4) of the benzothiazole series.[3] Absorption and sensitising curves were subsequently given for I (n=1, Y=S, R=Et, R′=Me, X=I) of the benzothiazole series, and for III (n=1, R=Et, R′=Me, X=I) of the 2-linked pyridine series.[12] The dye, I (n=1, Y=CMe_2, R=R′=Me, X=I), of the indolenine series, was more strongly adsorbed by alumina from an aqueous pyridine solution than was its lower vinylene homologue.[51] The 1,3-butadienyl salts, I (n=1, Y=CH:CH, S, or O, R=Et, R′=Me, X=I; and n=1, Y=CMe_2 or NMe, R=R′=Me, X=I), the 6,7-benzo-derivative of I (n=1, Y=S R=R′=Me, X=I), III (n=1, R=R′=Me, X=I), LVII (n=1, R=R′=Me), LVIII (n=1, R=R′=Me, R^1=H or Me, R^2=H), and LX (n=1, R=R′=Me) were compared with the corresponding styryl salts.[13,14] The butadienyl salt, I (n=1, Y=CH:CH, R=R′=Me, X=I), was obtained in 12 % yield by boiling quinaldine methotoluene-*p*-sulphonate and *p*-dimethylaminocinnamaldehyde in acetic anhydride for 5 minutes, precipitating with ether, converting into iodide, and recrystallising thrice from methanol.[17] In the benzothiazole series and with nitromethane as solvent, absorption maxima for I (n=1, Y=S, R=Et, Ph, or *o*-$C_6H_4NO_2$, R′=Me, X=I or ClO_4), and the 6-nitro-derivative of I (n=1, Y=S, R=Et, R′=Me, X=Br), were compared with those of the related pairs of symmetrical dyes, and also with the corresponding styryl analogues.[18, 52] The three dyes with negative substituents were prepared by boiling a quaternary salt with the cinnamaldehyde in ethanol, with addition of piperidine as catalyst for the last two.[18] A *p*-dimethylaminophenylbutadienyl salt having a dihydrothiopyranothiazole nucleus was described.[151]

O. Styryl and Phenylbutadienyl Analogues in which the Carbon Chain which Links the Nuclei, or Part or it, is Cyclic

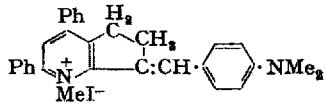
3-*p*-Dimethylaminobenzylidene-2-methylindolenine methoperchlorate is analogous to *p*-dimethylaminostyryl compounds and its absorption maximum was compared with theirs.[88]

Dihydro-β-quinindene methiodide on heating with *p*-dimethylaminobenzaldehyde in acetic anhydride gave the benzylidene salt, XXXI (R=Me),[10] and the corresponding ethiodide was prepared later.[152]

Similarly tetrahydroacridine methiodide was condensed with the aldehyde by heating in acetic anhydride for a few minutes to give

XXXII (R=H), but prolonged heating gave another product. The methochloride was also prepared, as well as the 7-substituted salts, XXXII (R=MeO or NHAc).[10]

The *p*-dimethylaminobenzylidene salt, LXIII, was prepared from 2,3-diphenyldihydropyrindine methiodide, by heating it with the aldehyde and piperidine in ethanol for 15 hours.[152]



(LXIII)

The benzylidene salt, XXXIII (*n*=0, R=Ph, R'=Et, X=ClO_4), was prepared by boiling 2,3-diphenylpyrrocoline with *p*-diethylaminobenzaldehyde, acetic acid, and sodium perchlorate for 5 minutes. The 7,8-benzo-derivative of XXXIII (*n*=0, R=H, R'=Me, X=ClO_4) was prepared similarly. The 6,7-benzo-derivative of XXXIII (*n*=0, R=H, R'=Me, X=I) was prepared by use of 10 % hydriodic acid in ethanol, whilst use of 10 % hydrochloric acid in ethanol, followed by sodium perchlorate, gave the corresponding perchlorate. These reaction mixtures were purple. The blue cinnamylidene salts, XXXIII (*n*=1, R=H or Ph, R'=Me, X=ClO_4), were prepared by reaction of the pyrrocoline with *p*-dimethylaminocinnamaldehyde, acetic acid, and sodium perchlorate, the latter salt being obtained in 65 % yield after recrystallisation from methanol. The 6,7- and 7,8-benzo-derivatives of XXXIII (*n*=1, R=H, R'=Me, X=ClO_4) were prepared similarly.[53]

The benzylidene compound, XXXIV, was prepared by stirring together 1,2-dimethylindole, *p*-dimethylaminobenzaldehyde, and aqueous perchloric acid at room temperature; the blue product solidified, in 33 % yield, on treatment with acetone, but was unstable.[17] Its absorption maximum in nitromethane was recorded.[19, 52]

The salt, XXXV, was prepared by boiling 2-*p*-tolylbenzothiazole ethotoluene-*p*-sulphonate with *p*-dimethylaminobenzaldehyde in pyridine, and converting into iodide.[54]

P. Styryl and Phenylbutadienyl Salts with Substituents on the Chain

(*1*) 2-p-*Dialkylaminostyryl Salts*

In the indolenine series, 2-benzoylmethylene-1,3,3-trimethylindoline was heated with diethylaniline and phosphorus oxychloride,

the mixture was treated with water and alkali, unchanged ketone was filtered off, and the violet-red salt, XXXVI, was salted out.[55]

In the benzothiazole series, the salt, XXXVII (R=R′=Me, R^1=CO_2H, R^2=H, X=I), was prepared by heating together 2-carboxymethylbenzothiazole methiodide and *p*-dimethylaminobenzaldehyde in acetic anhydride, but was found to decompose during recrystallisation.[57] The salts, XXXVII (R=Me or Et, R′=Me, R^1=OPh, R^2=H, X=ClO_4), were prepared, in yields of 31 % and 24 %, respectively, by boiling 2-phenoxymethylbenzothiazole alkotoluene-*p*-sulphonate and *p*-dimethylaminobenzaldehyde with piperidine in ethanol for 4 hours, converting into perchlorate, and recrystallising twice from methanol. The analogue, XXXVII (R=Et, R′=Me, R^1=OEt, R^2=H, X=ClO_4), was made similarly. The compounds did not sensitise appreciably but might be used as filter dyes.[58] For preparing XXXVII (R=Et, R′=Me, R^1=OAc, R^2=H, X=I), 2-acetoxymethylbenzothiazole ethotoluene-*p*-sulphonate was condensed with the aldehyde in acetic anhydride.[59] To prepare XXXVII (R=Et, R′=R^1=Me, R^2=H, X=ClO_4), 2-ethylbenzothiazole ethiodide and *p*-dimethylaminobenzaldehyde were boiled together in acetic anhydride for an hour, and the reaction mixture was treated with ethanol and aqueous sodium perchlorate solution, giving a 54 % yield; of the analogues, XXXVII (R=Et, R′=Me, R^1=Et or Ph, R^2=H, X=ClO_4), the former was not obtained pure and the latter was obtained in 18 % yield. The compounds, XXXVII (R=Ph, R′=Me, R^1=Me, Et, or Ph, R^2=H, X=ClO_4), were also made. The *β*-substituted salt, XXXVII (R=Et, R′=R^2=Me, R^1=H, X=ClO_4), was prepared in 16 % yield by heating 2-methylbenzothiazole ethotoluene-*p*-sulphonate with *p*-dimethylaminoacetophenone in acetic anhydride, and similarly for XXXVII (R=Ph, R′=Me, R^1=H, R^2=Me or Ph, X=ClO_4).[61] The 6-methyl derivative of XXXVII (R=*p*-C_6H_4Me, R′=R^1=Me, R^2=H, X=I) was prepared, in a medium of acetic anhydride, in 28 % yield; the yields for the perchlorates, XXXVII (R=*p*-C_6H_4Me, R′=Me, R^1=Et, isoPr, Ph, or OMe, R^2=H, X=ClO_4) varied from 28–66 %, whilst XXXVII (R=*p*-C_6H_4Me, R′=Me, R^1=H, R^2=*p*-$C_6H_4NMe_2$, X=ClO_4) resulted in 18 % yield.[62] Starting from benzothiazolium cyclohexochlorides, having a 2-CH_2R^1 group, and with acetic anhydride as medium, the cyclohexoperchlorates, XXXVII (R=C_6H_{11}, R′=Me, R^1=Me, Et, isoPr, OMe, or Ph, R^2=H, X=ClO_4), were prepared in yields of 21–50 %.[63] *p*-Dimethylaminostyrylbenzothiazolium salts, having a 3,4-trimethylene group, and as α-substituent

Me, Et, isoPr, or Ph, were prepared in yields of 74 %, 80 %, 13 %, and 76 %, respectively, the first three as perchlorates, the last as iodide.[64] In preparing XXXVII (R=Et, R′=Me or Et, R^1=Me, R^2=H, X=I), 2-ethylbenzothiazole ethiodide was condensed with *p*-dialkylaminobenzaldehyde by boiling with acetic anhydride, and the final yields of pure dyes, after removal of a basic by-product from each (see section 1-Q.3) were 57 % and 18 %. The styryl compounds, XXXVII (R=Et, R′=Me, R^1=Ph, or *p*-$C_6H_4NO_2$, R^2=H, X=I), were similarly prepared in yields of 56 % and 36 %, the latter being accompanied by a base. Through dibenzothiazolylmethane ethiodide and the aldehyde in acetic anhydride, XXXVII (R=Et, R′=Me, R^1=2-benzothiazolyl, R^2=H, X=I) was obtained in 43 % yield after three recrystallisations. For preparing XXXVII (R=Et, R′=Me, R^1=CO_2Et, R^2=H, X=I) from 2-carbethoxymethylbenzothiazole ethiodide, 5 hours' boiling with the aldehyde and triethylamine in ethanol was applied and the yield was 24 %.[65]

In the benzoxazole series, XXXVIII (R=Me) was prepared in 57 % yield by boiling 2-ethylbenzoxazole ethiodide with *p*-dimethylaminobenzaldehyde in acetic anhydride, and recrystallising from methanol. The corresponding α-phenyl salt was prepared, in 7% yield, through 2-benzylbenzoxazole ethotoluene-*p*-sulphonate, which was boiled with the aldehyde and triethylamine in ethanol for 4 hours.[65]

(*2*) *4-p-Dimethylaminophenyl-1,3-butadienyl Salts*

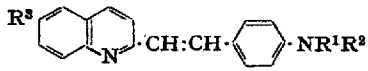
The β-(methylthio)butadienyl salt, XXXIX (R=SMe), was prepared by heating 2-(β-methyl)(β-methylthio)vinylbenzothiazole ethoethylsulphate (cf. VI-1 and 15; VII-8) with *p*-dimethylaminobenzaldehyde in acetic anhydride, and converting into iodide.[66] The β-methyl salt, XXXIX (R=Me), was prepared, in 2 % yield, by heating 2-methylbenzothiazole ethiodide with *p*-dimethylaminostyryl methyl ketone in acetic anhydride for 15 minutes. The β-(*p*-dimethylaminostyryl) salt, XXXIX (R=*p*-CH:CH·($C_6H_4NMe_2$), was similarly prepared in 5 % yield, by use of di-(*p*-dimethylaminostyryl) ketone.[67]

Q. Styryl Bases and their Higher Vinylene Analogues

(*I*) *Bases of the 2- and 4-Linked Quinoline, Benzothiazole, and 2-Linked Pyridine Series*

In the 2-linked quinoline series, the base, V (*n*=0, Y=CH:CH), was prepared over fifty years ago by heating 2,6-dimethylquinoline and

p-dimethylaminobenzaldehyde with zinc chloride. Analogues with a *m*- or *p*-amino-group were also made.[153] In a study of the antiseptic



(LXIV)

action of certain styryl salts, there were included the bases, LXIV (R^1=R^2=Me; and R^1=H, R^2=Ac), besides the hydrochloride of the former and of LXIV (R^1=R^2=H).[83] The base, V (*n*=0, Y=CH:CH),[16] sensitised a chloride emulsion, as did its 4-linked quinoline analogue.[70] The higher vinylene analogue of the former was prepared in 9 % yield by heating quinaldine with *p*-dimethylaminocinnamaldehyde and hydrochloric acid at 100° for 16 hours, making alkaline, and recrystallising the product four times.[17]

The base, V (*n*=0, Y=S), of the benzothiazole series was similarly prepared from 2-methylbenzothiazole, *p*-dimethylaminobenzaldehyde, and hydrochloric acid, the yield of once recrystallised product being 78 %.[17] Its sensitising action and that of its 5-dimethylamino- and 4,5-benzo-derivatives, were described.[70] Its higher vinylene analogue, V (*n*=1, Y=S), was prepared by hydrolysis of its α-cyano-derivative (section 1-Q.3).[72]

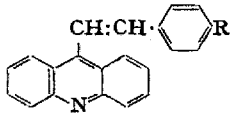
In the 2-linked pyridine series, methyl iodide was eliminated from 2-*p*-dimethylaminostyrylpyridine methiodide by boiling it with diethylaniline for 1 hour, or with dimethylaniline for 2 hours.[71] Bases of the pinaflavol series were described as better sensitisers than the salts, but with the maximum at a shorter wavelength.[154]

(2) *Styryl Bases with Unusual Nuclei*

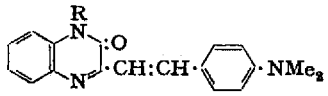
Of styryl bases with unusual nuclei, having nitrogen as the one hetero-atom, LXV (R=NMe_2) was prepared at a very early date by heating 9-methylacridine and the aldehyde with zinc chloride; analogues with a *m*- or *p*-NH_2, or *p*-NO_2, were also made.[153] The base, LXV (R=NMe_2), was again prepared later, also LXV (R=NH_2 or NO_2), and analogues with a *m*-NHAc or *m*-NO_2 group.[31]

Of styryl bases having a nucleus with two nitrogen atoms as the only hetero-atoms, those of type XLI with a 4-oxodihydroquinazoline nucleus were described in 1924,[69] but the corresponding quaternary

salts are unknown. Styryl bases, LXVI (R=Me or Ph), with a 3-oxodihydroquinoxaline nucleus were prepared by heating the appropriate 2-methyldihydroquinoxalone with *p*-dimethylaminobenzaldehyde in acetic anhydride (cf. section 1-M.2); with acid or with methyl sulphate they gave intensely coloured solutions.[37] When 2-methylindolo(3',2'-3,4)quinoline methotoluene-*p*-sulphonate and *p*-dimethylaminobenzaldehyde were subjected to prolonged boiling with piperidine in meth-

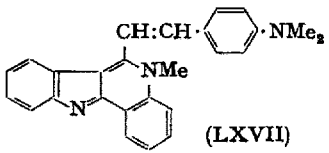


(LXV)

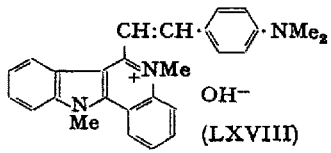


(LXVI)

anol, a procedure resembling that used for preparing the dye, XX (R=Me) (see section 1-M.2), from the 2,1-dimethyl salt, the product was a base. This was probably LXVII, formed by loss of acid; alternatively, it might be LXVIII, formed by the union of methanol with LXVII, and that would account for its great stability.[41]

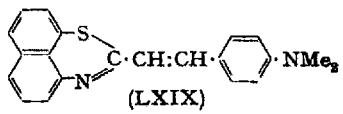


(LXVII)



(LXVIII)

Of nuclei with one nitrogen and one sulphur as hetero-atoms, the perinaphtho-1,3-thiazine nucleus was introduced into styryl bases as well as into salts (cf. section 1-M.5). Thus from 2-methylperinaphtho-1,3-thiazine hydriodide and *p*-dimethylaminobenzaldehyde there resulted the hydriodide of LXIX, said to have its absorption maximum at



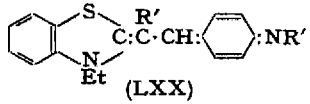
(LXIX)

4500 Å and to sensitise weakly.[45] The hydriodide was later prepared in 38% yield by boiling the reactants in ethanol for 5 minutes; its principal absorption maximum lay at 5430 Å, with a weaker one at 5100 Å, whilst the base, LXIX, had its absorption maximum at 4170 Å.[139]

(3) *Bases with Substituents on the Chain*

In the 4-linked quinoline series, XLII (R=CN) was prepared by heating 4-quinolylacetonitrile with *p*-dimethylaminobenzaldehyde in acetic anhydride.[72] The base, XLII ($R=CO_2Et$), was similarly prepared from ethyl 4-quinolylacetate.[56]

In the benzothiazole series, the 1-cyano-4-*p*-dimethylaminophenyl-1,3-butadienyl base, XLIII ($n=1$, Y=S, R=CN), was prepared from 2-benzothiazolylacetonitrile, *p*-dimethylaminocinnamaldehyde, and piperidine in ethanol.[72] 2-Benzoylmethylbenzothiazole was condensed with *p*-dimethylaminobenzaldehyde in acetic anhydride to give the chain-substituted styryl base, XLIII ($n=0$, Y=S, R=COPh); that and the corresponding bases having as α-substituent CO_2Et, $COCO_2Et$, CO_2CH_2Ph, CSNHPh, or CONHPh were weak sensitisers. The last of them was converted into methiodide (see section 1-P);[56] absorption maxima were quoted for that base and for analogues having an α-CO_2Et or α-$CONH\cdot N:CH\cdot C_6H_4\cdot NMe_2$ group.[57] Each of the three *p*-dimethylaminostyryl salts, XXXVII (R=Et, R′=Me or Et, R^1=Me, R^2=H, X=I; and R=Et, R′=Me, $R^1=p$-$C_6H_4NO_2$, R^2=H, X=I), (see section 1-P), was accompanied by a basic by-product: analyses indicated that the three bases were, respectively, the imines, LXX (R′=H or Et, R^1=Me; and R′=H, $R^1=p$-$C_6H_4NO_2$), each of which had a sharp absorption maximum, due to the chain of conjugated double bonds.[65]

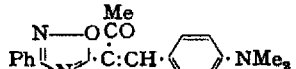


(LXX)

A chain-substituted styryl base, LXXI, with a benzimidazole nucleus had its absorption maximum at 4300 Å, and quaternary salt formation caused a bathochromic shift of 100 Å.[73]



(LXXI)



(LXXII)

In the 1,2,4-oxadiazole series, the chain-substituted base, LXXII, was described.[56]

R. Bis-(*p*-dialkylaminostyryl) Salts and a Higher Vinylene Analogue

In the pyridine series, heating 2,6-dimethylpyridine alkiodide (1 mol.) and *p*-dialkylaminobenzaldehyde (2 mols.) with piperidine in ethanol gave the bis-styryl salts, XLIV (n=0, R=Et, R′=Me;[29,74] n=0, R=R′=Me;[29,155] n=0, R=R′=Et;[74] and n=0, R=Me, R′=Et).[155] The *p*-dimethylamino-compounds melted at a higher temperature than the *p*-diethylamino-compounds and were more resistant to decolorisation by acids.[155] By use of 2,4,6-trimethylpyridine ethiodide, the 4-methyl derivative of XLIV (n=0, R=Et, R′=Me) was obtained[74] but subsequently tri-(*p*-dialkylaminostyryl) salts were prepared from 2,4,6-trimethylpyridine methiodide and ethiodide.[155] A bis-styryl salt was also prepared from 2,6-dimethylpyridine methomethylsulphate and *m*-nitrobenzaldehyde.[74] By boiling *p*-dimethylaminobenzaldehyde and 2,4-dimethylpyridine methiodide with piperidine in methanol for 21 hours, the bis-styryl salt, XLV, was prepared.[15] By condensing 2,6-dimethylpyridine ethiodide with *p*-dimethylaminocinnamaldehyde, a higher vinylene analogue, XLIV (n=1, R=Et, R′=Me), of a bis-styryl salt was prepared.[74]

In the quinoline series, a bis-(*p*-dimethylamino)styryl salt, prepared from 2,4-dimethylquinoline ethiodide, was compared with the corresponding dianil (See section 2).[12]

By boiling bis-[5-(3-benzyl-2-methylbenzoxazolium)] dibromide with *p*-dimethylaminobenzaldehyde in acetic anhydride, the salt, XLVI, was obtained.[75]

Polymeric *p*-dimethylaminostyryl compounds, in which individual dye units were linked through their nitrogen atoms by a chain $(CH_2)_n$ were patented (see XV-7).

TABLE I. Some Properties of *p*-Dimethylaminostyryl Salts

(1) *Ethiodides with Unsubstituted Chain*

Nature of nucleus	Formula	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å) in MeOH		$\varepsilon_{max.}$ × 10^{-4}	Sensitising (Å) Maximum	Extent	Ref.
2-quinoline	I (n=0, Y=CH:CH)	blue prisms	249[a]	5300		5.6	6300	6750	3, 12, 13, 156
4-quinoline	II	almost black	124[a]	5500		—	6500	6800	12, 13
benzoxazole	I (n=0, Y=O)	red and blue	248–249	5000		—	5500	6200	4, 12
benzothiazole	I (n=0, Y=S)	purple	255–257	5250		7.9	5650	7050	12, 65
benzoselenazole	I (n=0, Y=Se)	dark needles	250–253	5410[b]		—	—	—	19
indolenine	I (n=0, Y=CMe_2)	green and gold	222	5450		—	6000[c]	6500	12, 13
benzimidazole	I (n=0, Y=NEt)	orange needles	245–247	4140[b]		—	5300[d]	—	13, 19
2-pyridine	III (n=0)	red prisms[e]	275[a,c]	4700	—	—	5550	6500	4, 12
4-pyridine	LVII (n=0, R′=Me)	red plates	257–259	4830[b]		—	6300[c]	—	13, 19
thiazole	LVIII (n=0, R′=Me, R^1=R^2=H)	red	142–145	4830[b]		—	5700[c]	—	13, 19
thiazoline	LX (n=0, Y=S)	orange	219–220	4775		—	5300[c]	5870[e]	131, 132
pyrroline	LX (n=0, Y=CH_2)	red[f]	203[f]	—		—	5060[f]	5450[f]	134

(2) *Benzothiazolium Salts with Substituents on the Chain,* (Formula XXXVII; R=Et)

R^1	Nature of salt R^2	X	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å) in MeOH	Hypsochromic shift (Å) on substitution	$\varepsilon_{max.} \times 10^{-4}$	Sensitising (Å) Maximum	Extent	Ref.
OPh	H	ClO_4	dark red	254–256	—	—	—	—	—	58
OEt	H	ClO_4	dark blue	157–158	—	—	—	—	—	58
OAc	H	I	violet needles	184[a]	4980	270	—	—	—	59
Me	H	ClO_4	—	234	4810[g]	440	6.2	—	—	61
Me	H	I	dark blue	197	4600	650	2.1	5300, 5700	6300	65
Et	H	ClO_4	not isolated pure	—	4820[g]	430	—	—	—	61
Ph	H	ClO_4	cherry red	172	5080[g]	170	2.5	—	—	61
Ph	H	I	red	180	4910	340	2.5	5800	6800	65
p-$C_6H_4NO_2$	H	I	terracotta	203	4820	430	2.8	desensitiser		65
CO_2Et	H	I	orange	199	4180	1070	2.5	5250	5600	65
2-Benzothiazolyl	H	I	red	210	4380	870	3.3	5200	5600	65
H	Me	ClO_4	red	203	5180[g]	70	2.1	—	—	61

[a] Decomp. not recorded. [b] In nitromethane. [c] Data for methiodide. [d] Value for *N*Me methiodide.
[e] Nature of *N*-alkyl and halide not specified. [f] Data for perchlorate. [g] Solvent not recorded.

TABLE II. Some Particulars about Styrylpyridine Methiodides

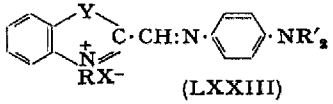
Nature of substituents in benzene ring	M.p. (°C)	% Yield after recrystallisation	Absorption maximum (Å)	Ref.
Series with 2-Linked Pyridine Nucleus				
none	230–231	73	3340[a]	80
p-MeO	242–243	92	3590[a]	80
p-OH	269–270	70	3630[a], 4350[b]	80
o,o'-diMeO	244–245	88	3270[a]	80
p-NMe_2	273–274	97	4440[a], 3230[c]	80
p-NMe_3I	272–273	67	3200[a]	80
m-Br, *p*-NMe_2	232–233	73	3600[a]	80
p-NEt_2	246–247	95	—	80
Series with 4-Linked Pyridine Nucleus				
none	220–221	82	3350[a]	125
p-MeO	214–215	98	3680[a]	125
o-OH	218–219	78	3660[a], 4510[b]	125
m-OH	260–261	90	3430[a], 3450[b]	125
p-OH	265–266	80	3750[a], 4450[b]	125
p-NMe_2	258–259	100	4540[a], 3275[c]	125
p-NEt_2	221–222	100	4710[a], 3310[c]	125

[a] in aqueous solution. [b] in aqueous NaOH. [c] in aqueous HCl.

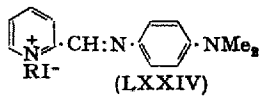
2. Aza Analogues of *p*-Dialkylaminostyryl Heterocyclic Compounds

A. General Survey

The first aza analogues of the styryl salts considered in the foregoing sections were described in 1912, when quinaldine ethiodide was condensed with *p*-nitrosodimethylaniline to give the reddish-violet anil, LXXIII (Y=CH:CH, R=Et, R'=Me, X=I); the red salt, LXXIV

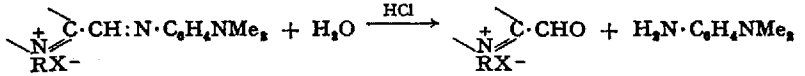


(LXXIII)



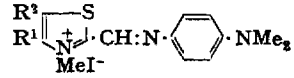
(LXXIV)

(R=Me), of the pyridine class was similarly made. Their molecules were broken down by acid to give the salts of heterocyclic aldehydes, which could be isolated as phenylhydrazones, together with dimethyl-*p*-phenylenediamine (equation 7).[156]



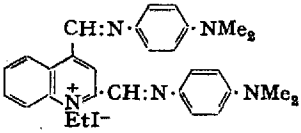
The subsequent hydrolysis of various anils, to liberate salts of heterocyclic aldehydes, which were forthwith condensed with the hydrazones of heterocyclic ketones to yield $\alpha\beta$-diazatrimethincyanines (see XII-5),[157] is interesting.

The preparation of the first *p*-dimethylaminoanil of the thiazole series, LXXV, was described in 1922,[25] and was followed by others in 1923, at which date it was recorded that these anils are useless as dyes



(LXXV)

and, unlike the corresponding styryl salts, decrease the sensitivity of photographic emulsions.[96] As practical desensitisers, for developing in the light, the anils seemed unsafe to use, as they were liable to give rise to decomposition products having a destructive effect on the latent image.[158] In 1930 absorption curves were given for a series of ten anils, all of them desensitisers, and including the dianil, LXXVI; the absorption bands were broader than those of the corresponding *p*-dimethylaminostyryl salts and lay at a longer wavelength by 250–600 Å.[12]

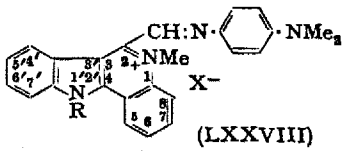


(LXXVI)

Unusual nuclei which were introduced into *p*-dimethylaminostyryl salts (see section 1-M.2), and also into the corresponding anils, were the indolo(3′,2′-3,4)isoquinoline nucleus, in LXXVII,[40] and the indolo(3′,2′-3,4)quinoline nucleus, in LXXVIII[41] (section 2-B.2). Both these salts gave rise to bases (section 2-B.4).

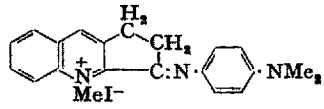


(LXXVII)



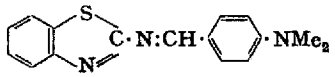
(LXXVIII)

Another anil, LXXIX, is abnormal in that part of the azadimethin chain, which usually links the nuclei, is cyclic, participating in the dihydro-β-quinindene nucleus; that compound is analogous with the *p*-dimethylaminobenzylidene salt, XXXI (section 2-B.3).[152]

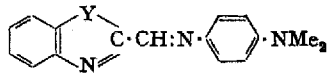


(LXXIX)

It was pointed out in 1935 that *p*-dialkylaminostyryl heterocyclic salts, which are photographic sensitisers, have an odd-numbered carbon chain linking the two nitrogen atoms, whereas the corresponding *p*-dialkylamino anils, which are desensitisers, have an even-numbered carbon chain linking the nitrogen atom of the nucleus to that of the chain. In connection with this generalisation, azadimethin bases were examined, in which the position of nitrogen in the chain was reversed, so that the carbon chain linking the two nitrogen atoms was odd-numbered, and it seemed at that time particularly interesting that bases of type LXXX were sensitisers;[154,159] a quaternary salt was unstable (section 2-C.1).[159] However it was subsequently observed that three out of four bases of type LXXXI, with an even-numbered chain

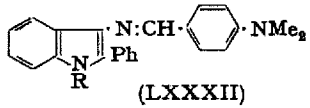


(LXXX)



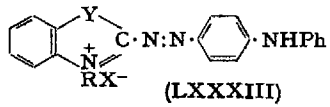
(LXXXI)

(section 2-B.4), are also sensitisers.[160] In 1949 the α-azadimethin bases, LXXXII (R=Et or Ph), were prepared by condensing 3-aminoindoles with *p*-dimethylaminobenzaldehyde.[161]



(LXXXII)

According to a patent of 1954, diazadimethin compounds of type LXXXIII were prepared by coupling diphenylamine with a hetero-



(LXXXIII)

cyclic hydrazone, under the action of an oxidising agent. The colours of the products varied through reddish brown, orange, violet, and blue (see section 2-D).[162]

B. *p*-Dialkylaminoanils of Heterocyclic Aldehyde Quaternary Salts, etc.

(1) Anils of the 2- and 4-Linked Quinoline, Benzothiazole, 2-Linked Pyridine, and Thiazole Series

In the 2-linked quinoline series, quinaldine ethiodide and *p*-nitrosodimethylaniline were boiled together in ethanol, with piperidine as catalyst, to give LXXIII (Y=CH:CH, R=Et, R′=Me). This was broken down by acid (see equation 7).[156] Its absorption maximum lay at 5680 Å and it is remarkable that that of its 5,6-benzo-derivative was at a shorter wavelength by 80 Å; the former substance desensitised more powerfully than the latter.[163] Absorption curves for both were published.[12] In 1926 the antiseptic properties of forty-five anils, mostly methochlorides, and including LXXIII (Y=CH:CH, R=R′=Me, X=Cl), of the 2-linked quinoline series were compared; some had a substituent such as a 7,8-benzo-, 6-amino-, -acylamino-, -dimethylamino-, -bromo-, -chloro-, -methyl, or -nitro-group, and in some the *p*-NMe_2 group was replaced by *p*-NH_2, -NHAc, or -NEt_2.[83] Another twenty-three, examined later, included anils with other substituents in the nuclei, and two with an *o,m*-benzo-group as well as a *p*-NR_2 group, obtained by condensing 2,6-dimethylquinoline methochloride with 1-dialkylamino-4-nitrosonaphthol in the absence of a catalyst.[164] Thirty-seven anils were tested as trypanocidal agents but were in general less effective than the corresponding styryl compounds, though their bactericidal action was powerful.[84] Subsequently six anils of type LXXIII (R=R′=Me, X=Cl), but with a substituted amino-group in the 6-position, proved to have only slight trypanocidal action.[85] Twenty-five of the foregoing anils were tested for desensitising properties, also LXXIII (Y=CH:CH, R=Me or Et, R′=Me or Et, X=I), and the 6-methyl derivatives of LXXIII (Y=CH:CH, R=Me or Et, R′=Me, X=I).[158]

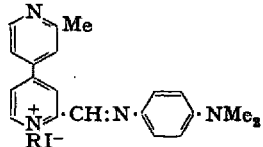
In the 4-linked quinoline series, an analogue of LXXIII (R=Et, R′=Me, X=I) was prepared from 6-methoxylepidine ethiodide.[165] The antiseptic properties of the 6-methyl derivative of the 4-linked analogue of LXXIII (R=R′=Me, X=Cl) were tested, together with those of the dyes of the 2-linked quinoline series.[83] In the 4-linked

quinoline series, the absorption maximum of the anil analogous with LXXIII (R=Et, R′=Me, X=I) lay at 5850 Å.[12] Its desensitising properties were compared with those of the corresponding methiodide.[158]

In the benzothiazole series, the anil, LXXIII (Y=S, R=Et, R′=Me, X=I), had its absorption maximum at 5570 Å, whilst its 4,5- and 6,7-benzo-derivatives absorbed in much the same region, the broadness of the curves making the maxima indefinite.[12] The former derivative was prepared in 24 % yield and the latter in 43 % yield by boiling the appropriate ethiodide and *p*-nitrosodimethylaniline with piperidine in alcohol for 7 hours and recrystallising.[99] The parent anil, LXXIII (Y=S, R=Et, R′=Me, X=I), desensitised strongly but produced chemical fog.[158]

The anil, LXXIII (Y=Se, R=Et, R′=Me, X=Br), was prepared in 26 % yield by boiling 2-methylbenzoselenazole ethobromide and *p*-nitrosodimethylaniline with piperidine in ethanol for 3 hours and recrystallising.[166]

Anils, LXXIV (R=Me or Et), of the 2-linked pyridine type were prepared by heating 2-picoline alkiodide and *p*-nitrosodimethylaniline with piperidine in ethanol. The aldehydes liberated by hydrochloric acid could not be isolated but could be converted into phenylhydrazones.[156] The absorption maximum of LXXIV (R=Et) lay at 5000 Å.[12] Both of the salts, LXXIV (R=Me or Et), desensitised.[158] From 2,2′-dimethyl-4,4′-bipyridine alkiodide there were prepared the anils, LXXXIV (R=Me or Et), both of which were desensitisers.[123] They are analogous with certain styryl salts (see section 1-I).



(LXXXIV)

In the thiazole group, the anil, LXXV (R^1=Ph, R^2=H), was described in 1922.[25] In the following year there were added LXXV (R^1=Me, R^2=Ph; and R^1=Ph, R^2=Me or Ph).[96] The absorption curve of LXXV (R=Et, R^1=Me, R^2=H) was published.[12]

(2) *Anils with Unusual Nuclei*

1-Methyl-1′-phenylindolo(3′,2′-3,4)isoquinoline methiodide on heating with *p*-nitrosodimethylaniline, in ethanol containing a trace of

piperidine, for 10 hours gave LXXVII, which was extracted with acetone, leaving a basic by-product undissolved (see section 2-B.4).[40] Similarly 2-methylindolo(3',2'-3,4)quinoline methotoluene-*p*-sulphonate gave the crimson salt, LXXVIII (R=H, X=$SO_3 \cdot C_7H_7$), which was a desensitiser but, on repeating with excess of piperidine, the product was a base (see section 2-B.4). From 1',2-dimethylindolo(3',2'-3,4)quinoline methotoluene-*p*-sulphonate and *p*-nitrosodimethylaniline, the sole product was LXXVIII (R=Me, X=$SO_3 \cdot C_7H_7$), in 62 % yield.[41]

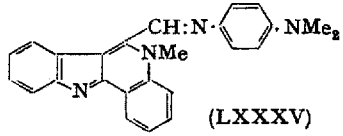
(3) *Anil in which Part of the Azadimethin Chain is Cyclic*

The anil, LXXIX, was prepared by boiling dihydro-*β*-quinindene methiodide and *p*-nitrosodimethylaniline with piperidine in ethanol for 10 minutes. It was so unstable that it was decomposed even on heating its alcoholic solution.[152]

(4) *Anil Bases, Including Those with Substituents on the Chain*

The base, LXXXI (Y=CH:CH), with a 2-linked quinoline nucleus was prepared by melting together 2-formylquinoline and dimethyl-*p*-phenylenediamine at 100°; the *p*-diethylamino-base was also made.[167] The yield of the former, on heating the reactants at 115–120° for 5 minutes, and recrystallising the product from methanol, was 64 %. The 4-linked quinoline analogue was similarly prepared.[160,168] The bases, LXXXI (Y=S or Se), were prepared from 2-formyl-benzothiazole[160,168] or -benzoselenazole[160] and dimethyl-*p*-phenylenediamine and both were strong sensitisers. Bases without the dimethylamino-group were also described.[160]

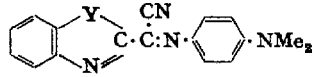
The basic by-product accompanying LXXVII was recrystallised from ethanol and it proved to be the base formed by elimination of methyl iodide.[40] The base of the indolo(3',2'-3,4)quinoline series gave no sign of an :NH band in the 2.9 μ region and was therefore regarded



(LXXXV)

as LXXXV, a conclusion which was confirmed by its readily combining with toluene-*p*-sulphonic acid to give LXXVIII (R=H, X=$SO_3 \cdot C_7H_7$).[41]

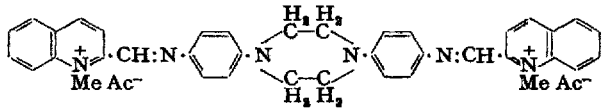
2-Cyanomethylbenzothiazole condensed with *p*-nitrosodimethylaniline to give the chain-substituted anil base, LXXXVI (Y=S), although 2-methylbenzothiazole did not condense thus. Similarly 2-cyanomethylbenzimidazole condensed to give LXXXVI (Y=NH).[73]



(LXXXVI)

(5) *Bis*-(p-*dimethylaminoanils*)

Only one bis-(*p*-dimethylaminoanil) has been described, LXXVI,[12] though another type of dianil was prepared earlier, *viz.*, the 6,6′-dimethyl- and 5,6,5′,6′-dibenzo-derivatives of LXXXVII, which were prepared through di(nitrosophenyl)piperazine.[164]



(LXXXVII)

C. α-Aza-*p*-dimethylaminostyryl Heterocyclic Bases

(1) *Bases of the Benzothiazole and Thiazole Series*

The base, LXXX, m.p. 188°, was prepared by heating 2-aminobenzothiazole with *p*-dimethylaminobenzaldehyde at 140° for 1 hour. Although the product added on ethyl iodide, the resultant salt was very unstable. The 6-ethoxy- and 4,5- and 6,7-benzo-derivatives of the base were also prepared. An analogue was made from 2-methylthiazole.[159]

(2) *Bases with a 3-Linked Indole Nucleus*

By heating 3-amino-1-ethyl-2-phenylindole and *p*-dimethylaminobenzaldehyde at 150–160° for 8 hours, and treating the product with ethanol, there resulted the base, LXXXII (R=Et). The analogue, LXXXII (R=Ph), was similarly made, also two corresponding bases by use of benzaldehyde.[161]

D. Diaza-*p*-anilinostyryl Heterocyclic Salts

The 4,5,6,7-tetrahydro-derivative of the diaza-compound, LXXXIII (Y=S, R=Me, X=Cl), was obtained by adding aqueous ferric chloride to a methanolic solution containing diphenylamine, hydrochloric acid, and the hydrazone hydrochloride of *N*-methyl-4,5,6,7-tetrahydrobenzothiazolone; the dye was isolated from the deep blue solution by adding water and sodium chloride. The shades given by dyes, of series such as LXXXIII (Y=CH:CH, S, Se, or NMe, X=Cl), were tabulated, also those of a 5-nitro-dye of the 2-linked pyridine series, four compounds of the 4-linked quinoline, and twelve of the 4-linked pyridine series, with various substituents in the heterocyclic nucleus.[162]

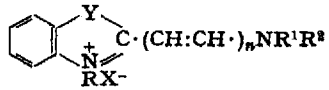
3. Hemicyanines: Heterocyclic Quaternary Salts Having the Group $\cdot(CH{:}CH\cdot)_nNR^1R^2$

A. General Survey

The name hemicyanine was applied in 1939 to quaternary heterocyclic salts, in which the nitrogen atom of the ring was linked by an odd-numbered carbon chain to a substituted amino-group: i.e., the salts had an α- or γ-$\cdot(CH{:}CH\cdot)_nNR^1R^2$ group. Those with a dimethin-chain were designated hemicarbocyanines, whilst higher vinylene homologues with a tetra- or hexa-methin chain were called hemidi- and hemitri-carbocyanines, respectively.[169] These terms referred to the use of salts, such as $\cdot(CH{:}CH\cdot)_nNAcPh$ or $\cdot(CH{:}CH\cdot)_nNHPh$ (where n=1–3) as intermediates in the preparation of carbocyanines[170] (see V-6), dicarbocyanines[171,172] (see VII-1), and tricarbocyanines[173,174] (see VIII-2), respectively. An extension of the term to *p*-dimethylamino-styryl salts[67] can be justified by regarding them as hemicyanines in which part of the polymethin chain is cyclic, but they have already been considered separately (section 1). Applications of the salts $\cdot(CH{:}CH\cdot)_nNR^1R^2$ have already been dealt with, so that only some additional aspects will be mentioned here.

It was noted in 1937 that deeply coloured hexamethin quaternary salts with the group $\cdot(CH{:}CH\cdot)_3NR^1R^2$ could be obtained from others, with the group $\cdot(CH{:}CH\cdot)_3NAcPh$ by reaction with a primary amine, such as aniline, or a secondary one, such as dimethylamine or piperidine, and it was proposed as a colour test for the identification of amines.[175]

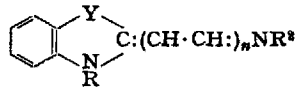
The salts, LXXXVIII (n=3, Y=CH:CH, S, or Se, R=Et, R^1=Ac, R^2=Ph, X=I), were applied in detecting the presence of primary or secondary amines in commercial samples of tertiary amines; for detecting aniline, the most sensitive salt was the corresponding



(LXXXVIII)

methiodide of the 3,3-dimethylindolenine series.[176] The general method of preparing salts by the action of primary or secondary non-aromatic amines on quaternary heterocyclic salts, having an α- or γ- ·(CH:CH·)$_n$NAcPh group (where n=1–3) was patented and the sensitising properties of the products were stressed.[169] Salts with a substituted anilino-group were also patented as sensitisers; it was possible to replace, not only an acetanilido-, but also an anilino-group, by means of a strongly basic amine (see section 3-D).[177] Tetramethin salts with an anilino-group were conveniently prepared by condensing a salt having a 4-ethoxy-1,3-butadienyl group[178] with aniline.[179]

In the benzothiazole series, the absorption maxima of methanolic solutions of six salts, LXXXVIII (n=1, 2, or 3, Y=S, R=Et, R^1=H or Ac, R^2=Ph, X=I), were compared. The shift on passing from an anilino-salt to its next higher vinylene analogue was about 1000 Å. With the acetanilido-salts, the shifts were less and diminished as the series was ascended: here the marked difference in basicity of the two nitrogen atoms caused the two extreme resonance configurations to differ widely in stability. By treating the anilino-salts, LXXXVIII (n=0, 1, 2, or 3, Y=S, R=Et, R^1=H, R^2=Ph, X=I), with alkali, four bases, LXXXIX (n=0, 1, 2, or 3, Y=S, R=Et, R^2=Ph), were

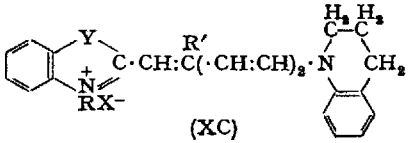


(LXXXIX)

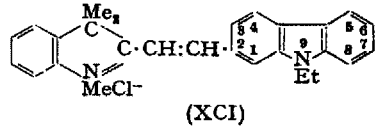
prepared (section 3-F) and absorption curves were given. From the bases, by use of methyl toluene-p-sulphonate, followed by iodide, four methylanilino-salts, LXXXVIII (n=0, 1, 2, or 3, Y=S, R=Et,

R^1=Me, R^2=Ph, X=I), were made: they absorbed at a wavelength shorter by about 135 Å than the anilino-salts. Absorption data were also given for four salts, LXXXVIII (n=0, 1, 2, or 3, Y=S, R=Et, R^1R^2=C_5H_{10}, X=I), with a piperidine group.[180] Absorption maxima of two salts of the quinoline series, LXXXVIII (n=2, Y=CH:CH, R=Me, R^1=H or Me, R^2=Ph, X=I), were compared with those of the related pairs of symmetrical dyes.[17,180]

A chain-substituted hemicyanine with the group ·CH:CR′·NHAr was formulated in 1932 as a probable intermediate stage in the production of a *meso*-alkylcarbocyanine by heating an arylthioimide with a quaternary salt having a reactive methyl group (see VI-5).[181] Ten years later, chain-substituted salts of this kind were prepared by reaction of a primary or secondary aromatic amine with a salt having a β-halogenovinyl group.[182] The preparation of certain β-substituted hexamethin salts of type XC was accomplished by reaction of a quaternary salt having a ·CH:CR′·Me group with β-*N*-(1,2,3,4-tetrahydroquinolyl)-acraldehyde (section 3-E).[183]



(XC)

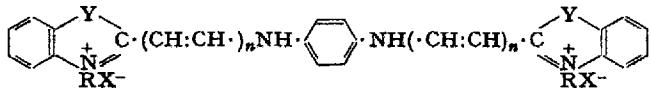


(XCI)

The salt, XCI, was prepared by condensing *N*-ethylcarbazole-3-aldehyde with 1,3,3-trimethyl-2-methyleneindoline by heating with phosphorus oxychloride in a solvent.[184] It may be regarded as a hemicyanine, in which part of the odd-numbered polymethin chain linking the nitrogen atoms is cyclic.

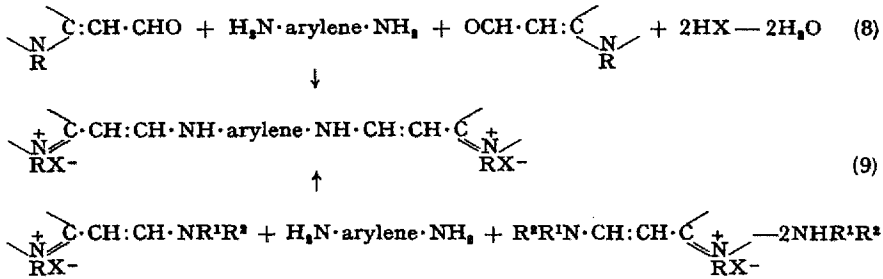
Hemicyanines having a group ·$(CH:CH·)_nNHR^2$ could be converted into bases, e.g. of type LXXXIX, by removal of acid, and this was preferably effected by treatment with alkali hydroxide in the presence of a diluent which dissolved the base but not the salt.[185] Its application to a benzothiazolium salt in which the NHR^2 group was directly linked to the nucleus, as well as to others with a di-, tetra-, or hexa-methin chain, has already been mentioned.[180] Some of the bases had sensitising properties.[185] Purification of crude anilinobutadienyl salts was conveniently accomplished by converting them into bases, and then reconverting to salts, and these pure salts further afforded a source of pure acetanilidobutadienyl salts.[179]

Double hemicyanines, such as XCII ($n=1$), were described in 1935 as sensitisers[188] and were prepared by condensing a diamine, in the presence of acid, with two mols. of a heterocyclic *N*-alkyl-2-formyl-

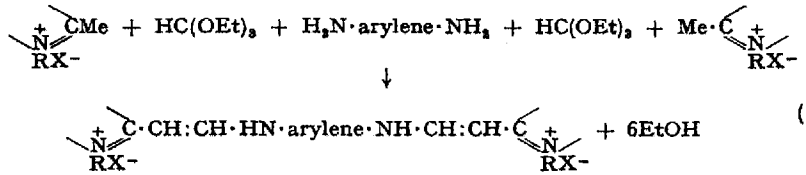


(XCII)

methylene base (equation 8).[187] An alternative route consisted in reaction of a diamine with two mols. of a quaternary salt having a ·CH:CH·NR¹R²group (equation 9),[188] though the product prepared by use of pyridine was formulated as, e.g., XCII ($n=1$) minus HX, as



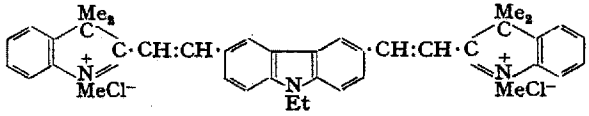
also was an analogue of type XCII ($n=0$), prepared by reaction of a diamine with a quaternary salt having an alkylthio-group.[188] Double hemicyanines were said to be particularly valuable sensitisers when they had as substituent a CO_2H or SO_3H group.[189] Besides the two preceding methods of synthesising double hemicyanines, two others were used later. One of them consisted in condensing two mols. of a quaternary salt, having a reactive methyl group, with two of ethyl orthoformate and one of a diamine (equation 10).[190]



The fourth method was a modification of the second, in that excess of diamine was condensed with a quaternary salt, having the

group ·CH:CH·NAcPh, to give an intermediate salt with the group ·CH:CH·NH·arylene·NH_2, and that could subsequently be condensed with another molecule of quaternary salt having a reactive group.[190] Double hemicyanines with two pyrroline nuclei were prepared by the first two methods and also by a modification of the first (equation 8), in which the formylmethylene compound was replaced by its anil.[191]

The double hemicyanine, XCIII, was prepared by condensing *N*-ethylcarbazole-3,6-dialdehyde with 1,3,3-trimethyl-2-methyleneindoline by heating with phosphorus oxychloride and a diluent.[184] In this trinuclear salt, as in XCI, part of the polymethin chain is cyclic.



(XCIII)

Quaternary heterocyclic salts, having a reactive ·CH:CR(SR') group, were condensed with *p*-phenylenediamine to give intermediate salts with the chain ·CH:CR·NH·C_6H_4·NH_2, whence unsymmetrical double hemicyanines with one or two alkyl groups on the chain were prepared (section 3-G.7).[192]

Bases prepared by removal of two mols. of acid from one mol. of double hemicyanine were photographic sensitisers (section 3-G.8).[193]

Some properties of some hemicyanines are given in Table III.

B. Salts of the 2- and 4-Linked Quinoline Series

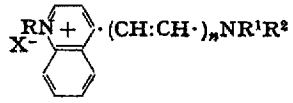
In the 2-linked quinoline series, 2-*β*-acetanilidovinylquinoline ethiodide was heated with piperidine in ethanol for 30 minutes, to give LXXXVIII (n=1, Y=CH:CH, R=Et, $R^1R^2=C_5H_{10}$, X=I), which gave a yellow alcoholic solution. The analogue with a tetramethin chain was made by use of 2-(4-acetanilido-1,3-butadienyl)-quinoline ethiodide and gave a pinkish orange solution.[169] The tetramethin salt, LXXXVIII (n=2, Y=CH:CH, R=Et, R^1=H, R^2=Ph, X=I), was prepared in 9 % yield by heating the acetanilido-salt with aniline in ethanol, and recrystallising the product twice from methanol,[180] and similarly for the methiodide: the latter was converted into base (section 3-F) and that, by use of methyl toluene-*p*-sulphonate, into the methylanilino-salt, LXXXVIII (n=2, Y=CH:CH, R=Et, R^1=

TABLE III. Properties of Some Hemicyanines (Formula LXXXVIII; R=Et, X=I)

Nature of substance	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å) of MeOH solution, or colour	Sensitising (Å) Maximum	Extent	Ref.
$n=0$, Y=S, R^1=H, R^2=Ph	cream coloured	197–198	2985	—	—	180
$n=1$, Y=S, R^1=H, R^2=Ph	brownish needles; blue reflex	265–266	4140	5400, 6200	6700	177, 180
$n=1$, Y=S, R^1=Ac, R^2=Ph	almost colourless	231–233	3640	—		180
$n=2$, Y=O, $R^1R^2=C_5H_{10}$	yellow	192–195	yellow	4700	5100	169
$n=2$, Y=S, R^1=H, R^2=o-C_6H_4Me	reddish; blue reflex	212–214	—	5400	6100	177
$n=2$, Y=S, R^1=Ac, R^2=Ph	brownish	233–234	4260	—	—	180
$n=2$, Y=S, $R^1=R^2$=Et	reddish needles	209–211	deep yellow	4650, 5200	5800	169
$n=2$, Y=S, $R^1R^2=C_4H_8O$	reddish	248–251	deep yellow	4700, 5200	5900	169
$n=2$, Y=Se, R^1=H, R^2=Ph	dark needles; green reflex	225–226	—	5600	6200	177
$n=2$, Y=Se, $R^1R^2=C_5H_{10}$	reddish	120–122	deep yellow	4700, 5200	5900	169
$n=2$, Y=CH:CH, $R^1R^2=C_5H_{10}$	reddish	237–239	pinkish orange	5400	6100	169
$n=3$, Y=S, R^1=H, R^2=Ph	dark needles; greenish bronze reflex	161–163	6125	6600	6900	177, 180
$n=3$, Y=S, R^1=Ac, R^2=Ph	reddish brown	203–205	4610	—	—	180
$n=3$, Y=S, $R^1R^2=C_5H_{10}$	dark blue	120·5–123·5	purple	6100	6600	169

Me, R^2=Ph, X=I).[17] By reaction of quinaldine ethiodide with β-ethoxyacraldehyde diethyl acetal in acetic acid,[178] and heating the crude 2-(4-ethoxy-1,3-butadienyl)quinoline ethiodide with aniline, it was obtained in 36% yield.[179] Of hexamethin salts, 2-(6-acetanilido-1,3,5-hexatrienyl)quinoline ethiodide was used to detect the presence of primary or secondary amines in tertiary amines.[176]

In the 4-linked quinoline series, 4-(4-acetanilido-1,3-butadienyl)-quinoline ethiodide was heated with piperidine in ethanol to form XCIV (n=2, R=Et, $R^1R^2=C_5H_{10}$, X=I), which gave a bluish-red alcoholic solution.[169] A 21% yield of XCIV (n=2, R=Et, R^1=H,



(XCIV)

R^2=Ph, X=I) was prepared by reaction of lepidine ethiodide with β-ethoxyacraldehyde diethyl acetal in acetic acid,[178] heating the resultant salt with aniline in ethanol, and recrystallising from methanol.[179]

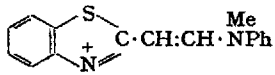
C. Salts of the Indolenine Series

A pure specimen of the tetramethin salt, LXXXVIII (n=2, Y=CMe_2, R=Me, R^1=H, R^2=Ph, X=ClO_4), was prepared by condensing 2,3,3-trimethylindolenine methiodide with β-anilinoacraldehyde anil hydrochloride by boiling in pyridine, converting the corresponding salt into base, acidifying, and treating with aqueous sodium perchlorate solution.[179] For detecting the presence of primary or secondary amines in samples of tertiary amines, the hexamethin salt, LXXXVIII (n=3, Y=CMe_2, R=Me, R^1=Ac, R^2=Ph, X=I), was more sensitive than analogues with other heterocyclic nuclei.[176]

D. Salts of the Benzothiazole, Benzoxazole, and Benzoselenazole Series

In the benzothiazole series, the salt, LXXXVIII (n=0, Y=S, R=Et, R^1=H, R^2=Ph, X=I), with the nuclei directly linked, was prepared in 3% yield by heating 2-phenylthiobenzothiazole ethiodide with aniline in ethanol, and recrystallising repeatedly from ethanol, but in 43% yield by heating 2-anilinobenzothiazole with excess of ethyl iodide at 100° for 44 hours. The base prepared from this salt

(section 3-F) was heated with methyl toluene-*p*-sulphonate at 100° for 24 hours and converted into the colourless perchlorate, LXXXVIII (n=0, Y=S, R=Et, R^1=Me, R^2=Ph, X=ClO_4), which resulted in 62% yield after two recrystallisations.[180] The dimethin salt, LXXXVIII (n=1, Y=S, R=Et, R^1=H, R^2=Ph, X=I), was prepared in 54% yield by heating the acetanilidovinyl salt with aniline in ethanol, precipitating with ether, and recrystallising from methanol.[177,180] The base prepared from this salt (section 3-F) was heated with methyl toluene-*p*-sulphonate at 100° for 2 hours, and sodium iodide was used to precipitate the yellow LXXXVIII (n=1, Y=S, R=Et, R^1=Me, R^2=Ph, X=I) in 70% yield.[180] The acetanilido-salt on heating with piperidine or morpholine in ethanol gave LXXXVIII (n=1, Y=S, R=Et, R^1R^2=C_5H_{10} or $C_4H_{10}O$, X=I), and the 4,5-benzo-derivative of the former was also made: all gave yellow solutions.[169] A patent on betaine cyanine dyes included a hemicyanine, XCV, which was prepared by reaction of 2-methylbenzothiazole *N*-(sulphobutyl)betaine with methyldiphenylformamidine.[102]



(XCV)

In the benzothiazole group, the tetramethin iodide, LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=Ph, X=I), was prepared in 34% yield from the acetanilido-salt and aniline and was converted into the base (section 3-F),[180] through which a pure specimen of perchlorate was prepared.[179] The base was also converted, in 60% yield, into LXXXVIII (n=2, Y=S, R=Et, R^1=Me, R^2=Ph, X=ClO_4).[180] The product obtained by reaction of β-ethoxyacraldehyde diethyl acetal in acetic acid[178] on 2-methyl-6,7-benzobenzothiazole ethiodide was converted by aniline into the 6,7-benzo-derivative of LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=Ph, X=I)[179]. Reaction of 4-acetanilido-1,3-butadienylbenzothiazole ethiodide with n-butylamine gave LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=n-C_4H_9, X=I). Its reaction with the secondary amines, diethylamine, diethanolamine, diallylamine, di-n-butylamine, dibenzylamine, or di-(tetrahydrofurfuryl)amine, gave the six tetramethin salts, LXXXVIII (n=2, Y=S, R=Et, R^1=R^2=Et, CH_2CH_2OH, $\cdot CH_2\cdot CH{:}CH_2$, n-$C_4H_9$, $\cdot CH_2Ph$, or C_5H_9O, X=I, but

for the last X=ClO_4); 4,5-benzo-derivatives of the first and last, both as iodides, were also made. Use of the cyclic amines, piperidine, morpholine, and 6-methoxy-1,2,3,4-tetrahydroquinoline, gave LXXXVIII (n=2, Y=S, R=Et, R^1R^2=C_5H_{10}, C_4H_8O, or $C_{10}H_{12}O$, X=I); the 4,5-benzo-derivative of the first was obtained similarly.[169] Salts with a substituted anilino-group, LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=o-C_6H_4Me, o-$C_6H_4NO_2$, o-C_6H_4OEt, p-C_6H_4Cl, or p-C_6H_4OMe, X=I), were prepared by heating 4-acetanilido-1,3-butadienylbenzothiazole ethiodide, usually for 20–30 minutes, with 1¼–2 mols. of the appropriate amine. By means of β-naphthylamine, 2-amino-α-naphthathiazole, and p-aminoazobenzene, there were prepared LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=β-$C_{10}H_7$, $C_{11}H_6NS$, or p-C_6H_4N:NPh, X=I). Moreover the anilino-group of 4-anilino-1,3-butadienylbenzothiazole ethiodide was replaced on heating the salt with p-aminodiethylaniline in ethanol, to give LXXXVIII (n=2, Y=S, R=Et, R^1=H, R^2=p-$C_6H_4NEt_2$, X=I).[177]

The hexatrienylacetanilido-salt, LXXXVIII (n=3, Y=S, R=Et, R^1=Ac, R^2=Ph, X=I), was converted by aniline into the anilino-salt, LXXXVIII (n=3, Y=S, R=Et, R^1=H, R^2=Ph, X=I),[175,177,180] and that into base (section 3-F), whence the methylanilino-salt, LXXXVIII (n=3, Y=S, R=Et, R^1=Me, R^2=Ph, X=I), resulted in 19% yield by heating with 2 mols. of methyl toluene-p-sulphonate, conversion into iodide, and recrystallisation from methanol.[180] This methylanilino-salt was later synthesised from 2-methylbenzothiazole ethiodide by two different methods. One consisted in heating the ethiodide in pyridine with 1-methylanilino-1,3-butadienyl-4-aldehyde (H_2O eliminated), the other in heating it with 1-anilo-5-piperidino-2,4-pentadienyl methochloride ($C_5H_{11}N$,HCl eliminated).[194] On heating the acetanilido-compound with piperidine[169,180] or morpholine,[169] it gave the hexamethin salts, LXXXVIII (n=3, Y=S, R=Et, R^1R^2=C_5H_{10} or C_4H_8O, X=I), which gave purple alcoholic solutions. The piperidine salt was later prepared by the action of piperidine hydrochloride, followed by iodide, on 3-ethyl-2-(5-formyl-2,4-pentadienyl)benzothiazoline, which was prepared from the acetanilido-salt by means of potassium carbonate.[194] Reaction of the formyl compound with the calcium chloride double salt of streptomycin gave a purple colour, and tryptophan also gave purple, whilst m-hydroxyaniline gave a blue colour in methanol.[195]

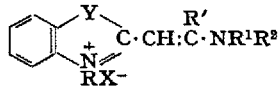
In the benzoxazole series, the colourless dimethin salt, LXXXVIII (n=1, Y=O, R=Et, R^1R^2=C_4H_8O, X=I), was prepared by heating

2-β-acetanilidovinylbenzoxazole ethiodide with morpholine in ethanol for 30 minutes. The yellow tetramethin salt, LXXXVIII (n=2, Y=O, R=Et, $R^1R^2=C_5H_{10}$, X=I), was prepared from 4-acetanilido-1,3-butadienylbenzoxazole ethiodide and piperidine in ethanol.[169] Similarly aniline gave LXXXVIII (n=2, Y=O, R=Et, R^1=H, R^2=Ph, X=I) and the 6,7-benzo-derivative of this was also made.[177]

In the benzoselenazole series, the tetramethin salts, LXXXVIII (n=2, Y=Se, R=R^1=R^2=Et, X=I) and LXXXVIII (n=2, Y=Se, R=Et, R^1=H, R^2=Ph, X=I), were prepared by heating the corresponding acetanilido-salt in ethanol with diethylamine[169] or with aniline.[177] Similarly the hexamethin salts, LXXXVIII (n=3, Y=Se, R=Et, R^1=R^2=Me, or $R^1R^2=C_5H_{10}$, X=I), were prepared by reaction of dimethylamine or piperidine with the corresponding acetanilido-salt,[175] and this was a useful means of detecting the presence of primary or secondary amines in tertiary amines.[176]

E. Salts with Substituents on the Chain

On heating 2-methylbenzothiazole methiodide with ethyl isopropionanilide, formation of a methiodide with the group ·CH:CEt·NHPh was postulated, as an intermediate giving a *meso*-ethylthiacarbocyanine.[181] Reaction of 2-(β-chloropropenyl)benzothiazole ethochloride[196] with aniline in ethanol, followed by potassium iodide, gave XCVI (Y=S, R=Et, R'=Me, R^1=H, R^2=Ph, X=I). Its 4,5-benzoderivative was similarly made, also the *p*-chloro-, *p*-methoxy-, and *p*-methyl derivatives



(XCVI)

of that, and the 4,5-benzo-derivative of XCVI (Y=S, R=Et, R'=Me, $R^1R^2=C_5H_{10}$, X=I): these benzo-derivatives sensitised.[182] The preparation of β-substituted hexamethin salts, XC (Y=S, R'=alkyl, alkoxy, or alkylthio), was effected by heating a benzothiazolium salt, having a ·CH:CMeR' group, with β-*N*-(1,2,3,4-tetrahydroquinolyl)acraldehyde in a mixture of pyridine and acetic anhydride below 100° for 2–5 minutes.[183]

Reaction of 2-(β-chlorobutenyl)benzoselenazole ethochloride and

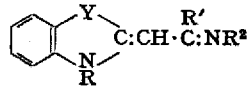
p-chloroaniline in ethanol, followed by iodide, gave the β-substituted dimethin salt, XCVI (Y=Se, R=R′=Et, R^1=H, R^2=*p*-C_6H_4Cl, X=I), which did not sensitise.[182] The preparation of β-substituted hexamethin salts, XC (Y=Se, R′=alkyl, alkoxy, or alkylthio), analogous with those of the benzothiazole series, was claimed.[183]

F. Bases Prepared from Hemicyanines, Including Some with Substituents on the Chain

In the 2-linked quinoline series, the dimethin base, LXXXIX (*n*=1, Y=CH:CH, R=Et, R^2=Ph), was prepared by heating 2-β-anilinovinylquinoline ethiodide with sodium hydroxide in the presence of aqueous acetone, the base being recovered from the acetone and recrystallised.[185] The tetramethin base, LXXXIX (*n*=2, Y=CH:CH, R=Me, R^2=Ph), was prepared in 55 % yield by shaking 2-(4-anilino-1,3-butadienyl)quinoline methiodide with acetone and 10 % sodium hydroxide solution, precipitating from the acetone layer with water, and recrystallising from ligroin.[17]

In the 4-linked quinoline series, a dimethin base was prepared by the action of aqueous sodium hydroxide, in the presence of acetone, on 4-β-anilinovinylquinoline methiodide.[185] 4-(4-Anilinobuta-1,3-dienyl)quinoline ethiodide was converted into the tetramethin base, whence a pure sample of ethoperchlorate was obtained.[179]

In the benzothiazole series, 2-anilo-3-ethylbenzothiazoline, LXXXIX (*n*=0, Y=S, R=Et, R^2=Ph), was prepared by heating 2-anilinobenzothiazole ethiodide with aqueous sodium hydroxide in the presence of acetone, being precipitated from the acetone extract by water, and resulting in 63 % yield after two recrystallisations from petroleum ether. Its dimethin analogue, LXXXIX (*n*=1, Y=S, R=Et, R^2=Ph), was similarly prepared, in 80 % yield after two recrystallisations from ligroin, from 2-β-anilinovinylbenzothiazole ethiodide;[180, 185]



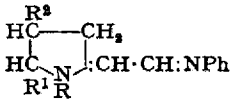
(XCVII)

the 4,5-benzo-derivative of the dimethin base was made, also LXXXIX (*n*=1, Y=S, R=R^2=Ph). The β-substituted dimethin base, XCVII (Y=S, R=Et, R′=Me, R^2=$C_{10}H_7$), was prepared by the action of

alkali in aqueous acetone on [2-(2-β-naphthylamino)]propenylbenzothiazole ethiodide; its 4,5-benzo-derivative was made, also the 4,5-benzo-derivative of XCVII (Y=S, R=Et, R′=Me, R^2=Ph), and the *p*-methoxy and *p*-methyl derivatives of that.[185] The tetramethin base, LXXXIX (*n*=2, Y=S, R=Et, R^2=Ph), was prepared from the anilinobutadienyl salt.[180, 185] It was used for arriving at a pure sample of ethoperchlorate.[179] The hexamethin base, LXXXIX (*n*=3, Y=S, R=Et, R^2=Ph), was likewise prepared from the anilinohexatrienyl salt.[180, 185]

In the benzoselenazole series, the β-ethyldimethin base, XCVII (Y=Se, R=R′=Et, R^2=*p*-C_6H_4Cl), did not sensitise.[185]

In the thiazoline group, a base was prepared by the action of alkali on 2-β-anilinovinylthiazoline methiodide.[185]



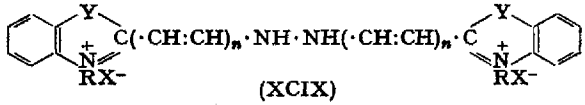
(XCVIII)

In the pyrroline series, the dimethin base, XCVIII (R=R^2=Me, R^1=H), m.p. 93°, was obtained by removal of acid from the corresponding anilinovinylpyrroline methotoluene-*p*-sulphonate, but the corresponding *N*-ethyl base was an oil, as also were XCVIII (R=Me or Et, R^1=Me, R^2=H). The base, XCVIII (R=Et, R^1=H, R^2=Ph), had m.p. 84°, but XCVIII (R=Et, R^1=CH_2Ph, R^2=Ph) was an oil.[135]

G. Double Hemicyanines and Related Bases

(*1*) *Salts of the 2- and 4-Linked Quinoline Series*

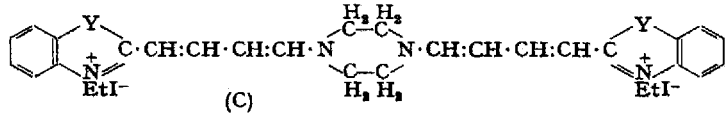
With two 2-linked quinoline nuclei, the scarlet salt, XCIX (*n*=0, Y=CH:CH, R=Et), was prepared by heating 2-ethylthioquinoline ethotoluene-*p*-sulphonate with hydrazine hydrochloride and then with



(XCIX)

pyridine.[188] A higher vinylene homologue, XCIX (*n*=1, Y=CH:CH, R=Me, X=I), was prepared through 2-β-ethylthiovinylquinoline methotoluene-*p*-sulphonate.[197] The sensitising properties of XCII (*n*=1,

Y=CH:CH, R=Et, X=Cl) were described.[186] A double hemicyanine, C (Y=CH:CH), comprising a piperazine nucleus, was prepared by heating 2-(4-acetanilido-1,3-butadienyl)quinoline ethiodide with piperazine hexahydrate in ethanol; it gave a crimson solution.[169]

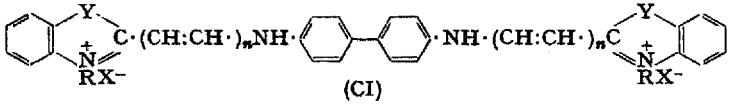


(C)

The 4-linked quinoline analogue of XCIX (n=0, Y=CH:CH, R=Me) was prepared as a coppery solid by heating 1-methyl-4-thiodihydroquinoline with methyl toluene-p-sulphonate, followed by hydrazine hydrochloride and pyridine.[188]

(2) *Salts of the Indolenine Series*

The simplest double hemicyanine with two substituted indolenine nuclei was XCIX (n=1, Y=CMe_2, R=Me, X=I), prepared by heating 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide with hydrazine hydrochloride and pyridine. The same methiodide condensed with p-phenylenediamine to give XCII (n=1, Y=CMe_2, R=Me, X=I),[188] whilst the corresponding dimethochloride was prepared by condensation of 2-formylmethylene-1,3,3-trimethylindoline with p-phenylenediamine in aqueous hydrochloric acid;[187] products obtained from this aldehyde with o- and m-phenylenediamine also sensitised.[186] The 2-β-acetanilidovinyl salt was condensed with benzidine to give CI (n=1,



(CI)

Y=CMe_2, R=Me, X=I) and the o,o'-dimethoxy-derivative was made from dianisidine.[188] Sensitising properties of the dimethochloride corresponding with the former, and with the o,o'-dimethyl derivative of that, were described, both of them obtained by the aldehyde method. Other sensitisers were prepared by condensing the aldehyde with 1,5-diaminonaphthol, 4,4'-diaminodibenzophenone, 4,4'-diaminostilbene, 4,4'-diaminodiphenylamine, derivatives of di-(p-aminophenyl)methane, and di-(p-aminophenyl)methane-o,o'-sulphone.[186]

(3) *Salts of the Benzothiazole, Benzoxazole, and Benzoselenazole Series*

With two benzothiazole nuclei, the double hemicyanine, XCIX (n=0, Y=S, R=Me), was prepared by boiling 2-methylthiobenzothiazole methotoluene-p-sulphonate with hydrazine hydrochloride and pyridine, and pouring into water. Similarly the salt with p-phenylenediamine hydrochloride gave XCII (n=0), and o-phenylenediamine was also used. The same salt with benzidine in ethanol gave CI (n=0, Y=S, R=Me, X=$SO_3 \cdot C_6H_4Me$). The compound, XCIX (n=1, Y=S, R=Et, X=I), with two dimethin units, was prepared by heating 2-β-acetanilidovinylbenzothiazole ethiodide and hydrazine hydrochloride with sodium acetate in ethanol, whilst heating the same ethiodide with p-phenylenediamine hydrochloride in pyridine gave XCII (n=1, Y=S, R=Et, X=I).[188] The dimethochloride corresponding with the last dye was prepared by use of a formylmethylene compound and had its sensitising maximum at 5300 Å.[186] Condensation of 2-β-acetanilidovinylbenzothiazole ethiodide by heating with benzidine in ethanol gave CI (n=1, Y=S, R=Et, X=I).[188] Its o,o'-dicarboxy- or o,o'-disulpho-derivatives were described as good sensitisers. One carboxy-group was introduced into the molecule of a double hemicyanine by the use of 1,3-diamino-5-carboxy-4-hydroxybenzene, and two by the use of *sym*-di-(4-amino-2-carboxyphenyl)carbamide.[189] The diethiodide, C (Y=S), with two tetramethin chains, was prepared, as was its 2-linked quinoline analogue, through piperazine hexahydrate.[169]

The double hemicyanine, XCIX (n=0, Y=O, R=Me), with two benzoxazole nuclei, was prepared by heating 2-methylthiobenzoxazole methotoluene-p-sulphonate with hydrazine hydrochloride and pyridine. The analogues, XCII and CI (n=1, Y=O, R=Me, X=I), with two dimethin linkings, were prepared by heating 2-β-acetanilidovinylbenzoxazole ethiodide with p-phenylenediamine hydrochloride in pyridine, or with benzidine in alcohol, respectively;[188] the former was also made by reaction of 2-methylbenzoxazole ethiodide, ethyl orthoformate, and p-phenylenediamine.[190] The diethiodide, C (Y=O), with two tetra- methin chains, was prepared as was its 2-linked quinoline analogue.[169]

With two benzoselenazole nuclei, a salt, XCII (n=1, Y=Se, R=Me, X=Cl), prepared through a formylmethylene compound, had its sensitising maximum at 5400 Å.[186]

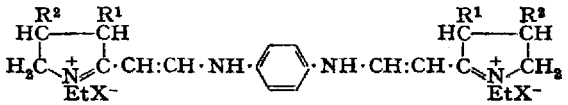
(4) *Salts of the Thiazoline and Selenazoline Series*

In the thiazoline series, diethiodides with an acidic group were obtained by reaction of *N*-ethyl-2-formylmethylenethiazolidine with *o*-carboxy- or *o*-sulpho-*p*-phenylenediamine; 2-methoxy-5-sulphophenylene-1,4-diamine was also used, whilst two carboxy-groups were introduced by means of *m*-dicarboxy-*p*-phenylenediamine. Carboxymethyl groups attached to both nitrogen atoms of the chain were introduced by use of *p*-phenylenedi(aminoacetic acid) and that salt also sensitised.[189]

In the selenazoline series, a diethiodide with a carboxyl group was obtained through *N*-ethyl-2-formylmethyleneselenazolidine and *o*-carboxy-*p*-phenylenediamine.[189]

(5) *Salts with Less Usual Nuclei*

The preparation of fifteen double hemicyanines, mostly diethiodides, with two pyrroline nuclei, was described. Those of type CII (R^1=H, Me, or Ph, R^2=H, Me, or Ph) were prepared by heating an *N*-ethyl-2-formylmethylenepyrrolidine, or its anil, with *p*-phenylene-



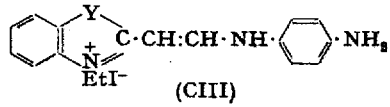
(CII)

diamine in aqueous hydrochloric acid, or, alternatively, a 2-*β*-anilinovinylpyrroline ethiodide was used. Substituted *p*-phenylenediamines, with an *o*-methoxy-, *o*-carboxy-, or *o*-sulpho-group were used, also benzidine, a dicarboxybenzidine, and 2,6-diaminonaphthalene: the products were photographic sensitisers.[191]

Hydrazine hydrochloride was condensed with two mols. of the methotoluene-*p*-sulphonates of each of the three bases 4-methylthioquinazoline, 2,5-di(methylthio)-1,3,4-thiadiazole, and 4,5-di(methylthio)-1,2,3-thiadiazole.[188] The sensitising action of diethiodides prepared by condensation of *o*-carboxy-*p*-phenylenediamine with 3-ethyl-2-formylmethylene-5-methyl-1,3,4-thiadiazole, and with 2-formylmethylene-*N*-methyldihydro-1,3,4-thiazine, was described.[189]

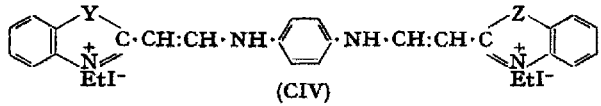
(6) *Unsymmetrical Salts*

The intermediate salt, CIII (Y=O), was prepared by heating 2-β-acetanilidovinylbenzoxazole ethiodide with *p*-phenylenediamine in ethanol, and the ethiodide, CIII (Y=S), of the benzothiazole series was



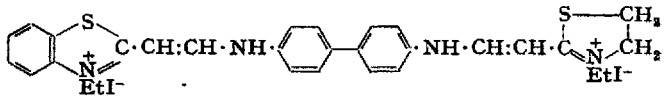
(CIII)

made similarly.[192] The former salt yielded the symmetrical CIV (Y=Z=O) either by reaction with 2-methylbenzoxazole ethiodide and ethyl orthoformate, or by reaction with 2-β-acetanilidovinylbenzoxazole ethiodide,[190] whilst the unsymmetrical 5-methyl derivative of CIV (Y=Z=O) was prepared by a modification of the latter procedure. Analogously, from CIII (Y=S) there were prepared the two unsymmetrical



(CIV)

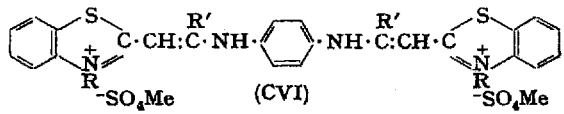
salts, CIV (Y=S, Z=O or CH:CH). Another intermediate salt was prepared by heating *N*-ethyl-2-formylmethylenebenzothiazoline with benzidine in methanol, in a current of hydrochloric acid, and converting into iodide; heating this ethiodide with 2-β-anilinovinylthiazoline ethiodide in ethanol gave the unsymmetrical salt, CV[192].



(CV)

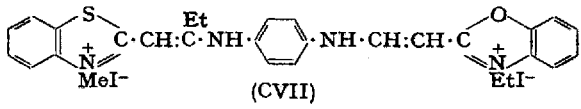
(7) *Salts with Substituents on the Chain*

By condensation in ethanol of one mol. of *p*-phenylenediamine with two mols. of a benzothiazolium salt, having the group ·CH:CR'·SMe, there were prepared two symmetrical double hemicyanines, CVI



(CVI)

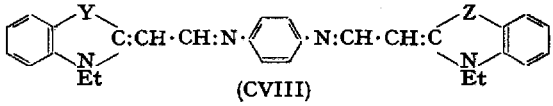
(R=Et, R′=Me; and R=Me, R′=Et), with a substituent on each chain. A benzothiazolium salt of this type was also condensed with one mol. of *p*-phenylenediamine to give an intermediate salt, whence there was derived the unsymmetrical double hemicyanine, CVII, with a substituent on one chain only.[192]



(CVII)

(8) Symmetrical and Unsymmetrical Bases

From the double hemicyanine, XCII (*n*=1, Y=O, R=Et, X=I), by the action of sodium hydroxide and acetone, the base, CVIII (Y=Z=O), was made, and was found to sensitise. Similarly the unsymmetrical double hemicyanine, CIV (Y=O, Z=S), yielded the unsymmetrical base, CVIII (Y=O, Z=S). From the diethiodide corresponding to CVI (R=Et, R′=Me), there was prepared a symmetrical base with a methyl group on each chain.[193]



(CVIII)

4. Oxonols and Related Compounds

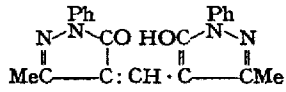
A. General Survey

The oxonols, like the dyes of the next chapter, require consideration because of their connection with trinuclear cyanines. This useful name was proposed[198] for dyes characterised by having an odd-numbered methin chain, comprising the following structure:

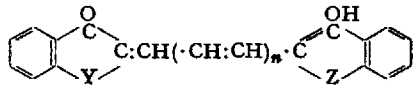


In the present section, only those derived from cyclic ketomethylene compounds and so having two residues of this kind are considered.

Many substances which condensed with quaternary salts having a reactive group to give symmetrical trimethincyanines (see Chapters IV and VI) also condensed with cyclic ketomethylene compounds to give methinoxonols. The first representative of this class of product was prepared from 3-methyl-1-phenyl-5-pyrazolone,[199] and its constitution was recognized in 1897 as being what would now be written CIX.[200,201] Nine years later, other such dyes, including some with a *meso*-substituent, were prepared from substituted pyrazolones.[202] The dye, CIX,

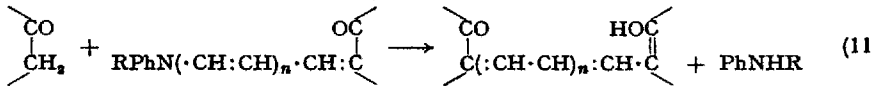


(CIX)



(CX)

occurred as a secondary product on heating 3-methyl-1-phenyl-5-pyrazolone with diphenylformamidine.[203] A method capable of yielding unsymmetrical oxonols was described in 1911 when CX (n=0, Y=Z=S) was prepared by reaction of 3-oxodihydrothianaphthene with its 2-formyl derivative in sulphuric acid.[204] The same dye was subsequently made from 3-oxodihydrothianaphthene with chloroform and alkali,[205] or with formic acid,[206] but it was not until 1932 that the sensitising properties of oxonols having two 3-oxodihydrothia-(or selena-)naphthene nuclei were patented: the sensitisers included methinoxonols, which might be *meso*-substituted, also tri- and pentamethinoxonols, CX (n=1 or 2, Y=Z=S or Se).[207] The methinoxonols were prepared by action of an ortho-ester or a tetrahalogenomethane on the cyclic ketomethylene compound,[208] but the latter procedure requires confirmation, especially in view of the fact that *meso*-halogenocarbocyanines, prepared by an analogous method, have not been authenticated (cf. VI-1). Some symmetrical methinoxonols that were unobtainable by the original method,[200] involving ethyl orthoformate and a ketomethylene compound, could be prepared by reaction of such a compound with another in which the cyclic methylene group carried an acetanilidomethylene substituent, in the presence of a basic condensing agent, and unsymmetrical oxonols could be prepared likewise[209] (equation 11, n=0).

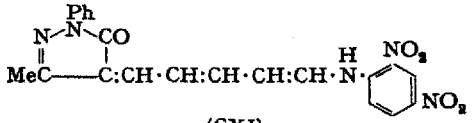


(11)

This method was later extended to the preparation of certain unsymmetrical pentamethinoxonols, which were valuable for anti-halation,[210] also of certain unsymmetrical methin- and trimethin-oxonols, which had the same application.[211] In 1937 certain symmetrical methin-, trimethin-, and pentamethin-oxonols, which were yellow, red, and blue, respectively, had been described as useful filter dyes, which were easily bleached by photographic processing solutions.[212]

On the type of intermediate compound, with a substituent aminomethylene group, of which the first representative had been made in 1909, from 3-methyl-1-phenyl-5-pyrazolone and diphenylformamidine,[203] the name hemicarboxonol was later conferred. Analogous substances with three or five methin groups were found to be photographic sensitisers. They were prepared from cyclic ketomethylene compounds by reaction of the hydrochloride of 1-anilino-3-aniloprop-1-ene or of 1-anilino-5-anilopenta-1,3-diene, which had been used in the synthesis of di- and tri-carbocyanines, respectively (see VII-1, VIII-2). The compounds were called hemidi- and hemitri-carboxonols,[213] but these terms have been misused.[214,215] The general term hemioxonol is useful and, if that be accepted, the names methin-, trimethin-, and pentamethin-hemioxonols are not liable to misinterpretation. The analogy between the hemicyanines (section 3) and the hemioxonols (section 4-G) is apparent. Just as the acetanilido-group of hemicyanines may be replaced by treatment with a secondary amine, giving products which are sensitisers, so may that of hemioxonols (section 4-G). Hemioxonols are valuable intermediate substances in the preparation of various types of merocyanines, including chain-substituted di- and tetra-methin-merocyanines, and azadimethinmerocyanines (see Chapter XIV).

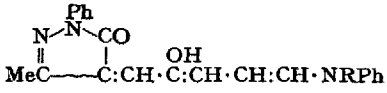
Pentamethinhemioxonols of a rather different type, such as CXI, were prepared by heating a cyclic ketomethylene compound with 2,4-dinitrophenylpyridinium chloride in the presence of a base, whereby



(CXI)

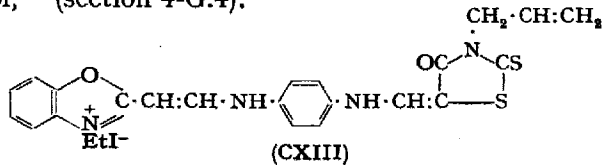
the pyridine ring was ruptured.[216] Blue compounds, useful for anti-halation layers, were produced by the action of aniline on 4-furfurylidene-3-methyl-1-phenyl-5-pyrazolone and were formulated as β-

hydroxypentamethinhemioxonols, CXII (R=H or Me), produced by rupture of the furfural ring.[217] Double hemioxonols have been de-



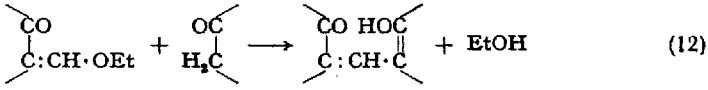
(CXII)

scribed, also a compound CXIII, which is both a hemicyanine and a hemioxonol,[193] (section 4-G.4).



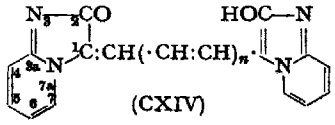
(CXIII)

To return to methinoxonols, it is interesting that, instead of ethyl orthoformate to provide the methin bridge, there may alternatively be used diethoxymethyl acetate[218] or ethylisoformanilide,[219] which have also been used in preparing carbocyanines (see IV-13, V-7). Another method, applicable to unsymmetrical dyes, consisted in the reaction of a heterocyclic compound having an ethoxymethylene substituent[220,221] with another having an unsubstituted methylene group[221,222] (equation 12).



(12)

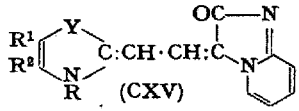
The symmetrical methinoxonol, CXIV (n=0), having two 3,7a-diazaindan-2-one residues, was prepared by two straightforward methods.[219,223] Besides this, two unsymmetrical methinoxonols, having

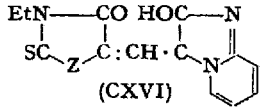


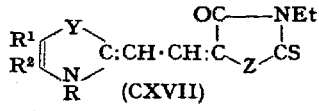
(CXIV)

one nucleus of this kind, were prepared by a remarkable process, which consisted in the rupture of the molecule of a dimethinmerocyanine, having one such nucleus, by means of a ketomethylene compound. Thus the dimethinmerocyanine, CXV (Y=CH:CH, R=Me, R^1=R^2=H), on heating with 3-ethyl-4-oxo-2-thio-oxazolidine in ethanol, gave

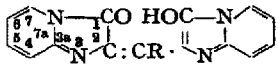
the methinoxonol, CXVI (Z=O), accompanied by the dimethinmerocyanine, CXVII (Y=CH:CH, Z=O, R=Me, R^1=R^2=H). Similarly the dimethinmerocyanine, CXV (Y=O, R=Et, R^1R^2=C_6H_4), by the action of 3-ethylrhodanine, gives the methinoxonol, CXVI (Z=S), accompanied by the dimethinmerocyanine, CXVII (Y=O, Z=S, R=Et, R^1R^2=C_6H_4). The yields of methinoxonols were higher than those

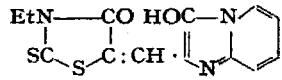

(CXV)


(CXVI)


(CXVII)

of the dimethinmerocyanines. When the symmetrical methinoxonol, CXIV (n=0), was boiled with 3-ethyl-4-oxo-2-thio-oxazolidine and potassium hydroxide in ethanol, its molecule also was ruptured, to give the unsymmetrical methinoxonol, CXVI (Z=O).[219] Rupture of the chains of methin- and trimethin-cyanines by quaternary salts, which has been recorded elsewhere (see II-6-E and V-12-A), seems somewhat analogous. Subsequently 3-7a,diazaindan-1-one was synthesised and the symmetrical methinoxonol, CXVIII (R=H), isomeric with CXIV (n=0) was prepared. From scale drawings it was concluded that CXVIII (R=H) has a planar molecule, whilst the two nuclei in CXIV must be distorted from co-planarity. An unsymmetrical methinoxonol, CXIX, was also made.[224]


(CXVIII)


(CXIX)

It was noted in 1952 that methinoxonols are often poor photographic sensitisers, and this was attributed to the prevention of co-planarity of the two nuclei by steric hindrance, as shown in Figure 1 for the methinoxonol, CIX.

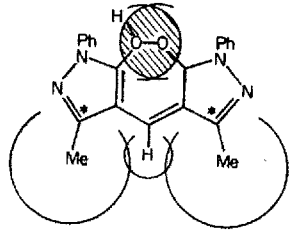
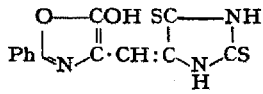


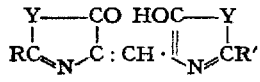
Fig. 1. Oxonol molecule. [From Knott (225). By courtesy of the author and the Chemical Society.]

For such a compound to have a planar molecule, one or both of the positions marked * must be unsubstituted, i.e., hetero-atoms. Nuclei regarded as suitable had already been used.[225] Such were the residues of 3-ethylrhodanine and of 2-diphenylamino-4-oxothiazoline;[209] another was 5-oxo-2-phenyloxazoline in the methinthio-oxonol, CXX (cf. XIV-4),[226] and another was 2-ethylthio-5-oxothiazoline.[222] As regards the last



(CXX)

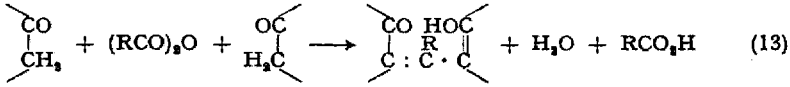
type, the methinoxonols, CXXI (Y=S, R=R'=SEt or SCH_2Ph), were powerful orthochromatic sensitisers. Besides the symmetrical methinoxonol, CXXI (Y=S, R=R'=OEt), other unsymmetrical methinoxonols of type CXXI (Y=S) were prepared by use of ethoxymethylene compounds. A progressive hypsochromic shift of the absorption



(CXXI)

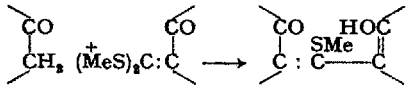
maximum of CXXI (Y=S, R=R'=SEt) occurred on replacement of first one ethylthio-group, and then the second by ethoxy.[225] In the oxothiazoline series, various methinoxonols of type CXXI (Y=S) were described, also analogues having one oxo-oxazoline and one oxothiazoline residue. Some of these oxonols sensitised as powerfully as merocyanines, which was remarkable.[227] The symmetrical methinoxonol, CXXI (Y=O, R=R'=Ph), and related unsymmetrical dyes showed abnormal colour reactions.[225]

Meso-substituted methinoxonols were first referred to in 1932.[207,208] In 1940 the reaction of a rhodanine with an acid anhydride, in the presence of triethylamine, to give a *meso*-alkylmethinoxonol (equation 13) was patented.[228] By condensation of a ketomethylene compound



(13)

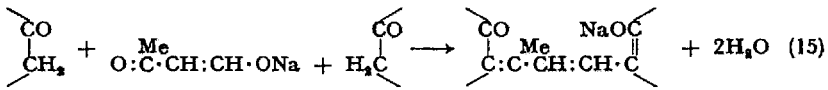
with an oxothiothiazolidine having a 5-di(methylthio)methylene substituent,[229] there resulted a *meso*-(methylthio)methinoxonol[230] (equation 14) (cf. XIV-8-A.7).



(14)

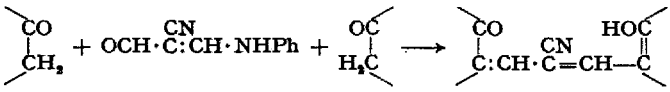
Certain substances, such as 1,3,3-triethoxyprop-1-ene and 1-anilino-3-aniloprop-1-ene hydrochloride, which were used in the preparation of pentamethincyanines (see VII-2 and 1), were also condensed with heterocyclic ketomethylene compounds to give symmetrical trimethinoxonols. These were also reached by a two stage process involving a trimethinhemioxonol (equation 11, $n=1$), whilst an intermediate compound prepared from 1,3,3-triethoxyprop-1-ene was used to give an unsymmetrical trimethinoxonol (see section 4-C).

α-Substituted trimethinoxonols were prepared by condensation of 2 mols. of a cyclic ketomethylene compound with one of a 1,3-ketone aldehyde, such as sodium formylacetone (equation 15). By means of



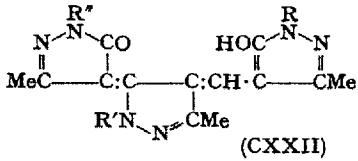
(15)

acetylacetone or benzoylacetone, products with substituents in the αα′-positions were obtained. Condensation of one mol. of ketomethylene compound with one of sodium formylacetone gave an intermediate compound having the group ·CH:CH·COMe, whence unsymmetrical α-methyltrimethinoxonols were obtainable. These dyes were described as useful for sensitising or for antihalation.[231] Just as 3-anilino-2-cyano-1-oxoprop-2-ene could be used in the preparation of a *meso*-cyanopentamethincyanine (see VII-7-A), so it could be condensed with two mols. of a cyclic compound having a ketomethylene group, to give a *meso*-cyanotrimethinoxonol[232] (equation 16). Symmetrical trimethinoxonols with a β-substituent and 3,7a-diazaindan-2-one nuclei, have been described.[233]



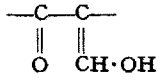
(16)

In 1941, trimethinoxonols, in which two carbon atoms of the chain were cyclic, were described. They were obtained by the action of alcoholic potassium hydroxide on a mixture of methinoxonol and substituted pyrazolone, e.g. CIX (n=0), with 3-methyl-1-phenyl-5-pyrazolone gave CXXII (R=R′=R″=Ph), as its purple red potassium

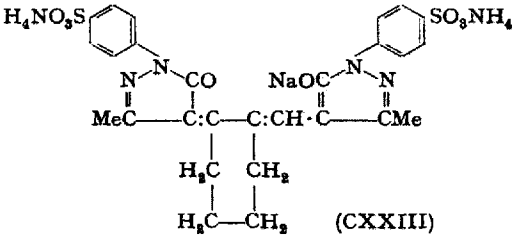


(CXXII)

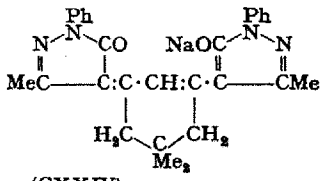
salt, which was converted by hydrochloric acid into the orange red dye. The trinuclear dye was alternatively prepared by heating 3-methyl-1-phenyl-5-pyrazolone and diphenylformamidine with methanolic potassium hydroxide. A method of obtaining other trimethinoxonols, in which the $\alpha\beta$-carbon atoms were cyclic, consisted in heating a substituted pyrazolone with a carbocyclic compound comprising the structure



For instance, by means of 2-hydroxymethylenecyclohexanone, CXXIII was prepared. The trimethinoxonol, CXXIV, in which the $\alpha\gamma$-carbon atoms were cyclic, was prepared through 1,1-dimethylcyclohexane-3,5-

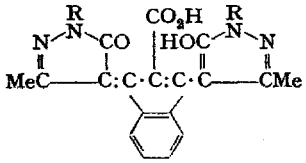


(CXXIII)

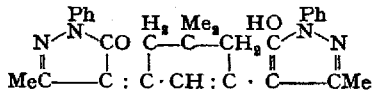


(CXXIV)

dione. The trimethinoxonol, CXXV (R=Ph), in which the $\alpha\gamma$-carbon atoms were cyclic and the β-carbon carried a substituent, was prepared through sodium 1,3-indandione-2-carboxylate. Dyes of this kind were useful for anti-halation.[234] In 1945 trimethinoxonols, e.g. CXXVI, in which the $\alpha\gamma$-carbon atoms of the chain were cyclic, were prepared by use of 3-ethylthio-5,5-dimethylcyclohex-2-en-1-one (section 4-C) (cf. IX-5).

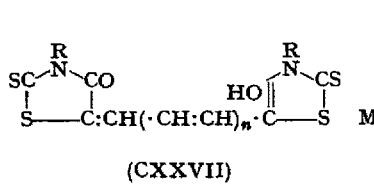


(CXXV)

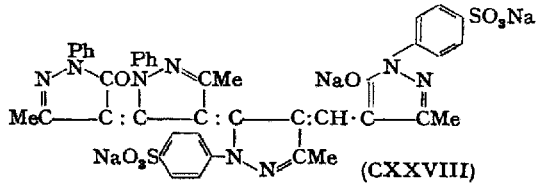


(CXXVI)

When the sensitising properties of pentamethinoxonols, CX (n=2, Y=Z=S or Se), were described in 1932, the dyes were prepared in one step.[207] Subsequently the former was prepared by the method involving a pentamethinhemioxonol (equation 11, n=2); the absorption maximum of the dye in acetic acid was compared with those of the corresponding methin- and trimethin-oxonols.[235] Pentamethinhemioxonols were again used in the preparation of unsymmetrical pentamethinoxonols, which gave purplish red layers useful for anti-halation.[210] Pentamethinhemioxonols, such as CXI and its analogues, were also used in the preparation of unsymmetrical pentamethinoxonols, whilst symmetrical pentamethinoxonols were prepared from ketomethylene compounds and 2,4-dinitrophenylpyridinium chloride.[216] The salts of the pentamethinoxonol, CXXVII (n=2, R=Et), were very unstable, but



(CXXVII)



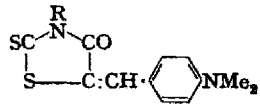
(CXXVIII)

the free dye was more stable.[236] The pentamethinoxonol with two 3-methyl-1-phenyl-5-pyrazolone residues was described.[237]

A pentamethinoxonol, CXXVIII, in which two pairs of carbon atoms of the chain are cyclic, was formulated.[234]

Some properties of four groups of symmetrical methin-, trimethin-, and pentamethin-oxonols are given in Table IV.

The *p*-dialkylaminobenzylidene derivatives of heterocyclic ketomethylene compounds bear some analogy to the *p*-dialkylaminostyryl derivatives prepared from heterocyclic quaternary salts having a re-



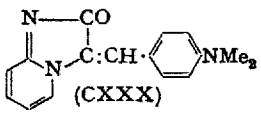
(CXXIX)

TABLE IV. Some Properties of Four Series of Symmetrical Methin-, Trimethin-, and Pentamethin-oxonols

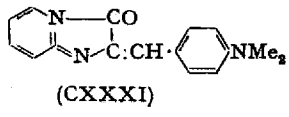
Nature of nucleus and of linking		Formula	Appearance of crystals	M.p. (°C) (decomp.)	Colour of alcoholic solution or absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
Pyrazolone	CH	CIX	orange-yellow needles	180–181[a]	—	—	—	200
Pyrazolone	5CH	—	—	205[a]	blue; 5300[b]	—	—	216, 237
3-oxodiH-thianaphthene;	CH	CX (Y=Z=S, n=0)	red needles	270–271[a]	violet; 5850[b] yellow; 4850[c]	5990	6550	204, 207, 235, 255, 256
3-oxodiH-thianaphthene	3CH	CX (Y=Z=S, n=1)	green needles[d]	255–257	6500[b], 4920[c]	6900	7400	207, 235
3-oxodiH-thianaphthene	5CH	CX (Y=Z=S, n=2)	green[d]	240–242	5020[c]	7850	8800	207, 235
3-Et-rhodanine	CH	CXXVII (R=Et, n=0)	blue needles	163	5400[b]	—	6200	219, 227, 255, 256
3-Et-rhodanine	3CH	CXXVII (R=Et, n=1)	black —	no definite m.p.	6130[b]	no sensitising		88, 254
3-Et-rhodanine	5CH	CXXVII (R=Et, n=2)	—	—	7140[b]	—	—	236
3,7a-diazaindan-2-one	CH	CXIV (n=0)	brick red	300[a]	5070[b], 4900[c]	—	—	219, 223, 224
3,7a-diazaindan-2-one	3CH	CXIV (n=1)	purple needles	284[a]	6000[b], 5850[e]	—	—	233
3,7a-diazaindan-2-one	5CH	CXIV (n=2)	green needles	218[f]	5900[b], 6850[e]	—	—	233

[a] decomp. not recorded. [b] for salt with NEt_3, NH_4OH, or NaOH. [c] in acid.
[d] sodium salt. [e] for methotoluene-p-sulphonate in MeOH. [f] for hydrochloride.

active methyl group (see section 1). The first representatives, CXXIX, of this type were prepared in 1905, by reaction of *p*-dimethylaminobenzaldehyde with rhodanine and its *N*-substituted derivatives.[238] Many years later, after an examination of numerous compounds of this type, CXXIX (R=H) was proposed as a specific reagent for silver, because of the red salt which it gave[239] and it was also used in testing for other metals.[240] In 1933 examples of such *p*-dimethylaminobenzylidene compounds were included amongst other photographic sensitisers having a nucleus with the ·NR·CO·C:structure (cf. XIV-1).[241,242] An independent discovery of the sensitising action of analogues of CXXIX included some with a *p*-diethylaminobenzylidene group.[243,244] The absorption maxima of methanolic solutions of ten *p*-dimethylaminobenzylidene compounds having different heterocyclic nuclei were recorded.[88] Just as aldehydes, $OCH \cdot C_6H_4 \cdot NR^1R^2$, in which one or both of the alkyl groups R^1 and R^2 were halogenated, were used in the preparation of substituted *p*-dialkylaminostyryl salts (See section 1-A), so they were used in the preparation of *p*-dialkylaminobenzylidene compounds.[20] Again, just as *m*-dimethylaminobenzaldehyde was condensed with various quaternary salts having a reactive methyl group, so was it with 3-methyl-1-phenyl-5-pyrazolone.[23] The hydrobromide of 3,7a-diazaindan-2-one was condensed with *p*-dimethylaminobenzaldehyde to give the hydrobromide of CXXX.[222] Its absorption maxima in pyridine, ethanol, and aqueous pyridine lay always at a shorter wavelength than the corresponding maxima of CXXXI, having a 3,7a-diazaindan-1-one nucleus.[223]

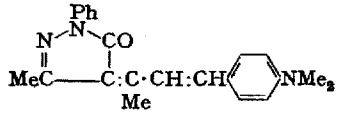


(CXXX)

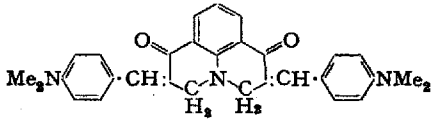


(CXXXI)

A higher vinylene analogue of CXXIX (R=H) was prepared by condensing rhodanine with *p*-dimethylaminocinnamic aldehyde.[241] The dye CXXXII, with a substituent on the chain, was prepared by condensing 4-isopropylidene-3-methyl-1-phenyl-5-pyrazolone (cf. XIV-8-A.6) with *p*-dimethylaminobenzaldehyde.[245]



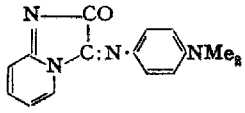
(CXXXII)



(CXXXIII)

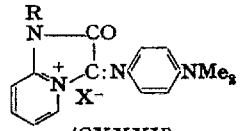
The bis-*p*-dimethylaminobenzylidene compound, CXXXIII, was prepared by condensation of 1,6-dioxo-julolidine with *p*-dimethylaminobenzaldehyde.[246]

Whereas *p*-nitrosodimethylaniline was condensed with numerous heterocyclic salts, having a reactive methyl group, to give *p*-dialkylaminoanils of heterocyclic aldehydes (see section 2-B), analogous condensations with heterocyclic ketomethylene compounds are comparatively rare. In 1926 an intensive blue colour was observed on condensing 3,7a-diazaindan-2-one with *p*-nitrosodimethylaniline: although the product gave a nitrogen value agreeing with CXXXIV, it was regarded



(CXXXIV)

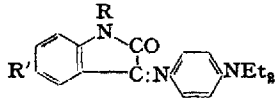
with suspicion because it was amorphous.[247] Eighteen years later it was identified as one of the products of reaction of *p*-nitrosodimethylaniline with 2-acylacetaminopyridines, its formation involving cleavage and ring closure.[248] It was obtainable by condensation of *p*-nitrosodimethylaniline, not only with 3,7a-diazaindan-2-one, but with its acetyl and diacetyl derivatives. *p*-Nitrosodimethylaniline was also condensed with the methiodide and perchlorate of the ketomethylene compound, the products being formulated as CXXXV (R=Me, X=I or ClO_4).[249] The absorption maximum of CXXXIV lay at 5250 Å, whilst that of a salt, CXXXV (R=H or Me), lay at 5930 Å.[223] Magenta azamethin dyes of the pyrazolone series are formed in certain colour processes and in 1951 the absorption maxima of a series of twenty-six, in three solvents of



(CXXXV)

varying dielectric constant, were compared. The two absorption bands in the visible region were regarded as *x* and *y* bands, the former, at 5300–5500 Å, being associated with structures in which the pyrazolone 2-*N* atom is negatively charged, and the latter, at 4400–4500 Å, with structures in which the *O* atom is negatively charged. The secondary

band, at shorter wavelength, was disadvantageous in the photographic application of the dyes, but could be reduced by modification of the pyrazolone.[250] In 1956 the aza-compound, CXXXVI (R=R'=H), was prepared from 2-oxoindoline, besides eight of its *N*-substituted derivatives, and their absorption maxima were recorded.[251] Subsequently



(CXXXVI)

similar substances with substituents in the 5-position were prepared. Whilst weakly electropositive groups gave a slight hypsochromic shift, a bathochromic shift was caused by a bromo- or a nitro-substituent.[252] An analogue of the bis-(*p*-dimethylaminobenzylidene) compound, CXXXIII, was prepared, in which both :CH· groups were replaced by :N (see section 4-F).[246]

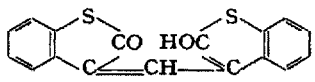
B. Methinoxonols, Including those with a Substituent on the Chain

The symmetrical methinoxonol, CX (*n*=0, Y=Z=S), was prepared at an early date from the ketomethylene compound, by warming with chloroform and sodium hydroxide, whereupon a blue-violet colour developed and the sodium salt crystallised.[205] The chloroform method was later applied to the preparation of CX (*n*=0, Y=Z=S or Se).[207,208] Use of formic acid to provide the methin bridge was applied to the former dye,[206] and, much later, gave a 90 % yield.[253] The use of formamide to provide the methin bridge of the symmetrical methinoxonol, CIX,[202,254] later gave an 85 % yield of this and a 97 % yield of CX (*n*=0, Y=Z=S), also 58 % and 56 % yields of CXXVII (*n*=0, R=Et or Ph). The red acid solutions of the last two turned violet with silver, mercuric, and cupric salts, and sparingly soluble metallic salts separated. Formamide reacted with barbituric and thiobarbituric acid to give products other than oxonols.[255] As examples of methinoxonols which were useful filter dyes, there were mentioned in 1937 the compound, CIX, and its analogues with *NN'*-di-$C_6H_4SO_3H(p)$, -di-$C_6H_4CO_2H(p)$, -di-α-$C_{10}H_7$, and -diH.[212]

One of the first preparations of CIX by means of ethyl orthoformate was effected in acetic acid,[200] and a recent one in a medium

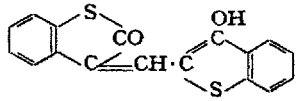
of acetic anhydride gave an 80% yield; also diphenylformamidine in acetic anhydride was used for CIX, and for a methinoxonol from 4-oxo-3-phenyl-2-thiothiazolidine.[237] By means of an ortho-ester in the presence of triethylamine, methinoxonols were prepared from 3-methyl- and 3-ethyl-rhodanine.[227] By condensation of ethyl orthoformate with the hydrobromide of 3,7a-diazaindan-2-one a symmetrical methinoxonol, CXIV (n=0), with two such nuclei was obtained, in the form of its hydrobromide.[223] The free dye was prepared independently by reaction of ethylisoformanilide with the ketomethylene compound, by heating with triethylamine in ethanol, and the hydrochloride dihydrate was also isolated.[219] The isomeric CXVIII (R=H) was prepared by boiling 3,7a-diazaindan-1-one with ethyl orthoformate in pyridine for 2–3 minutes.[224] The preparation of symmetrical methinoxonols by means of diethoxymethyl acetate was effected by heating it with a ketomethylene compound in piperidine at 120° for 17 hours; substances used were 3-ethyl-1-phenyl-2-thiohydantoin, 2-diphenylamino-4-oxothiazoline, 3-ethylrhodanine, 3-methyl-1-phenyl-5-pyrazolone, and 1-ethyl-2-oxoindoline. The free dyes were sometimes stronger sensitisers than their salts with triethylamine or pyridine.[218]

Condensation of a cyclic ketomethylene compound with its formyl derivative was applied at an early date to the preparation of the symmetrical methinoxonols, CX (n=0, Y=Z=S or NH),[204] and, later, to give an unsymmetrical dye, a chloromethyl derivative of CX (n=0, Y=S, Z=Se).[207,208] In 1955, the symmetrical dye, CXXXVII, isomeric



(CXXXVII)

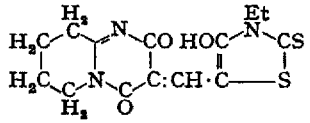
with CX (n=0, Y=Z=S), was prepared by condensing 2-oxodihydrothianaphthene with its 3-formyl derivative, by boiling for 3 hours with triethylamine in ethanol. The unsymmetrical methinoxonol, CXXXVIII, was prepared by condensing 2-formyl-3-oxodihydrothianaphthene with 2-oxodihydrothianaphthene, under acid or basic



(CXXXVIII)

conditions, but could not be obtained by certain other methods. CXXXVII absorbs at 5000 Å and is markedly more soluble than CXXXVIII, with its absorption maximum at 5660 Å, or CX (n=0, Y=Z=S), with its absorption maximum at 5920 Å. A pair of unsymmetrical oxonols of type CXXXVIII were prepared, with a 6-ethoxy-group in one ring or the other.[256]

In 1940, the method of equation 11 (n=0) gave the symmetrical methinoxonol, CX (n=0, Y=Z=S), by heating 3-oxodihydrothianaphthene and its anilinomethylene derivative (see section 4-G) with hydrochloric acid in ethanol.[235] The procedure of condensing a compound having a reactive cyclic methylene group with another having an acetanilidomethylene substituent, e.g., by use of triethylamine in pyridine, was applied to symmetrical and unsymmetrical methinoxonols, having such nuclei as rhodanine, thiohydantoin, or thiooxazolidine-2,4-dione.[209] Subsequently CXXVII (n=0, R=H or Et) were thus synthesised, for comparison of their absorption maxima with those of related dimethinmerocyanines.[257] Besides merocyanines having a complex dioxotetrahydropyrimidine nucleus (see XIV-10-C.2e), the methinoxonol, CXXXIX, was prepared, by reaction of the ketomethylene compound with 5-acetanilidomethylene-3-ethylrhodanine.[258]

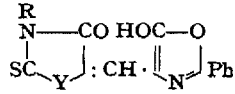


(CXXXIX)

Unsymmetrical methinoxonols were made by condensing 4-acetanilidomethylene-3-methyl-1-phenyl-5-pyrazolone with compounds such as 1,3-diethyl-2-thiobarbituric acid, 1-ethylbarbituric acid, or 1,3-di-(*p*-ethoxyphenyl)barbituric acid.[211]

The method of equation 12, involving an ethoxymethylene compound, was first applied to the preparation of a symmetrical methinoxonol, when 5-oxo-2-phenyloxazoline was condensed with its 4-ethoxymethylene derivative by heating with triethylamine in ethanol.[221] Another was made by condensing 2-ethylthio-5-oxothiazoline with its 4-ethoxymethylene derivative to give CXXI (Y=S, R=R'=SEt), though in that instance the ethyl orthoformate method was considered more convenient.[222] The method was also applied in preparing the thio-

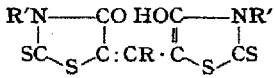
oxonol, CXX, by condensation of 4-ethoxymethylene-5-oxo-2-phenyl-oxazoline with 2,4-dithioimidazolidine by means of triethylamine in cold methanol, being isolated as triethylamine salt; with more vigorous conditions, decolorisation occurred, and this was attributed to opening of the ring. Another such compound was prepared by use of 4-ethoxy-methylene-5-oxo-2-thiothiazolidine and the same ·CS·CH_2· compound.[226] The symmetrical methinoxonol, CXXI (Y=S, R=R'=OEt), was prepared by condensing 2-ethoxy-4-ethoxymethylene-5-oxothiazoline[259] with 2-ethoxy-5-oxothiazoline by heating with triethylamine in ethanol. Use of ethoxymethylene compounds was applied to the preparation of the unsymmetrical methinoxonols, CXXI (Y=S, R=SEt, R'=$OC_{14}H_{29}$, SC_8H_{17}, or $SC_{12}H_{25}$; and Y=S, R=SC_8H_{17}, R'=NHAc). Other unsymmetrical methinoxonols included CXL (Y=S, R=Et or



(CXL)

CH_2CO_2H; and Y=NPh, R=Et).[225,228] In preparing the unsymmetrical methinoxonol, CXIX, 3,7a-diazaindan-1-one hydrochloride and 5-ethoxymethylene-3-ethylrhodanine were boiled for 30 minutes in pyridine containing triethylamine; the product was twice purified by converting into a salt and precipitating with acetic acid.[224] Absorption maxima, in methanol containing piperidine, were given for symmetrical methinoxonols with indan-1,3-dione, 5-isoxazolone, 3-oxo-indoline, 4-oxo-2-thio-oxazolidine, pyrazolone, rhodanine, thiohydantoin, barbituric acid and thiobarbituric acid nuclei.[88]

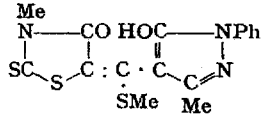
Methinoxonols of type CX (*n*=0, Y=Z=S), but with a *meso*-methyl or -chloro substituent, were described as obtainable by condensing the ketomethylene compound with ethyl orthoacetate or carbon



(CXLI)

tetrachloride.[207,208] Reaction of 3-methyl- or 3-ethyl-rhodanine with acetic anhydride and triethylamine (equation 13) gave CXLI (R=Me, R'=Me or Et), whilst by means of propionic anhydride there was

made CXLI (R=Et, R'=Me), all of them photographic sensitisers.[228] Reaction of 3-methyl-1-phenyl-5-pyrazolone with 3-methyl-5-(dimethylthio)methylenerhodanine gave the very insoluble CXLII, which

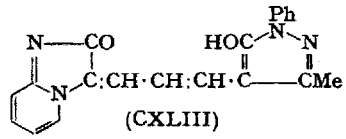


(CXLII)

formed a pink insoluble silver salt.[230] The *meso*-methylmethinoxonol, CXVIII (R=Me), was believed to result by ring-closure when 2-pyridylaminoacetic acid hydrochloride was boiled with acetic anhydride; its properties were almost identical with those of the unsubstituted CXVIII (R=H).[224]

C. Trimethinoxonols, Including Those with a Substituent on the Chain, and Others in which Part of the Chain is Cyclic

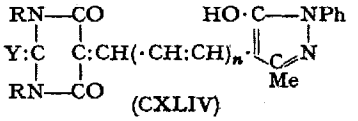
When the sensitising action of the trimethinoxonol, CX (n=1, Y=Z=S), was patented in 1932, the dye was prepared by heating 3-oxodihydrothianaphthene and 1,3,3-triethoxyprop-1-ene with piperidine in pyridine; its 5,5'-dichloro-derivative was prepared by means of 1-anilino-3-aniloprop-1-ene hydrochloride and sodium methoxide.[207] The dye, CX (n=1, Y=Z=S), was prepared by the method of equation 11 (n=1) from 3-oxodihydrothianaphthene and its γ-anilinoallylidene derivative: it dissolved in alkali to a blue solution.[235] An attempt to make the symmetrical dye, CXIV (n=1), by condensing 3,7a-diazaindan-2-one hydrobromide with 1,3,3-triethoxyprop-1-ene gave an intense blue colour, but the product was too unstable to isolate. It was,



(CXLIII)

however, possible to condense equimolecular quantities of the reactants to give an intermediate compound, whence an unsymmetrical trimethinoxonol hydrobromide, CXLIII, was prepared.[223] The red trimethinoxonol, CXXVII (n=1, R=Et), was prepared in 12 % yield by boiling 3-ethylrhodanine and 1-anilino-3-aniloprop-1-ene hydrochloride

with triethylamine in ethanol for six hours, being isolated as its blue ammonium salt, which was decomposed by hydrochloric acid.[260] It was later prepared from 3-ethylrhodanine and its 5-acetanilidoallylidene derivative, with triethylamine in pyridine or with potassium carbonate in ethanol.[236] The absorption maximum of its triethylamine salt was recorded.[88] A trimethinoxonol, prepared from 3-ethyl-5-oxo-2-thiothiazolidine by heating it with 1,3,3-triethoxyprop-1-ene and triethylamine in ethanol, could not be recrystallised without decomposition.[261] By heating 4-γ-acetanilidoallylidene-3-methyl-1-phenyl-5-pyrazolone and 1,3-diethyl-barbituric, or -thiobarbituric, acid with triethylamine in pyridine, there resulted the unsymmetrical trimethinoxonols, CXLIV



(CXLIV)

(n=1, Y=O or S, R=Et). An analogue, CXLIV (n=1, Y=O, R=p-C_6H_4OEt), of the former was also described and all were suitable for filter dyes.[211] The suitability for this purpose of a symmetrical trimethinoxonol with 3-methyl-1-p-sulphophenyl-5-pyrazolone nuclei had been noted fifteen years before.[212]

The α-methyl derivative of a trimethinoxonol analogous with CIX was prepared, in the form of its sodium salt, by heating 3-methyl-1-phenyl-5-pyrazolone with sodioformylacetone in methanol at 60° for 10 hours (equation 15). The p-sulpho-derivative of this pyrazolone, or certain other ketomethylene compounds, could also be used. Instead of sodioformylacetone, there could be used, in conjunction with triethylamine, the anil of formylacetone, or hydroxy-methyleneacetone or -benzylideneacetone. αα′-Groups were introduced by condensation of the substituted pyrazolone with acetyl- or benzoyl-acetone. Moreover, with a shorter time of heating, 3-methyl-1-phenyl-5-pyrazolone condensed with 1 mol. of sodioformylacetone, or of the anil of formylacetone to give an intermediate compound with the group ·CH:CH·COMe in the 4-position, and thiobarbituric acid behaved similarly. From such intermediates there could be prepared α-methyltrimethinoxonols. In condensing 3-ethylrhodanine with 3-anilino-2-cyano-1-oxoprop-2-ene (equation 16), the method was to boil them in acetic anhydride with addition of triethylamine, which gave the *meso*-derivative of CXXVII (n=1, R=Et).[231] β-Methyl, β-chloro-, and

β-bromo-derivatives of CXIV (n=1) were obtained by condensing 3,7a-diazaindan-2-one hydrochloride with the corresponding 2-substituted 1-anilino-3-aniloprop-1-ene, or its hydrochloride, by heating with sodium carbonate in aqueous ethanol.

A symmetrical trimethinoxonol, CXXII (R=R′=R″=Ph), in which two carbon atoms of the chain were cyclic, was prepared, as potassium salt, by heating the methinoxonol, CIX, and 3-methyl-1-phenyl-5-pyrazolone with potassium hydroxide in methanol for 7 hours, whereas use of 3-methyl-1-*p*-sulphophenyl-5-pyrazolone gave the unsymmetrical dye, CXXII (R=R′=Ph, R″=$C_6H_4 \cdot SO_3H$), which was isolated as disodium salt. By heating the di-*p*-sulpho-derivative of CIX and 3-methyl-1-phenyl-5-pyrazolone with aqueous ammonia for 7 hours, there was prepared CXXII (R=R′=$C_6H_4SO_3H$, R″=Ph) in the form of triammonium salt. By heating the potassium salt of CXXII (R=R′=R″=Ph) with sodium acetate and acetic anhydride, an acetyl group replaced the potassium atom. The trinuclear dye, CXXII (R=R′=R″=Ph), could be prepared by heating 3-methyl-1-phenyl-5-pyrazolone with diphenylformamidine in ethanol for 3 hours, and an analogue was also made from 5-oxo-3-phenylisoxazoline and diphenylformamidine. For preparing CXXIII, the ammonium salt of 3-methyl-1-*p*-sulphophenyl-5-pyrazolone and sodium 2-hydroxymethylenecyclohexanone were heated in methanol for 7 hours; a similar trinuclear compound was prepared by use of hydroxymethylenecamphor. For preparing CXXIV, 3-methyl-1-phenyl-5-pyrazolone and 1,1-dimethylcyclohexane-3,5-dione were heated in methanol for 24 hours, then treated with sodium chloride. On heating the same pyrazolone with sodium indan-1,3-dione-2-carboxylate at 135–140° for an hour, and treating the green sodium salt with dilute hydrochloric acid, CXXV (R=Ph) resulted. The tetrasodium salt of CXXV (R=*p*-$C_6H_4SO_3H$) was prepared in two stages.[234]

The dye, CXXVI, was prepared by fusion of 3-methyl-1-phenyl-5-pyrazolone with 3-ethylthio-5,5-dimethylcyclohex-2-en-1-one, followed by boiling with triethylamine in pyridine, and acidification. An analogue with two 3-methylrhodanine residues was also made.[262]

D. Pentamethinoxonols, Including One in which Part of the Chain is Cyclic

When the pentamethinoxonols, CX (n=2, Y=Z=S or Se), were described in 1932, the dyes were prepared by heating the appropriate

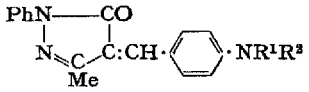
ketomethylene compound with 1-anilino-5-anilopenta-1,3-diene hydrobromide and diethylamine in ethanol.[207] The former was also prepared by condensing 3-oxodihydrothianaphthene with its 5-anilinopenta-1,3-dienyl derivative[235] (equation 11, $n=2$). Pentamethinhemioxonols were also used in the preparation of unsymmetrical pentamethinoxonols for anti-halation layers, condensation being effected by boiling with triethylamine in pyridine for 0·5–3 hours: nuclei such as substituted pyrazolone, substituted rhodanine, and thiobarbituric acid were introduced.[210] Analogous compounds were described later. The usefulness of symmetrical pentamethinoxonols as filter dyes was first noted in 1937, those described having two 3-methyl-1-*p*-sulphophenyl-5-pyrazolone or two thiobarbituric acid residues.[212] A symmetrical pentamethinoxonol was prepared by heating 3,7a-diazaindan-2-one hydrochloride and 1-anilino-5-anilopenta-1,3-diene hydrochloride with triethylamine in ethanol.[233] Unsymmetrical pentamethinoxonols were prepared by reaction of pentamethinhemioxonols of type CXI with ketomethylene compounds, such as substituted rhodanines or pyrazolones, by boiling with triethylamine in ethanol. Symmetrical pentamethinoxonols were made by heating 3-methyl-1-phenyl-5-pyrazolone, or its *p*-sulpho-derivative, with 2,4-dinitrophenylpyridinium chloride and triethylamine in alcohol.[216] The pyrazolone also reacted with pyridine cyanobromide, cyanochloride, or cyanuric chloride to give the pentamethinoxonol; boiling sodium carbonate solution converted the blue dye into a magenta one of unknown constitution.[233]

The tetranuclear pentamethinoxonol, CXXVIII, in which two pairs of carbon atoms of the chain are cyclic, was obtained as a by-product accompanying the trinuclear trimethinoxonol, CXXII ($R=R'=C_6H_4SO_3H$, $R''=Ph$), when this was prepared by condensing the methinoxonol from 3-methyl-1-*p*-sulphophenyl-5-pyrazolone with 3-methyl-1-phenyl-5-pyrazolone, by the action of sodium hydroxide.[234]

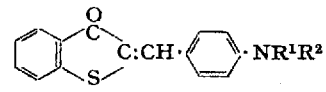
E. Dialkylaminobenzylidene Compounds, Higher Vinylene Analogues and a Bis-(*p*-Dialkylaminobenzylidene) Compound

p-Dimethylaminobenzaldehyde was originally condensed with rhodanine and its *N*-substituted derivatives to give CXXIX (R=H, Me, Et, Pr, Ph, *o*-C_6H_4Me, *p*-C_6H_4Me, and *m,m'*-$C_6H_3Me_2$).[238] Many other compounds were studied later.[239] The sensitising action of *p*-dimethylaminobenzylidene compounds was observed with CXXIX (R=H) and analogues with a 2,4-dioxothiazolidine, a thiohydantoin,

or an *N*-ethyl-2-oxoindoline nucleus, such compounds being made by use of *p*-dimethylaminobenzaldehyde and the appropriate ketomethylene compound. Methylation of CXXIX gave 5-*p*-dimethylaminobenzylidene-2-methylthio-4-oxothiazoline.[241] The compounds prepared by reaction of *p*-dimethylaminobenzaldehyde with 3-methyl-1-phenyl-5-pyrazolone[242] and with 3-methyl-5-oxo-2-thiothiazolidine[264] also sensitised. The sensitising action of such dyes was discovered independently.[243] Analogues with a 3-phenylrhodanine, 2,4,6-trioxohexahydropyrimidine, or 3-oxoindoline nucleus were described.[244] The absorption maxima of methanolic solutions of *p*-dimethylaminobenzylidene compounds having an indan-1,3-dione, 5-oxoisoxazoline, 2-oxoindoline, 4-oxo-2-thio-oxazolidine, pyrazolone, rhodanine, thiohydantoin, barbituric acid, or thiobarbituric acid nucleus were recorded.[88] *p*-Dialkylaminobenzylidene compounds with halogenated *N*-alkyl groups were described: such were CXLV (R^1=Me, R^2=CH_2CH_2Cl) or CXLVI (R^1=R^2=CH_2CH_2Cl); the aldehyde which gave the latter was also condensed

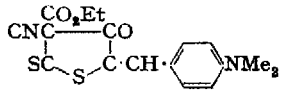


(CXLV)

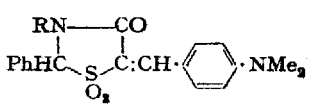


(CXLVI)

with *N*-methylindole in acetic acid.[20] The substances, CXLV (R^1=Me or Et, R^2=CH_2CH_2Cl; and R^1=R^2=CH_2CH_2Cl), the 6-ethoxy-derivative of CXLVI (R^1=Me, R^2=CH_2CH_2Cl), and the 6-chloro-4-methyl derivative of CXLVI (R^1=R^2=CH_2CH_2Cl), were prepared later.[22] The benzylidene compound, CXXX, was isolated as hydrobromide.[223] Its isomer, CXXXI, was obtained in 45% yield by heating 3,7a-diazaindan-1-one hydrochloride with *p*-dimethylaminobenzaldehyde and triethylamine in pyridine at 100° for 30 minutes.[224] Besides various types of merocyanines with a 3-carbethoxy-3-cyano-4-oxo-2-thiotetrahydrothiophene nucleus (see XIV-10-C.2d), CXLVII was described.[265] Together with dimethinmerocyanines having a sulphone group (see XIV-1), there were described two *p*-dimethylaminobenzylidene compounds, CXLVIII (R=Me or CH_2Ph), with this group.[266] 5-Oxo-1-



(CXLVII)



(CXLVIII)

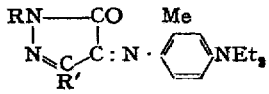
phenylimidazoline was condensed with *p*-dimethylaminobenzaldehyde (cf. XIV-1).[267] The reactivity of the methylene group in the 3-position of 2-methyl-4-oxo-1,2,3,4-tetrahydroisoquinoline was shown by its condensation with benzaldehyde and with *p*-dimethylaminobenzaldehyde; the latter stable product was orange, giving a colourless diperchlorate.[268]

The higher vinylene analogue of CXXIX (R=H) was prepared by condensing rhodanine with *p*-dimethylaminocinnamic aldehyde and had its sensitising maximum at 5800 Å.[241] The dye, CXXXII, with an α-methyl substituent, was prepared by heating *p*-dimethylaminobenzaldehyde and 4-isopropylidene-3-methyl-1-phenyl-5-pyrazolone with piperidine in ethanol.[245]

The bis-(*p*-dimethylaminobenzylidene) compound, CXXXIII, was prepared by heating 1,6-dioxojulolidine and *p*-dimethylaminobenzaldehyde with sodium hydroxide in aqueous ethanol for 15 minutes. Its orange needles gave a yellow solution in dioxan; there was no sensitising[246] (cf. section 4-F and IX-1).

F. Aza Analogues of Benzylidene Compounds and of a Bis-benzylidene Compound

Twenty-six azamethin dyes of type CXLIX were prepared from 2-amino-5-diethylaminotoluene and various pyrazolones by that method[269] which consisted in oxidising an alkaline solution of the



(CXLIX)

reactants with freshly precipitated silver chloride. They were purified by chromatography and recrystallisation, and resulted in 25–50 % yields. Their absorption was determined in cyclohexane, *n*-butyl acetate, and methanol.[250]

By boiling *p*-nitrosodiethylaniline and 2-oxoindoline in ethanol for 1 hour, with piperidine as catalyst, there resulted a 45 % yield of CXXXVI (R=R′=H). By use of *N*-substituted derivatives of the base, there were prepared CXXXVI (R′=H, R=Me, Et, Ph, Ac, OH, OMe, OAc, or OCH_2Ph). Absorption maxima varied from 4840 Å for CXXXVI (R=Me, R′=H), to 5160 Å for CXXXVI (R=Ac, R′=H).[251]

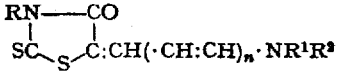
A similar procedure gave 5-substituted anils, such as CXXXVI (R=H, R'=NH_2, NHAc, or NO_2; R=Me, R'=NHAc, NO_2, Me, OH, or OMe; and R'=Br, R=H, Me, Et, Ph, or Ac), in yields varying from 33–70%. Absorption maxima varied from 4820 Å for CXXXVI (R=Me, R'=OH), to 5240 Å for CXXXVI (R'=NO_2, R=H or Me).[252]

A bis-aza compound, the analogue of CXXXIII in which both :CH· groups are replaced by :N·, resulted on gradually adding an aqueous solution of *p*-nitrosodimethylaniline hydrochloride at 60° to an aqueous ethanolic solution, also at 60°, of 1,6-dioxojulolidine containing sodium hydroxide; the product was recrystallised from acetone and gave blue-purple crystals (cf. section 4-F and IX-1).[246]

G. Hemioxonols

(*1*) *Methinhemioxonols*

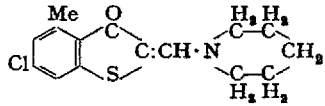
Methinhemioxonols with an anilinomethylene group were prepared in 1909 as yellow or red products, by heating 3-methyl-1-phenyl-5-pyrazolone, or other substituted pyrazolone, with diphenylformamidine.[203] The reaction with pyrazolones[270] was extended to isoxalones,[271] thiazolidones,[272,273] and 2-thio-4-imidazolones.[274] Subsequently 3-ethyl-(or phenyl-)rhodanine was condensed with diphenylformamidine by heating in kerosene and the anilinomethylene group was acetylated by means of triethylamine in acetic anhydride, and similarly with the product from 3-ethyl-4-oxo-2-thio-oxazolidine.[213] An acetanilidomethylene group was introduced directly into indan-1,3-dione by heating it with diphenylformamidine in acetic anhydride.[275] By heating the preceding acetanilidomethylene derivatives of rhodanines with piperidine in ethanol they were converted into CL (*n*=0, R=Et or Ph, R^1R^2=C_5H_{10}), whilst the dioxo-oxazolidine gave, with morpholine, 5-morpholylmethylene derivatives.[213] 4-Anilinomethylene-3-methyl-1-phenyl-



(CL)

5-pyrazolone was condensed with a phthalazine base to give a dimethinmerocyanine.[39] 2-Anilinomethylene-3-oxodihydrothianaphthene was used in the preparation of a symmetrical methinoxonol[235] and of di-

methinmerocyanines;[111–113,276,277] other dyes of the latter class were prepared through 5-acetanilidomethylenerhodanines[257,278,279] (see XIV-3-A), through the isomeric 4-acetanilidomethylene-5-oxo-2-thiothiazolidines,[261] and through 5-acetanilidomethylene-1,3-diethyl-2-thiobarbi-



(CLI)

turic acid.[280] The hemioxonol, CLI, was the main product in an attempt to prepare a methinoxonol by reaction of 6-chloro-2-formyl-4-methyl-3-oxodihydrothianaphthene and 2-oxodihydrothianaphthene in boiling ethanol containing piperidine.[256]

(2) *Trimethinhemioxonols*

Trimethinhemioxonols characterised by having a γ-anilinoallylidene group were prepared by heating together 1-anilino-3-aniloprop-1-ene hydrochloride, piperidine or triethylamine in ethanol, and a ketomethylene compound, such as 3-ethylrhodanine,—which gave CL (n=1, R=Et, R^1=H, R^2=Ph),—3-ethyl-2,4-dioxo-oxazolidine, 3-ethyl-4-oxo-2-thio-oxazolidine, or 3-ethyl-1-phenyl-2-thiohydantoin. Some corresponding γ-acetoanilidoallylidene compounds were prepared by heating 1-anilino-3-aniloprop-1-ene hydrochloride in acetic anhydride with a ketomethylene compound, such as 3-ethylrhodanine, —which gave CL (n=1, R=Et, R^1=Ac, R^2=Ph),—2-diphenylamino-4-oxothiazoline, or substituted pyrazolones; others were prepared by acetylating the anilinoallylidene compounds by heating with acetic anhydride.[213] A trimethinhemioxonol was prepared by boiling 3-oxodihydrothianaphthene and 1-anilino-3-aniloprop-1-ene hydrochloride with anhydrous sodium acetate in ethanol, and was used for preparing a symmetrical trimethinoxonol.[235] Absorption maxima of three γ-acetanilidoallylidene compounds lay at a shorter wavelength by 500–695 Å than those of the corresponding γ-anilinoallylidene compounds. One of them was used in the preparation of a dimethinmerocyanine.[260] By heating this type of acetanilidoallylidene compound in ethanol with a secondary amine, such as diethylamine, piperidine, or morpholine, products such as CL (n=1, R=Et, R^1=R^2=Et, or R^1R^2=C_5H_{10} or

C_4H_8O) were obtained,[213] and these were sensitisers.[215] In preparing tetramethinmerocyanines (see XIV-5-A), there were used the γ-acetanilidoallylidene derivatives of 3-ethylrhodanine[236] and of 1,3-diethyl-2-thiobarbituric acid,[280] and the γ-anilinoallylidene derivatives of 3-oxodihydrothianaphthene[277] and of 2-oxodihydrothianaphthene.[281,282]

(3) *Pentamethinhemioxonols*

Amongst sensitising cyclic compounds having a ketomethylene structure and a chain of conjugated double bonds were included the pentamethinhemioxonol, CL (n=2, R=H, R^1=Me, R^2=Ph), from rhodanine, and the corresponding compound from thiohydantoin.[241] They were prepared by the action of rhodanine or thiohydantoin with the methochloride of 5-anilo-1-methylanilinopenta-1,3-diene and sodium ethoxide in ethanol; the former was also obtained by reaction of rhodanine and 1-anilino-5-anilopenta-1,3-diene hydrochloride.[283] Pentamethinhemioxonols isomeric with CL (n=2, R=Et, or CH_2Ph, R^1=Ac, R^2=Ph), having a 5-oxo-2-thiothiazolidine nucleus, were sensitisers.[261] So was the compound prepared by condensing 1-anilino-5-anilopenta-1,3-diene hydrochloride with 2,4-dioxo-3-phenylthiazolidine, by means of piperidine in ethanol. A compound similarly made from 3-ethylrhodanine was acetylated by boiling with acetic anhydride. This acetanilido-compound on heating in ethanol with diethylamine, piperidine, or morpholine gave the pentamethinhemioxonols, CL (n=2, R=Et, R^1=R^2=Et, or R^1R^2=C_5H_{10} or C_4H_8O),[213] which were sensitisers.[215] A pentamethinhemioxonol with a 2-(5-anilino-1,3-pentadienyl) group was prepared from 3-oxodihydrothianaphthene and 1-anilino-5-anilopenta-1,3-diene.[235] Others were obtained from 3-methyl-1-phenyl-5-pyrazolone, or from 3-methylrhodanine, by boiling with the pentadiene hydrochloride and triethylamine in ethanol for 3–5 minutes;[211] yet another was prepared from 2-oxodihydrothianaphthene.[281] The pentamethinhemioxonol, CXI, was prepared by boiling 3-methyl-1-phenyl-5-pyrazolone and 2,4-dinitrophenylpyridinium chloride with triethylamine in ethanol; similar compounds were made from 3-methyl-1-*p*-sulphophenyl-5-pyrazolone and from thiobarbituric acid and they were used in preparing pentamethinoxonols.[216] 5-(5-Acetanilidopenta-2,4-dienylidene)-1,3-diethyl-2-thiobarbituric acid was used in preparing hexamethinmerocyanines,[280] as was CL (n=2, R=Et, R^1=Ac, R^2=Ph).[236,284]

(4) *Double Hemioxonols, etc.*

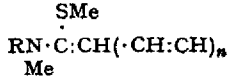
Certain double hemioxonols were prepared by condensing cyclic ketomethylene compounds, such as 2-allylrhodanine, barbituric acid, 3-methyl-1-phenyl-5-pyrazolone, 3-ethyl-4-oxo-2-thio-oxazolidine, and 2,4-dioxo-3-phenylthiazolidine, with hydrazine, *p*-phenylenediamine, etc.[285] Their silver salts were useful for anti-halation,[286] and some of the hemioxonols themselves were sensitisers.[287] In a patent on the sensitising action of the bases of double hemicyanines, the compound CXIII, which is both a dimethinhemicyanine and a methinhemioxonol, was said to sensitise strongly, with the maximum at 5100 Å.[193]

5. Dyes with an Open Chain Instead of a Cyclic Nucleus

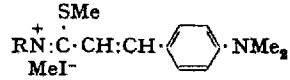
A. General Survey

Apart from the *p*-dialkylaminostyryl dyes (see section 1), which have only one heterocyclic nucleus and are, therefore, not regarded as true cyanines, there are certain other dyes which are related to cyanines but which do not have two heterocyclic nuclei.

In 1959, thioacetylbenzylamine, $PhCH_2 \cdot N{:}C(SMe) \cdot Me$, was prepared. Its methiodide was condensed with ethyl orthoformate, with 1-anilino-3-aniloprop-1-ene, and with 1-anilino-5-anilopenta-1,3-diene, to give dyes of formula CLII (n=0, 1, or 2, R=CH_2Ph), which were yellow, red, and blue-green, with absorption maxima at 4200 Å, 5800 Å, and 6300 Å, respectively. The methiodide was also condensed with *p*-dimethylaminobenzaldehyde to give the orange-red compound, CLIII

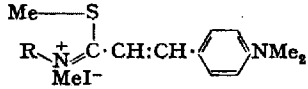


(CLII)



(CLIII)

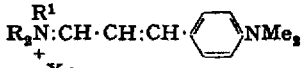
(R=CH_2Ph). The methiodide of thioacetylmethylamine was used in the preparation of CLII (n=0 or 1) and of CLIII (R=Me). By writing the open chain of the last as in CLIV, the relationship with dyes having



(CLIV)

a thiazoline nucleus was emphasised. The new dyes had their absorption maxima at a slightly shorter wavelength than had the thiazoline dyes; their sensitising action was similar.[133]

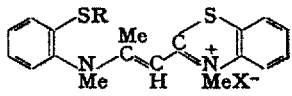
In 1942 filter dyes, which were completely removed during development, were patented; some of them were weak sensitisers. They were prepared by condensing *p*-dimethylaminocinnamic aldehyde with the salt of a secondary amine, and included eight examples of type CLV,



(CLV)

analogous with the higher vinylene analogues of styryl dyes (see section 1-N), also two analogous with the bis-compounds (section 5-B. Cf. 1-R).[288]

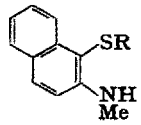
The behaviour of certain methylene bases in giving open-chain products is abnormal. The observation in 1890 that 1,3,3-trimethyl-2-methyleneindoline adds on methyl iodide, to give 2-ethyl-3,3-dimethylindolenine methiodide[289] perhaps needs reinvestigation. In 1925 it was suggested that the first product on reaction of 3-ethyl-2-methylenedihydroquinoline with benzyl iodide is benzylquinaldine ethiodide, though this undergoes further reactions to give dibenzylquinaldine ethiodide.[9] In 1939 addition of cyanogen bromide to 1,3,3-trimethyl-2-methyleneindoline gave 2-bromomethyl-2-cyano-1,3,3-trimethylindoline.[290] On the other hand, one mol. of methyl iodide added to two of 3-methyl-2-methylenebenzothiazoline to give an iodide.[291,292] The corresponding benzoselenazole compound was also made, and the 4,5-4′,5′-dibenzo-derivative of the benzothiazole one.[292] 3-Methyl-2-methylenebenzothiazoline exists as a dimer,[290] and the possibility that the new iodide was its methiodide was considered: it was rejected for various reasons, amongst them being the fact that such a formula would not



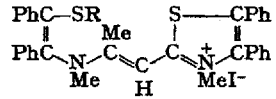
(CLVI)

account for the yellow colour of the iodide. The open-chain formula, CLVI (R=Me, X=I), does explain that, whilst both of them account for the hydrolysis of the iodide to 2-acetylmethylene-3-methylbenzo-

thiazoline.[291] An alternative formula, which was proposed on the basis of analysis,[292] does not explain the colour. The dimer 3-methyl-2-methylene-6,7-benzobenzothiazoline was treated with methyl or ethyl iodide to give the dibenzo-derivative of CLVI (R=Me or Et, X=I), both of which on hydrolysis gave 2-acetylmethylene-3-methyl-6,7-benzobenzothiazoline, together with CLVII (R=Me or Et). Addition of alkyl iodide to 4,5-diphenyl-3-methyl-2-methylenethiazoline gave CLVIII (R=Me or Et), the breakdown of which was studied. 3-Methyl-2-methylene-6-nitrobenzothiazoline did not give this type of salt either



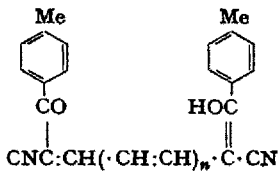
(CLVII)



(CLVIII)

with methyl iodide or methyl sulphate.[291] Reaction of 3-methyl-2-methylenebenzothiazoline with α-halogenoketones, $R' \cdot CO \cdot CH_2 \cdot X$, gave CLVI ($R=CH_2COR'$), and the 6,7-benzo-derivative behaved similarly. Reaction of 3-methyl-2-methylenebenzothiazoline with cyanogen bromide gave CLVI (R=CN, X=Br).[293] Subsequently additional evidence for the structure CLVI (R=Me, X=I), for the adduct from methylene base and methyl iodide, was provided by an examination of dyes prepared from it.[294]

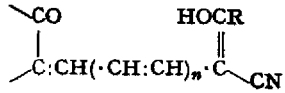
The structure characteristic of oxonols (see section 4) occurs also in open-chain compounds. Thus reaction of cyanoacetyl-*p*-toluene with ethyl orthoformate in acetic anhydride gave CLIX ($n=0$). One mol.



(CLIX)

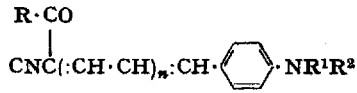
of cyanoacetyl-*p*-toluene was condensed with one of 1-anilino-5-anilopenta-1,3-diene hydrochloride, by heating with sodium acetate in ethanol, to give an intermediate compound, which was condensed with another mol. of the ketone, by heating in pyridine, to give CLIX ($n=2$), which had its absorption maximum at 6200 Å.[237] Dyes having an

oxonol structure, but with one end an open chain carrying an α-CN group, and the other a heterocyclic nucleus, comprised the structure CLX (n=0, 1, or 2, R=aryl or benzofuran); they were useful for anti-halation (section 5-C).[295]



(CLX)

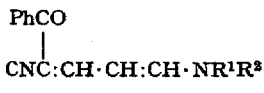
Not only was the aldehyde, p-OCH·C_6H_4·$\overset{Me}{N}$·CH_2CH_2CN, condensed with a 2-methyleneindoline (see section 1-A), but it was also condensed with ethyl cyanoacetate,[21] and aldehydes of type p-OCH·C_6H_4·$NR'CH_2CH_2Cl$ (R' = Me or Et), which were condensed with quaternary salts having a reactive methyl group (see section 1-A), were used similarly,[22] to give p-dialkylaminobenzylidene compounds of type CLXI (n = 0, R = OEt) (see section 5-D), which are open-chain



(CLXI)

compounds analogous with those of section 4-E. Subsequently a class of dyes, CLXI (n = 0 or 1, R = aryl), was described;[296] they were readily bleached by sulphite and were useful for anti-halation.[297]

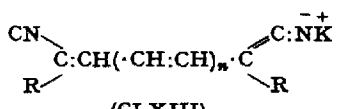
A patent on hemioxonols with the group :CH(·CH:CH)$_n$·NR^1R^2 (see section 4-G.1, 2, and 3) included open-chain compounds of type CLXII (R^1=H or Ac, R^2=Ph).[213] The acetanilido-group of such compounds, like that of their cyclic analogues, could be replaced by a piperidino-group (section 5-E).[214]



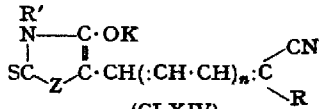
(CLXII)

In 1954 the observation was recorded that pyridine reacted with malonic dinitrile or with ethyl cyanoacetate, in the presence of alkali, to give a deep-red solution. Its absorption maximum lay at 5350 Å, whereas 1-anilino-5-anilopenta-1,3-diene absorbs at 4800 Å. Salts of

this type were named cyanomethins and they were formulated as CLXIII (n=2, R=CN or CO_2R').[298] They and other dyes of the same class, CLXIII (n=0, 1, or 2, R=CN or CO_2R'), possessed sensitising action, and were used in the form of their potassium salts.[299] By reaction of hemioxonols having the group $:CH(\cdot CH:CH)_{0-1}\cdot NRPh$ with malonic dinitrile or ethyl cyanoacetate and potassium hydroxide in ethanol, there resulted dyes, such as CLXIV (n=0 or 1), with one cyclic nucleus, and some of these were sensitisers.[300]



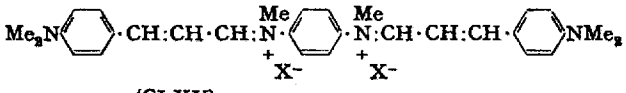
(CLXIII)



(CLXIV)

B. *p*-Dimethylaminocinnamylidene Salts

By heating methylaniline hydrochloride with *p*-dimethylaminocinnamic aldehyde in ethanol, and converting into iodide, there resulted CLV (R^1=Me, R^2=Ph, X=I), which gave very weak sensitising. The pink solution was bleached by developer. Analogues were CLV

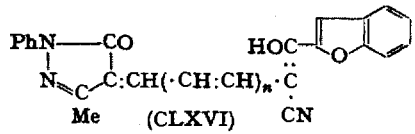


(CLXV)

(R^1=R^2=Ph, CH_2Ph, or β-$C_{10}H_7$), the first being perchlorate, the other two iodides, also CLV (R^1=Ph, R^2=CH_2Ph, X=I). Piperidine, morpholine, and 1,2,3,4-tetrahydroquinoline gave CLV (R^1R^2=C_5H_{10} C_4H_8O, or $C_9H_{10}N$), of which the last was isolated as iodide, the others as perchlorates. Condensation of *p*-dimethylaminocinnamic aldehyde with *NN'*-dimethyl-*p*-phenylenediamine dioxalate in ethanol gave CLXV (X=C_2O_4H). Similarly one mol. of piperazine hexahydrate was condensed with two of *p*-dimethylaminocinnamic aldehyde by heating with hydrochloric acid in aqueous ethanol.[288]

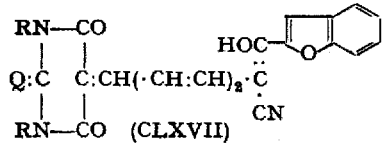
C. Oxonol Analogues

Dyes such as CLXVI (n=0) are analogous to methinoxonols. This yellow compound was prepared by heating 4-acetanilidomethylene-3-



(CLXVI)

methyl-1-phenyl-5-pyrazolone and 2-cyanoacetylbenzofuran with triethylamine in ethanol; an analogue with a *p*-tolyl, in place of a phenyl, group was made by the alternative route. Four dyes analogous to trimethinoxonols, but with only one heterocyclic nucleus, were described. Of these, CLXVI (n=1) was prepared from 4-acetanilidoallylidene-3-methyl-1-phenyl-5-pyrazolone and 2-cyanoacetylbenzofuran; one with a *p*-sulphophenyl, in place of a phenyl, group was reached through 2-(acetanilidoallylidenecyanoacetyl)benzofuran. An analogue of CLXVI (n=1) had a barbituric acid instead of a pyrazolone nucleus, whilst the fourth was analogous to CLXVI (n=1) but with 2,4-xylyl instead of benzofuran. Of ten examples analogous to pentamethinoxonols, some were prepared by one route and others by the alternative. The compound, CLXVII (Q=O, R=Et), was prepared from 1,3-diethylbarbituric acid and 2-(5-acetanilidopenta-2,4-dienylidenecyanoacetyl)-



(CLXVII)

benzofuran by heating with triethylamine in pyridine; its triethylamine salt gave a blue solution. Other such compounds were CLXVII (Q=O, R=*p*-C_6H_4OEt or *p*-C_6H_4OMe), and an analogue of the former with a 5-phenylbenzofuran nucleus. The dye, CLXVII (Z=S), was made, also its analogue with a phenyl group instead of benzofuran. Besides barbituric and thiobarbituric acids as in CLXVII, cyclic nuclei such as 1-ethyl-2-oxoindoline, 3-carboxymethyl-1-phenyl-5-pyrazolone, indan-1,3-dione, or 5-oxo-3-phenylisoxazoline were introduced.[295]

D. *p*-Dialkylaminobenzylidene Compounds

The compound, CLXI (n=0, R=OEt, R^1=Me, R^2=CH_2CH_2CN), was prepared by heating ethyl cyanoacetate and *p*-(*β*-cyanoethyl)-methylaminobenzaldehyde with piperidine in ethanol: it dyed acetate

silk a yellowish-green.[21] The dye, CLXI (n=0, R=Ph, R^1=R^2=Et), was prepared by heating benzoylacetonitrile and excess of *p*-diethylaminobenzaldehyde with piperidine in ethanol for 4 hours; compounds in which the phenyl group was substituted were described, also CLXI (n=0, R=*p*-C_6H_4·NH·CO·CH_2·CH_2·CO_2H or *p*-C_6H_4NH·SO_2Ph, R^1=R^2=Pr). A higher vinylene analogue, CLXI (n=1, R=Ph, R^1=R^2=Et), was prepared by heating benzoylacetonitrile and *p*-diethylaminocinnamic aldehyde with piperidine in ethanol.[206,207]

E. Hemioxonol Analogues

1-Anilino-3-aniloprop-1-ene hydrochloride and benzoylacetonitrile were heated with triethylamine in ethanol to give CLXII (R^1=H, R^2=Ph), which was acetylated by means of acetic anhydride containing triethylamine to yield CLXII (R^1=Ac, R^2=Ph).[212] The product, by heating with piperidine in ethanol, was converted into CLXII (R^1R^2=C_5H_{10}).[214]

F. Cyanomethin Dyes

Of cyanomethin dyes, an example of the simplest type was described, CLXIII (n=0, R=CN). Its higher vinylene analogue, CLXIII (n=1, R=CN), had its absorption and sensitising maxima at 4360 Å and 4700 Å, respectively. Again, two compounds, CLXIII (n=2, R=CN or CO_2Et), were described, of which the former had its absorption and sensitising maxima at 5400 Å and 5650 Å, respectively.[209]

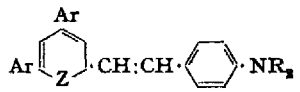
A dye with one heterocyclic nucleus and of the simplest type, CLXIV (n=0, Z=S, R'=Et, R=CN), was prepared by heating 5-anilomethylene-3-ethylrhodanine with malonic dinitrile and potassium hydroxide in ethanol; it had its absorption and sensitising maxima at 4490 Å and 4850 Å, respectively. A compound with a 3-methyl-1-phenyl-5-pyrazolone nucleus was made similarly, but the sodium salts of two others with different heterocyclic nuclei were made by an alternative route involving (dicyanomethylene-*N*-methyl)acetanilide. The higher vinylene analogue, CLXIV (n=1, Z=S, R'=Et, R=CN), prepared from 5-anilinoallylidene-3-ethylrhodanine and malonic dinitrile with potassium hydroxide in ethanol, had its absorption and sensitising maxima at 5290 Å and 5750 Å, respectively. Three other examples included the use of the alternative route, the introduction of other nuclei, and one instance of a reaction involving ethyl cyanoacetate.[300]

6. Cyanine Analogues Derived from Oxonium or Sulphonium Heterocyclic Salts

A. General

A few cyanine analogues in which oxygen, or sulphur, atoms take the place of NR in the heterocyclic nuclei are considered here.

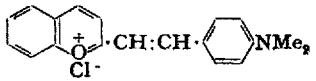
Oxonium salts are notably unstable: it was observed in 1911 that 2,4,6-trimethylpyrylium perchlorate is converted by ammonia into 2,4,6-trimethylpyridine.[301] In 1923 the reactivity of the 2-methyl group in a 4,6-diphenyl-2-methylpyrylium salt was demonstrated by its condensation with benzaldehyde;[302] the 4-methyl group likewise was reactive.[303] In a patent of 1935 there were described two *p*-diethylaminostyryl compounds of type CLXVIII (Z=O), prepared by virtue



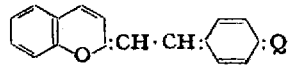
(CLXVIII)

of the reactive methyl group in 4,6-diaryl-2-methylpyrylium salts:[304] these are oxonium analogues of the styryl salts of section I-I. By the action of aniline their green colour changed to red owing to the formation of CLXVIII (Z=NPh).[304]

The reactivity of the 2-methyl group in 7-hydroxy-2-4,dimethylbenzopyrylium chloride had been recognized in 1916, when this salt was condensed with aldehydes, but all the products were isolated as ferric chloride double salts.[305] In 1922 various hydroxy-and methoxy-2-styrylbenzopyrylium chlorides were synthesised, under special conditions, from *o*-hydroxystyryl methyl ketones with aldehydes. Where a *p*-hydroxy-group was present, the red aqueous solution became blue on



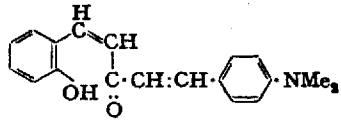
(CLXIX)



(CLXX)

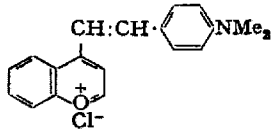
dilution. The greenish-yellow hydrochloric acid solution of the compound, CLXIX, likewise became blue. The colour change was attributed to a quinonoid structure, CLXX (Q=O or NMe_2Cl), the colours of anthocyanidins being explained similarly.[306] An additive product of

CLXXI[307] was oxidised to give the *p*-dimethylaminostyrylbenzopyrylium chloride, CLXIX.[308]

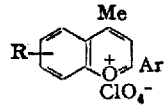


(CLXXI)

It was recorded in 1923 that 4-methylbenzopyrylium chlorides could, under special conditions, be condensed with aldehydes te give 4-styrylbenzopyrylium chlorides.[309, 310] In this series also, the red colour of salts with a *p*-hydroxy-substituent changed to blue, but only on addition of dilute alkali.[309] The 5,7-dimethoxy-2-phenyl derivative of CLXXII was isolated for analysis.[310]. Certain 2,4-distyrylbenzopyrylium salts were made from the corresponding 2,4-dimethyl salts, also

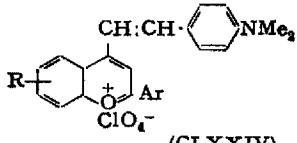


(CLXXII)



(CLXXIII)

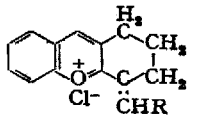
certain monostyryl salts, to which the 2-configuration was assigned. Those with a *p*-hydroxy-group became blue on addition of alkali.[311] In 1951 six 2-aryl-4-methylbenzopyrylium salts of type CLXXIII were synthesised. In one of them, which was rather unstable, the aryl group was *p*-dimethylaminophenyl,[312] and this may be regarded as a lower vinylene analogue of a *p*-dimethylaminostyryl salt. The other salts were



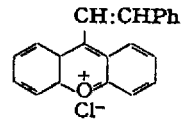
(CLXXIV)

condensed with *p*-dimethylaminobenzaldehyde to give six 4-*p*-dimethylaminostyrylbenzopyrylium salts of type CLXXIV. The absorption maxima of the green or blue-green substances were compared with those of the corresponding orange or red 2-arylbenzopyrylium or 2-aryl-4-methylbenzopyrylium salts.[313]

It was noted in 1912 that 3-methyl-1,2,3,4-tetrahydroxanthylium salts have a reactive 4-methylene group,[314] and in 1916 various salts of this kind were condensed with aldehydes to give compounds of type CLXXV, but these were all isolated as ferric chloride double salts.[305] In 1926 ten 9-styrylxanthylium salts of type CLXXVI were synthesised under anhydrous conditions.[315]



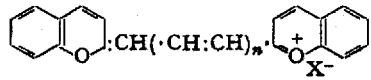
(CLXXV)



(CLXXVI)

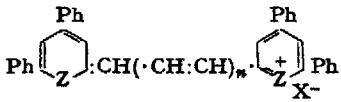
In 1932 twelve styryl derivatives of benzopyrylium or xanthylium salts were tested for photographic properties, but only two showed even a trace of sensitisation.[88] These were the 7-hydroxy-4-methyl derivative of CLXIX[311] and the 3,6-dihydroxy-derivative of CLXXVI.[315]

In 1938 the results of unpublished work on "pyrolocyanines", done in the previous eight years were summarised. The compound, CLXXVII (n=0), had its absorption maximum at a longer wavelength by 200 Å than that of a 2,2'-cyanine, whilst on comparing CLXXVII

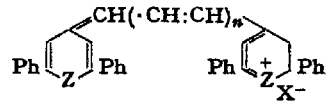


(CLXXVII)

(n=1) with a 2,2'-trimethincyanine, the bathochromic shift was as great as 960 Å for one of the three maxima. The methin- and trimethin-compounds, CLXXVIII (n=0 or 1, Z=O), were recorded as absorbing at a longer wavelength, by 1100 Å and 1600 Å, respectively, than the corresponding methin- and trimethin-cyanines having 1,2,4-triphenylpyridine nuclei. The absorption maxima of the heptamethin compound, CLXXIX (Z=O, n=3), were given as 7280 Å, 8220 Å, and 9380 Å. It was noted that these pyrylium dyes are less stable to hydrolysis than



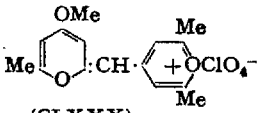
(CLXXVIII)



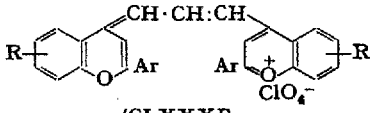
(CLXXIX)

are the cyanines,[316] so that it is particularly unfortunate that the methods of overcoming the experimental difficulties have not been communicated.

In 1946 2,6-dimethyl-4-oxopyran was converted, by means of methyl sulphate, into quaternary salts, which were regarded as 2,6-dimethyl-4-methoxypyrylium salts. Through its labile methoxy-group, such a salt condensed to give a red product, which was formulated as CLXXX,[317] a methincyanine analogue.



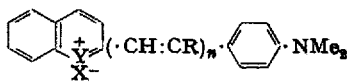
(CLXXX)



(CLXXXI)

In 1951 the condensation of two 2-aryl-4-methylbenzopyrylium salts with ethyl orthoformate, to give two trimethincyanine analogues of type CLXXXI was described.[318]

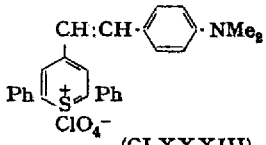
Further absorption maxima, including those of sulphonium salts, were published in 1945, but again without supporting experimental data. The sulphonium compounds were recorded as absorbing at a longer wavelength than the oxonium compounds. When a *p*-NMe_2 group was introduced into styryl salts of different series, to give CLXXXII (n=1, R=H, Y=NMe, O, or S), the bathochromic shifts



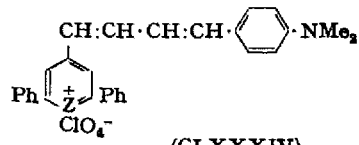
(CLXXXII)

were 1000 Å, 2500 Å, and 3600 Å, respectively. The compound, CLXXXII (n=0, Y=S, R=H), had its absorption maximum at 5900 Å, whilst CLXXXII (n=1, R=Ph, Y=NMe, O, or S) had their maxima at 5320 Å, 7220 Å, and 8320 Å, respectively. The bathochromic shift of 2420 Å, on introducing the group :CH·CPh: into CLXXXII (n=0, Y=S) was abnormally great.[318] In 1956 various 2,4,6-triarylpyrylium salts were converted into the corresponding 2,4,6-triarylthiopyrylium salts, including *p*-dimethylaminostyryl salts, such as CLXXXIII and type CLXVIII (Z=S), also a bis-styryl salt.[319] CLXXXIII was also prepared by use of *p*-dimethylaminobenzaldehyde, whilst the *p*-dimethylaminophenylbutadienyl salts, CLXXXIV (Z=S

or O), were prepared by use of *p*-dimethylaminocinnamic aldehyde.[320] For three *p*-dimethylaminostyryl salts with a thiopyrylium nucleus the absorption maxima were at a longer wavelength, by 350–420 Å, than

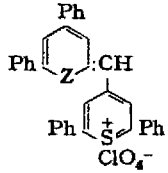


(CLXXXIII)

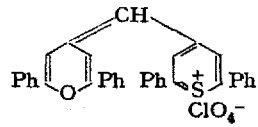


(CLXXXIV)

those of the corresponding salts with a pyrylium nucleus.[319] Methin- and trimethin-cyanine analogues, CLXXIX (n=0 or 1, Z=S, X=ClO_4), so-called "thiopyrolocyanines", were prepared from 4-methyl-2,6-diphenylthiopyrylium perchlorate; their absorption maxima, in acetone, were at 6280 Å and 7530 Å, respectively. The trimethincyanine analogue, CLXXVIII (n=1, Z=S), prepared from 2-methyl-4,6-diphenylthiopyrylium perchlorate, absorbed at 8200 Å, i.e., at a longer wavelength than any unsubstituted trimethincyanine. Three types of unsymmetrical methin compounds were also made, viz. CLXXXV (Z=O or S) and CLXXXVI. All four methin compounds were prepared by



(CLXXXV)



(CLXXXVI)

condensation of a diphenyl-pyrylium, or -thiopyrylium, salt, having a reactive methyl group, with 4-oxo-2,6-diphenylthiopyran,[320] a reaction which is without analogy in the methincyanine series.

B. Compounds with a Pyrylium, Benzopyrylium, or Xanthylium Nucleus

(*I*) p-*Dialkylaminostyryl Salts and* p-*Dimethylaminophenylbutadienyl Salts*

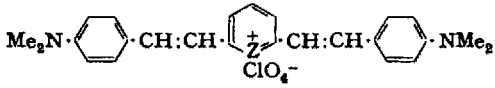
The green salt, CLXVIII (Z=O, Ar=C_6H_4OMe, R=Et), was produced by heating 4,6-dianisyl-2-methylpyrylium sulphoacetate with *p*-diethylaminobenzaldehyde in acetic anhydride, and treating with sodium perchlorate. Aniline converted it into the red CLXVIII (Z=

NPh, Ar=C_6H_4OMe, R=Et). A sulphoacetate corresponding with CLXVIII (Z=O, Ar=Ph, R=Et) was precipitated by ether as an oil and converted by aniline or methylamine into CLXVIII (Z=NPh or NMe, Ar=Ph, R=Et).[304]

Various hydroxy- and methoxy-2-styrylbenzopyrylium chlorides were prepared by condensation of an *o*-hydroxystyryl methyl ketone with an aldehyde, in the presence of formic acid and hydrogen chloride; the unstable chlorides were recrystallised from formic acid, but were not obtained free from adduct.[306] Reaction of *o*-hydroxystyryl methyl ketone, *p*-dimethylaminobenzaldehyde, and sodium hydroxide in aqueous ethanol gave a blood-red colour, but CLXXI could only be isolated as an additive product.[307] Its oxidation with ferric chloride and hydrogen chloride in ethanol gave the benzopyrylium salt, CLXIX, which was recrystallised from glacial acetic acid.[308]

4-Styrylbenzopyrylium chlorides were best prepared by condensation of 4-methylbenzopyrylium chlorides with aldehydes by passing dry hydrogen chloride into a hot alcoholic solution, being obtained in 50–60 % yields.[309] This method was applied to a series of such salts having 5,7-dimethoxy substituents.[310] Many years later, 2-aryl-4-methylbenzopyrylium salts of type CLXXIII (Ar=2,4-di$MeOC_6H_4$, 2,4-diOHC_6H_4, or 4-$OHC_{10}H_6$, R=7-OH, 7-NMe_2, or 7,8-diOH) were condensed with *p*-dimethylaminobenzaldehyde, by heating in acetic acid and acetic anhydride containing a little pyridine, to give six derivatives of type CLXXIV. They were recrystallised from acetic acid containing acetic anhydride (4:1), and the absorption maxima in ethanol containing perchloric acid were recorded.[313]

A bis-styryl salt, CLXXXVII (Z=O), had its absorption maximum at 7250 Å.[319]



(CLXXXVII)

A *p*-dimethylaminophenylbutadienyl compound, CLXXXIV (Z=O), was made by heating 4-methyl-2,6-diphenylpyrylium perchlorate with the cinnamic aldehyde in acetic anhydride; its absorption maximum was at 7550–7600 Å.[320]

Ten 9-styrylxanthylium salts of type CLXXVI were prepared by passing dry hydrogen chloride into an ethereal solution of the 9-methylxanthenol and the aldehyde.[315]

Non-diffusing, intensely coloured, compounds suitable for anti-halation layers included *p*-diethylamino-3,6-dihydroxy-derivatives of the xanthylium salt CLXXVI,[321] pyrylium salts of type CLXVIII (Z= O), a benzopyrylium salt of type CLXXIV, and its higher vinylene analogue.[322]

(*2*) *A Methincyanine Analogue with Pyrylium Nuclei*

On boiling 2,6-dimethyl-4-methoxypyrylium perchlorate with sodium acetate or triethylamine in methanol for 15 minutes, there resulted CLXXX, which could be recrystallised from methanol.[317]

(*3*) *Trimethincyanine Analogues with Benzopyrylium Nuclei*

The two compounds, CLXXXI (Ar=*o*,*p*-$C_6H_4(OH)_2$, R=7-OH; and Ar=*o*,*p*-$C_6H_4(OMe)_2$, R=7, 8-diOH), were prepared by heating the appropriate benzopyrylium perchlorate and ethyl orthoformate in a mixture of acetic acid and acetic anhydride, containing a little pyridine, at 100° for 15 minutes; they were recrystallised from an acetic acid/ anhydride mixture. Their absorption maxima in ethanol containing perchloric acid lay at 6950 Å and 7450 Å, respectively.[318]

C. Compounds with a Thiopyrylium Nucleus

(*1*) p-*Dimethylaminostyryl Salts and a* p-*Dimethylaminophenylbutadienyl Salt*

p-Dimethylaminostyrylthiopyrylium salts were prepared from the corresponding pyrylium salts by the action of sodium sulphide in aqueous acetone, followed by acidification with perchloric acid. Those prepared were CLXXXIII, CLXVIII (Z=S, Ar=Ph, R=Me), and its *p*-methoxy-analogue, and CLXVIII (Z=S, Ar=*p*-C_6H_4OMe, R=Me), and also the bis-styryl salt, CLXXXVII (Z=S), which had its absorption maximum at 7550 Å.[319] The first of the three styryl salts was also prepared from 4,6-diphenyl-2-methylthiopyrylium perchlorate and *p*-dimethylaminobenzaldehyde.[320]

The *p*-dimethylaminophenylbutadienyl compound, CLXXXIV (Z=S), was made by use of *p*-dimethylaminocinnamic aldehyde in acetic anhydride; it absorbed at 6900 Å.[320]

(2) *Methin- and Trimethin-cyanine Analogues with Thiopyrylium Nuclei*

The methin compound, CLXXIX (n=0, Z=S), was prepared by reaction of 4-methyl-2,6-diphenylthiopyrylium perchlorate with 4-oxo-2,6-diphenylthiopyran in acetic anhydride; the unsymmetrical analogue, CLXXXVI, was made similarly by use of 4-methyl-2,6-diphenylpyrylium perchlorate. The other unsymmetrical methin compounds, CLXXXV (Z=S or O), were prepared by reaction of 2-methyl-4,6-diphenyl-thiopyrylium, or -pyrylium, perchlorate with the same 4-oxothiopyran.[320]

The trimethin compounds, CLXXIX or CLXXVIII (n=1, Z=S), were prepared by reaction of 4-methyl-2,6-diphenyl-, or 2-methyl-4,6-diphenyl-, thiopyrylium perchlorate and ethyl orthoformate in acetic anhydride containing a little pyridine.[320]

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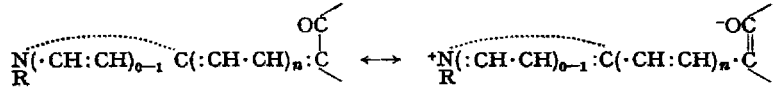
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CHAPTER XIV

Merocyanines

1. General Survey

The literature of the merocyanines is so vast that they might well form the subject of a separate book, but are perforce included here because of their bearing on trinuclear cyanines (see Chapter XV). They are non-ionic compounds comprising the structure

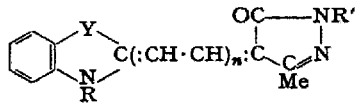


where n=0–3, and may be regarded as a cross between a cyanine and an oxonol. Their name was given because they were prepared from cyanine intermediates ($\mu\epsilon\rho o\varsigma$ = part) but in German patents the term neutrocyanines is used. In recent Russian literature, merocyanines in which the nuclei are directly linked have been called zeromethinmerocyanines. The merocyanines were discovered independently, about 1933, in America, England, and Japan, and the enormous development of the subject in the first two countries is apparent from the patent literature. Whereas in a true cyanine the methin chain which links the nuclei is odd-numbered, in simple merocyanines the nuclei are directly linked (eqn. above; n=0). Some of these are valuable sensitisers but the dimethinmerocyanines (n=1) are especially so. The difficulty of making tetra- and hexa-methinmerocyanines (n=2 or 3) is reflected in the comparatively small amount of information concerning them, and the six-membered chain is the longest which has been attained in merocyanines of the normal type, although octamethinmerocyanines, in which three members of the chain are cyclic, have recently been described (see section 9-A.4). Di-, tetra-, and hexa-methinmerocyanines have also been called mero-, merodi-, and merotri-carbocyanines.

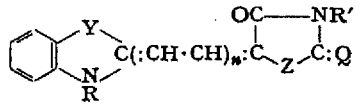
In the British discovery, sensitisers prepared from heterocyclic

compounds comprising the structure $H_2C{\cdot}\overset{\cdots}{\underset{\cdots}{C}}{\cdot}NR$ with a reactive methylene group included *p*-dimethylaminobenzylidene compounds (see XIII-4-E), simple merocyanines, and dimethinmerocyanines.[1] For preparing the merocyanines (see section 2), the other reactant was a quaternary salt having an alkylthio-group, such as had been used in the synthesis of methincyanines (see II-4), whilst for dimethinmerocyanines (see section 3-A) it was a salt having the group ·CH:CH·NRPh, such as had been used in synthesising trimethincyanines (see V-6). Alternatively dimethinmerocyanines were prepared by condensing a quaternary salt having a reactive methyl group with a methinhemioxonol (see XIII-4-G.1) having the group :CH·NRPh (see section 3-A).[2] Quaternary salts having a reactive alkylthio-group or iodine atom, or a *β*-acetanilidovinyl group, were moreover used in the preparation of mero- and dimethinmero-cyanines, respectively, in which the second nucleus was carbocyclic.[3] Just as quaternary heterocyclic salts having the group ·CH:CH·SR[4] or CH:CH·CH:CH·SR[5] could be condensed with others, having a reactive methyl group, to give, respectively, tri- and penta-methincyanines (see V-10 and VII-3), so they reacted with cyclic ketomethylene compounds to give dimethinmerocyanines[6,7] (see section 3-B) and tetramethinmerocyanines (see section 5-B).[8]

Another method of preparing dimethinmerocyanines, such as I ($n=1$) with a 5-pyrazolone residue, or II ($n=1$, Q=S, Z=S or O) with a rhodanine or 4-oxo-2-thio-oxazolidine residue (see section 3-E), including compounds with a *β*-substituent on the chain (see section 8-A.5),



(I)

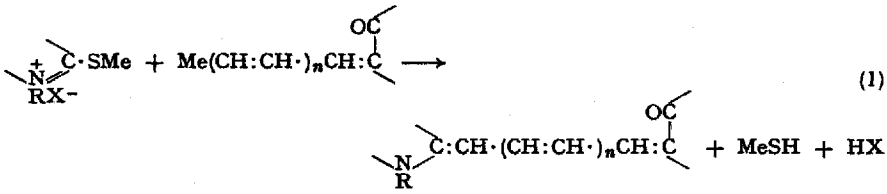


(II)

consisted in reaction of the ketomethylene compound, a quaternary salt having a methyl group, and an ortho-ester: it was remarkable that only small amounts of trimethincyanines or methinoxonols occurred as by-products.[9] Subsequently formamide, which had been used for providing a methin link in trimethincyanines (see IV-12) and in methinoxonols (see XIII-4-B) was found especially useful for synthesising dimethinmerocyanines, and diethoxymethyl acetate, which was used in the preparation of trimethincyanines (see IV-13), was applied to that of a dimethinmerocyanine (see section 3-E). Somewhat analogous

to such condensations is the reaction of a quaternary salt having a 2-methyl group, a ketomethylene compound, and a substance providing a pentamethin chain, which was used later to give a hexamethinmerocyanine (see section 6-D).

An interesting method, recorded in 1939, for preparing di- or tetra-methinmerocyanines, consisted in condensing a heterocyclic compound, having the structure $>C:CH\cdot CH_3$ or $>C:CH\cdot CH:CH\cdot CH_3$ adjacent to CO, with a 2-methylthiobenzothiazolium salt (see sections 3-F and 5-C) (equation 1). Moreover dimethinmerocyanines with substituents on the chain were described: one with an α-substituent, rela-



(1)

tive to the quaternary salt residue, was obtained by use of a heterocyclic compound having the group $:CH\cdot CH_2Ph$ (see section 8-B.3) and others with a β-substituent by use of compounds having the group :CRMe (see section 8-A.6).[10] The method was subsequently developed, to give β-OR- and β-SR-dimethinmerocyanines (see section 8-A.6) and, by use of a quaternary salt having the group $\cdot(CH:CH\cdot)_nNAcPh$, instead of SMe, gave δ-OR- and δ-SR-tetramethinmerocyanines (see section 8-D.3) and a δ-OEt-hexamethinmerocyanine (see section 8-F).

The American discovery of the sensitising action of merocyanines was first published in a patent, containing examples of four simple merocyanines and fifteen dimethinmerocyanines. The substances of the former type were made by reaction of heterocyclic ketomethylene compounds with 2-iodopyridinium or 2-iodoquinolinium salts, which had been used in preparing methincyanines (see II-2),[11] or with 2-alkylthio-quaternary salts of quinoline and other bases.[12] Many years later, from Russia, came a method of preparing simple merocyanines (see section 2) through the reactive imino-group of a heterocyclic compound, which was used in the preparation of methincyanines (see II-5) and of an azamethin base (see XII-8-A), and from France there was added a preparation from 2-alkylsulphonates of quaternary heterocyclic salts, or the corresponding betaines (see section 2), which were used in the synthesis of methincyanines (see II-2). Analogous with the preparation

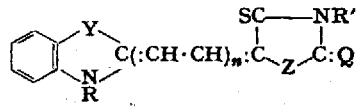
of 4′-cyanines by reaction of a quinolinium salt with a quaternary salt having a methyl group (see II-1) was one preparation of a simple merocyanine, having a 4-linked quinoline nucleus, from a quinolinium salt and a cyclic ketomethylene compound (see section 10-A.2a).

In America, dimethinmerocyanines were prepared from heterocyclic ketomethylene compounds either by their condensation with *N*-alkyldihydro-heterocyclic bases having a formylmethylene group (see section 3-C),[13] such as had been used in the preparation of trimethincyanines (see VI-8), or with quaternary salts having a *β*-anilinovinyl group (see section 3-A).[14] From Germany there came what was described as an improvement on the former method. It consisted in conversion of the group :CH·CRO to :CH·CRSe, whence there were prepared quaternary salts, having the group ·CH:CR(SeR′), which gave good yields in condensations. The method is analogous to that in which salts with the group ·CH:CH·SR are used (see section 3-B): it also gave *β*-substituted dimethinmerocyanines (see section 8-A.2). It is interesting that, at an early date, the first hexamethinmerocyanines, recorded from Germany, were prepared by use of *N*-alkyldihydro-heterocyclic bases, having the group :CH·CH:CH·CH:CH·CHO (see section 6-B),[15] which had been used in the preparation of heptamethincyanines (see VIII-4). The preparation of hexamethinmerocyanines from a pentamethinhemioxonol having the group :CH·CH:CH·CH:CH·NHR (XIII-4-G.3) and a salt having a methyl group followed later (see section 6-A).

In America, a comprehensive account of the merocyanines, which included the subject matter of the patents, was published in 1951.[16,17] Here also there was an instance of a preparation of a merocyanine involving a reaction with quinoline ethiodide and potassium hydroxide[18] by a method analogous to that of chapter II, 1. Thirteen different types of heterocyclic nuclei derived from quaternary salts were introduced and the numerous ketomethylene compounds included some in which this structure formed part of an open-chain system (see section 13). Details of syntheses were given for seven simple merocyanines, twenty-three dimethinmerocyanines, one tetra-, and one hexa-methinmerocyanine. Dimethinmerocyanines with a *β*-substituent on the chain (see section 8-A.2) were also described.[16] Synthetic details were further given for one merocyanine, forty-two dimethinmerocyanines, eleven tetramethin merocyanines, and two hexamethinmerocyanines, with absorption data for forty-two di- and nine tetra-methinmerocyanines.[17]

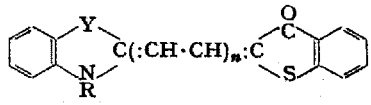
Dimethinmerocyanines with a 3-oxodihydrothianaphthene,[18] or with a barbituric or thiobarbituric acid nucleus[19] might be used as sensitisers or as filter dyes. At a later date di-, tetra-, and hexamethinmerocyanines with one benzimidazole and one thiobarbituric acid nucleus were prepared[20] (see sections 3-A, 5-A, and 6-A). Di- and tetra-methinmerocyanines with a 4-oxo-2-thio-oxazolidine nucleus included compounds said to be useful as filter dyes and for dyeing textiles,[21] and dimethinmerocyanines with a similarly substituted thiazolidine nucleus—rhodanines—were sensitisers.[22] Sensitisation for the far-red and infrared was attained by means of hexamethinmerocyanines, II (n=3, Q=S, Z=O or S), having one of these last two nuclei.[23] Di- and tetra-methinmerocyanines, II (n=1 or 2, Q=O, Z=NR″), with a hydantoin nucleus were described as useful for sensitisers and light filters, and the former type could be used for dyeing textiles. From 2-thiohydantoins there were prepared II (n=1 or 2, Q=S, Z=NR″).[24]

Not only that, but through 4-thiohydantoin there were prepared III (n=1, Y=S, Q=O, Z=NH), in which the cyclic CO group is replaced by CS.[24] 3-Methyl-1-phenyl-5-thiopyrazolone had been used



(III)

similarly.[11] Several years later, the CO group of certain dimethinmerocyanines, including β-substituted dyes, was converted to CS by the action of phosphorus pentasulphide (see section 4).[25] The preparation of a simple merocyanine from 3-ethyl-4-thiorhodanine has been mentioned (see section 10-C.1e) and that of an oxonol with one CS group has been noted (see XIII-4-A).

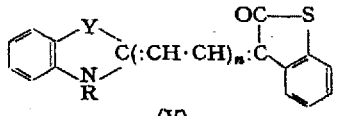


(IV)

The sensitising action of various dimethinmerocyanines, IV (n=1), having a 3-oxodihydrothianaphthene residue, was recorded in Japan in 1934.[27] Subsequently the absorption maxima of four such dyes of

the benzothiazole series, IV (n=0, 1, 2, or 3, Y=S), were compared;[28] their sensitising action was patented.[29] The effect of constitution on the colour of merocyanines having a 3-oxodihydrothianaphthene nucleus was studied (see section 12).

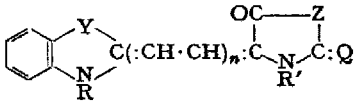
Through 3-formyl-2-oxodihydrothianaphthene[30] and quaternary salts having a reactive methyl group, dimethinmerocyanines, V (n=1),



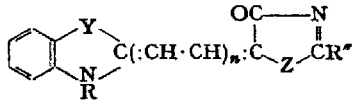
(V)

with that nucleus were made (see section 3-C). The thirty-two tabulated included four with a substituent on the chain.[31,32] A simple merocyanine[31] and tetra- and hexa-methinmerocyanines[33,34] were also described.

Compounds isomeric with rhodanines, namely 3-alkyl (or -cyclohexyl)-5-oxo-2-thiothiazolidines, were synthesised,[35–38] and were used for preparing merocyanines, di- and tetra-methinmerocyanines, and a hexamethinmerocyanine, of types VI (n=0–3, Q=Z=S), which were sensitisers.[38,39]

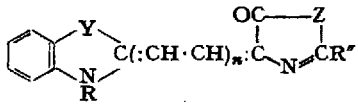


(VI)



(VII)

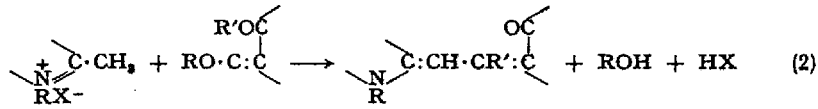
Mero- and dimethinmero-cyanines having a 2-alkylthio-4-oxo-oxazoline or -4-oxothiazoline nucleus, of type VII (Z=O or S, R″=SR), were prepared by alkylation of those of type II (Q=S, Z=O or S, R′=H).[22] Similarly those having a 2-alkylthio-4-oxoimidazoline nucleus, of type VIII (Z=NR′, R″=SR‴), were prepared by alkylation of those of type II (Q=S, Z=NH).[24]



(VIII)

By heating a 2-β-acetanilidovinyl quaternary salt with an acylaminoacetic acid, sodium acetate, and acetic anhydride, there resulted,

through substituted 5-oxo-oxazolines, dimethinmerocyanines of type VIII ($n=1$, $Z=O$), which were sensitisers.[16,26] Another method depended on 5-oxo-oxazolines having in the 4-position the group :CH·OR[40] or :CR'(OR),[41] which were condensed with salts having a reactive methyl group to give dimethinmerocyanines of type VIII ($n=1$, $Z=O$)[42] (see section 3-D) and their β-substituted derivatives (see section 8-A.4) (equation 2).



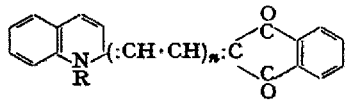
(2)

Through 5-oxo-oxazolines and 5-oxothiazolines, having a 4-ethoxymethylene and a 2-SR-substituent, there were prepared dimethinmerocyanines of type VIII ($n=1$, $Z=O$ or S, $R''=SR'''$), which were intensely coloured, and in which the normal instability of these nuclei seemed to be almost completely suppressed.[43] Subsequently a comparison was made of fourteen dimethinmerocyanines, in which different heterocyclic nuclei were coupled with a 3-methyl-5-oxo-2-phenyloxazoline residue (see section 3-D),[44] besides others with a β-methyl group on the chain (see section 8-A.4). A comparison was made of forty dimethinmerocyanines having a 5-oxothiazoline nucleus with a 2-SR-substituent, whilst two merocyanines and a tetramethinmerocyanine comprising this structure were also described.[44,45] They were non-wandering sensitisers.[45] Numerous dimethinmerocyanines with a 2-acylamino-5-oxothiazoline nucleus were compared, also a mero- and a tetramethinmero-cyanine with this nucleus.[44,46] Comparisons were also made in series of fourteen and twenty-eight dimethinmerocyanines having, respectively, a 2-NR^1R^2 or a 2-OR'-substituent in a 5-oxothiazoline nucleus. They were prepared either from a ketomethylene compound (see section 3-A) or from the 4-ethoxymethylene derivative of such a compound (see section 3-D).[44] To the absorption maxima of four series of dimethinmerocyanines having a 5-oxothiazoline nucleus with NHAc, SEt, NEt_2, or OEt in the 2-position, were added data for another series of seven compounds having that nucleus with a 2-NHEt group. Various properties were tabulated for numerous dimethinmerocyanines with a 2-NHR^1 group, and several of them were acylated.[47]

In the 4-oxo-2-thioimidazolidine series, 1-acyl-3-alkyl(or -aryl)-2-thiohydantoins were synthesised and were condensed with quaternary

salts having a β-acetanilidovinyl group, to give dimethinmerocyanines, of type II (n=1, Q=S, Z=N·COR'), which sensitised. Twenty such were described, also a mero- and a tetramethinmero-cyanine with a nucleus of this kind. Their absorption maxima were compared with those of analogues unsubstituted in the 1-position. The physical properties were tabulated for thirty-eight dimethinmerocyanines having a 1-, a 3-, or a 1,3-substituted-2-thiohydantoin nucleus.[47,48] 1,2-Disubstituted 4- or 5-oxoimidazolines were synthesised and were used in the preparation of dimethinmerocyanines (see sections 3-A and C), a merocyanine (see section 2) and a tetramethinmerocyanine (see section 5-A). The quaternary salt of a 4-oxoimidazoline was also used to give the salt of a dimethinmerocyanine (see section 3-C).[49]

A dye first made in 1882 was classed in 1951 as a simple merocyanine. Quinoline Yellow was the sulphonic acid of a yellow substance, which was first obtained by heating quinaldine and phthalic anhydride.[50] This dye was also called Quinophthalone.[51] To it there was assigned, in 1935, formula IX (n=0, R=H), which explained its conversion into an



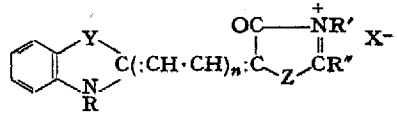
(IX)

N-methyl derivative, with a similar absorption curve. The latter was fairly soluble in water and was abnormal in absorbing at a longer wavelength in chloroform than in water. The analogous *N*-methyl compound with a 2-linked pyridine instead of a 2-linked quinoline nucleus was also prepared.[52] When, many years later, it was pointed out that the compound IX (n=0, R=Me) is a merocyanine, it was prepared by condensation of a 1-methyl-2-phenylthioquinolinium salt with indan-1,3-dione, whilst the pyridine analogue was similarly reached through 2-iodopyridine methiodide. The dimethin compounds corresponding with these two merocyanines were also made (see sections 2 and 3-A).[53]

A dimethinmerocyanine might be formed by the rupture of another dye molecule (see section 3-G). In the first instance of this kind, the molecule of a methinoxonol, having two pyrazolone nuclei, was split by heating with a quaternary salt having a reactive methyl group.[54] Secondly, the molecule of a 4,4'-carbocyanine was ruptured by 3-methyl-1-phenyl-5-pyrazolone giving a dimethincyanine[55] in a similar

way to the rupture of molecules of trimethincyanines when heated with quaternary salts having reactive methyl groups (see V-12). A dimethinmerocyanine was also produced on heating a mixture of a trimethincyanine and a methinoxonol with formamide.[56]

Salt formation in the merocyanine series (see section 7) was noted in 1936, when it was observed that alkylthio-quaternary salts, X (n=0 or 1, Z=S or O, R″=SAlk), were produced by the action of esters on simple mero- and dimethinmero-cyanines, II (n=0 or 1, Q=S, Z=S or 0), including chain-substituted derivatives of the latter, which possessed a rhodanine, or the corresponding oxazolidine nucleus. Through the reactivity of the alkylthio-group, trinuclear dyes were derived (see XV-5).[57] Independently, dimethinmerocyanines, which were prepared by condensing rhodanines with *N*-alkyldihydro-heterocyclic bases, having a 2-formylmethylene group (see section 3-C), were converted into water-soluble salts by alkyl sulphates, the absorption maxima thereby shifting to a longer wavelength.[58] The conversion of mero- and dimethinmero-cyanines, having an $-\underset{R}{N}\cdot C{:}S$ group, into salts, having the structure $-\overset{+}{\underset{RX^-}{N}}{:}C\cdot SR$, was conveniently effected by heating with an ester in nitrobenzene. Some of the salts had sensitising properties.[59] Not only was the salt, X (n=1, Y=Z=S, R=Et, R′=Me, R″=SMe,



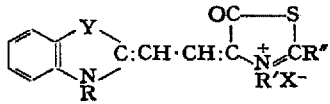
(X)

X=SO_4Me), prepared from II (n=1, Y=Q=Z=S, R=Et, R′=Me), by the action of methyl sulphate, but it was also prepared from VII (n=1, Y=Z=S, R=Et, R″=SMe), again by the action of methyl sulphate.[60]

By the action of ethyl malonate, the ·SR group of the salts was converted into $\cdot CH(CO_2Et)_2$, which could be hydrolysed to $\cdot CH_3$, and these salts also could be used in the synthesis of trinuclear dyes.[61] In the merocyanine series, a salt with a methylthio-group reacted with ethyl acetoacetate, etc., whereby merocyanines having the group $:C(COMe)(CO_2Et)$, etc., resulted; these also were hydrolysed to the salt having a methyl group. This salt could be converted into a methylene base; phenyl isothiocyanate converted the $:CH_2$ group of that mero-

cyanine into :CH·CS(NHPh), whilst carbon disulphide converted it into :CH·CS(SH). The last compound was converted by a methyl ester into a salt with the group ·CH:C(SMe)$_2$.[62] By the action of sodium selenide on quaternary salts having an alkylthio-group, prepared from mero- and dimethinmero-cyanines with a CS group, there resulted analogues with a CSe group, and these new compounds were especially useful in extending the sensitising range. The examples included two dimethinmerocyanines with a β-methyl group.[63]

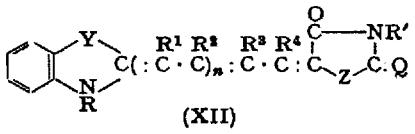
It was noted in 1949 that quaternary salts of merocyanines having an alkylthio-group were not improved by recrystallisation, and this instability was still more marked with salts, such as X (n=1, Y=Z=S, R″=SR‴), of dimethinmerocyanines, and was attributed to opening of the rhodanine nucleus.[64] Later work indicated that rupture of the nucleus does not occur, but that the decomposition products are dimethinmerocyanines in which the CS group of the original rhodanine nucleus has been replaced by CO.[60,65] When a salt, such as XI (Y=S,



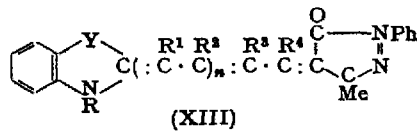
(XI)

R″=SR‴), having a 5-oxothiazolinium nucleus, and isomeric with X (n=1, Y=Z=S, R″=SR‴), was treated with primary amines, a complex series of reactions occurred and the products isolated comprised substances formed by opening the five-membered ring of the dimethinmerocyanines.[66] Salt formation of another kind occurred by reaction of esters with dimethinmerocyanines, VIII (n=1, Z=S, R″=NR^{1}R^2), in which a 5-oxothiazoline nucleus carried a substituted 2-amino-group, and the salts of type XI (R″=NR^{1}R^2) were sensitisers.[67]

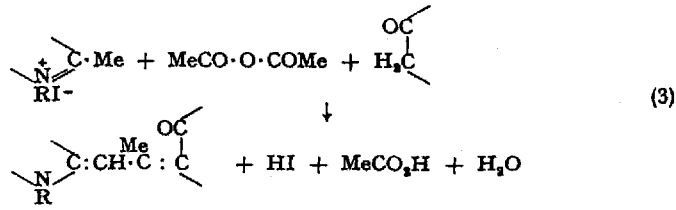
The earliest description of chain-substituted dimethinmerocyanines was in 1936 when, by heating a ketomethylene compound and a quaternary salt, having a reactive methyl group, with acetic anhydride and pyridine, there resulted dimethinmerocyanines, of types XII and XIII (n=0, R^3=H, R^4=Me), with a methyl group on the chain, in the β-position to the quaternary salt residue (equation 3).[68] There is no doubt that here the methyl substituent does come from the anhydride molecule (cf. VI-9). Subsequently a β-ethyl group was



(XII)



(XIII)



(3)

introduced by use of propionic anhydride (see section 8-A.1).[69] The sensitising action of other β-substituted dimethinmerocyanines was described; for their preparation (cf. section 3-C), a 2-acylmethylene-*N*-alkylbenzothiazoline was brought into reaction with certain ketomethylene compounds.[70] The alternative route in which a cyclic compound with >CH·CMeO adjacent to CO reacted with a 2-methyl quaternary salt was also used (see section 8-A.3). Instead of a base with an acylmethylene group, a quaternary salt having one of the groups ·CH:CR(SMe), ·CH:CRCl,[16] or ·CH:CR(SeMe)[71] could be condensed with a ketomethylene compound. Benzothiazolium salts having the group ·CH:C(C_3H_5)(SMe) were used to introduce a β-cyclopropyl group into dimethinmerocyanines, which were described as stronger sensitisers than those with an n-propyl group (see section 8-A.2). Just as compounds with >C:CHOEt adjacent to CO were used to give dimethinmerocyanines (see section 3-D), so 5-pyrazolones with the group >C:CR·OEt were used in the synthesis of β-substituted dimethinmerocyanines of the benzoxazole and benzothiazole series. The intermediate compounds were made by reaction of the ketomethylene compounds with ortho-esters.[72] The scope of this method was subsequently extended (see section 8-A.4). However instead of condensing a cyclic compound having the group >C:CMe(OEt) with a quaternary salt having a reactive methyl group, it could be condensed with one having an alkylthio-group, to give a β-ethoxydimethinmerocyanine. β-Ethylthio- and other groups were also introduced (see section 8-A.6). Cyclic compounds with >C:C$(SMe)_2$ adjacent to CO[73] were used not only in the preparation of a *meso*-(methylthio)methinoxonol (see XIII-4-B) but also in that of β-(methylthio)dimethinmerocyanines (see section 8-A.7).[74] By the

action of amines, NHR^1R^2, the β-SMe group was converted into β-NR^1R^2 (see section 8-A.8).[75] The preparation in 1938 of dimethinmerocyanines by heating a quaternary salt, having a reactive methyl group, with a ketomethylene compound and an ortho-ester, included the preparation of certain β-methyl and β-ethyl derivatives (see section 8-A.5).[9]

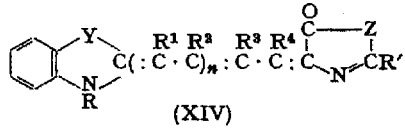
β-*o*-Carboxyphenyldimethinmerocyanines were prepared by heating a 2-methylthiazolinium salt with phthalic anhydride, a heterocyclic ketomethylene compound, and a base: for these sensitisers, the advantage of increased solubility was claimed (see section 8-A.9).[76] β-Methyldimethinmerocyanines were said to result on reaction of excess of 2-methylthiazolinium salt, part of which underwent fission, with certain types of ketomethylene compounds (see section 8-A.10).[77]

An α-phenyldimethinmerocyanine was prepared in 1939 by use of a pyrazolone having a 4-β-phenylethylidene group (see section 8-B.3).[10] In 1942 an α-methyldimethinmerocyanine was prepared from a quaternary salt having the group ·CMe:CH·SEt (see section 8-B.1).[6] An α-carbethoxydimethinmerocyanine, which was synthesised in 1948, from 2-carbethoxymethylbenzothiazole, was described as a supersensitiser (see section 8-B.5).[78] Just as quaternary salts with a 2-aryloxymethyl group were used to introduce an α-aryloxy-group into the chain of trimethincyanines and of styryl dyes (see VI-17 and XIII-1-P), so similarly they were used to give α-aryloxydimethinmerocyanines (see section 8-B.4).[79] In 1954 a 2-hydroxymethylbenzothiazolium salt was used, not only in the preparation of a *meso*-hydroxymethincyanine (see III-E) and of an α-hydroxytrimethincyanine (see VI-17-A), but also, by reaction with cyclic compounds having an ethoxymethylene group, it gave two α-hydroxydimethinmerocyanines. They were acetylated to the α-acetoxy-derivatives (see section 8-B.6 and section 12).[80]

α-Anilomethyldimethinmerocyanines were used in the synthesis of trinuclear dyes (see XV-3-C and E).

δ-Methyl- and δ-phenyl-tetramethinmerocyanines were obtained by condensation of a 5-pyrazolone having the group >C:CR·Me with a quaternary salt having the ·CH:CH·SR group (see section 8-D.2)[6] or the ·CH:CH·NR^1R^2 group (see section 8-D.3; cf. section 8-A.6).[10] Condensation of such a pyrazolone with a quaternary salt having the group ·CH:CH·CH:CH·SEt[5] gave a ζ-methylhexamethinmerocyanine (see section 8-F).[8] A quaternary salt having the group ·CH:CH·CH:CMe(SR),[81] which was used in the preparation of β-sub-

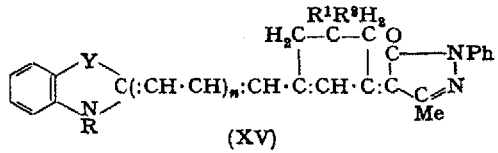
stituted pentamethincyanines (see VII-8), gave, on condensation with cyclic ketomethylene compounds, δ-methyltetramethinmerocyanines (see section 8-D.1).[82] δ-Ethoxytetramethinmerocyanines were obtained by condensation of a rhodanine having a 5-α-ethoxyethylidene group with a quaternary salt having the ·CH:CH·NAcPh group (section 8-D.3; cf. section 8-A.6).[83] Subsequently the method was extended by the use of α-ethoxyethylidene derivatives of other ketomethylene compounds, giving dyes of types XIV ($n=1$, $R^4=OEt$),[84,85] also δ-ethylthiotetramethinmerocyanines were made and a ζ-ethoxyhexamethinmerocyanine.[85]



(XIV)

β-Methyltetramethinmerocyanines were prepared by condensing a rhodanine having the 5-:CH·CH:CMe(SR) group[86] with a quaternary salt having a reactive methyl group (see section 8-E.1).[87] A β-(methylthio)tetramethinmerocyanine was prepared (see section 8-E.2)[88] by condensing a cyclic compound having >C:CH·NHPh adjacent to CO with a quaternary salt having the group ·CH:CMe(SR), such as were used in the preparation of β-SR-tri- and -penta-methincyanines and of a styryl compound with a β-SR-group (see VI-15, VII-8, and XIII-1-A).

Tetramethinmerocyanines, in which three units of the chain form part of a cyclohexene ring, are analogous to pentamethincyanines of this kind (see IX-5) and were prepared from the same intermediate salts.[89] A dye of type XV ($n=0$), and a rhodanine analogue, were

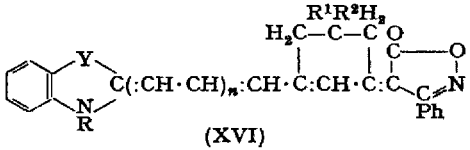


(XV)

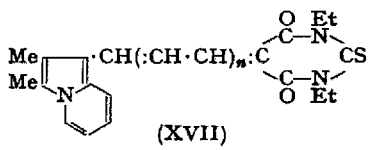
described in 1945 as valuable sensitisers (see section 9-A.1).[90] Several years later, intermediate compounds of a different type were prepared by reaction of cyclic ketomethylene compounds with a substituted 3-methylcyclohex-2-en-1-one. Their reaction with quaternary salts having an SR group gave dyes of type XV ($n=0$) (see section 9-A.2),

whilst reaction with a salt having the group ·CH:CH·NRPh gave a dye of type XV (n=1), which may be regarded as a hexamethinmerocyanine in which three members of the chain enter into a carbocyclic ring (see section 9-A.3); reaction with a salt having the group ·CH:CH·CH:CH·NRPh gave a dye of type XVI (n=2), which is an octamethinmerocyanine in which three units of the chain are cyclic (see section 9-A.4).[91]

The pyrrocoline nucleus has been introduced into the molecule of cyanines (see X-5-A), of *p*-dimethylamino-benzylidene and -cinnamylidene compounds (see XIII-1-O) and also, through 3-methylpyrrocoline, into that of tri- and penta-methin dyes of type XVII (n=1 or 2). These

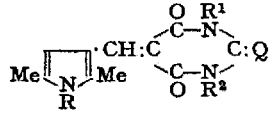


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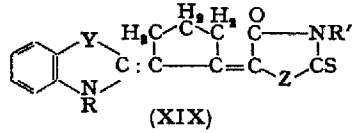
(XVII)

may be regarded as tetra- and hexa-methinmerocyanines in which one carbon atom of the normal chain linking the nuclei is cyclic. They were non-diffusing dyes, which were useful for anti-halation. Similarly methin dyes such as XVIII, with a pyrrole nucleus, may be regarded



(XVIII)

as dimethinmerocyanines in which one member of the chain is cyclic. They too were useful anti-halation dyes, being bleached by the developer (see sections 9-B.1, 2, and 3).[92] 1-Aryl-4-formylpyrazole was condensed with a couple of ketomethylene compounds, to give methin dyes (cf. X-5-B).[93] Dyes prepared by condensing heterocyclic methylene bases with quinones (section 9-B.3) have the same chromophore as dimethinmerocyanines but with one carbon atom of the chain cyclic. The absorption maxima of thirteen of them were compared (section 12).[94] A patent of 1959 covered the sensitising action of dimethinmerocyanines, such as XIX, in which the two carbon atoms of the chain formed part of a cyclo-pentane(or -hexane) ring (see section 9-C).[95]



(XIX)

Variations in the nuclei which enter into merocyanine molecules (see section 10) are considered, so far as is possible, in the same order as those entering into cyanine molecules, which formed the subject of Chapter X.

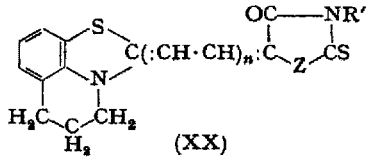
Among substituents that were introduced into the benzothiazole molecule and hence into those of cyanines (see X-2) and of dimethinmerocyanines of type IV ($n=1$, Y=S) (see section 10-A.1) were the 6-fluoro-,[96] the 5-trifluoromethyl,[97] and the 6-trifluoromethylthio-group;[98] the last was also introduced into that of a simple merocyanine by means of the appropriate 3-alkyl-2-iminobenzothiazoline (see section 2).[98] Ketomethylene compounds having a long-chain group were used in the preparation of mero-, dimethinmero-, and tetramethinmero-cyanines. Such a group conferred non-diffusing properties, without impairing the sensitising power, so that dyes thus substituted were especially useful for sensitising multi-layer films (see section 10-A.2).[99] On the other hand, certain merocyanines having in the ketomethylene residue a carboxyaryl,[100] a sulphoaryl,[101] a carboxyalkyl, or a sulphoalkyl group[102] were useful as filter dyes,[103] since such a group conferred solubility, so that the dye was easily removed by the developer (see sections 10-A.2a, b, and c).

3-Pyridyl-, 3-quinolyl-, and 3-thiazolyl-2-thiohydantoins were synthesised, also 3-heterocyclylrhodanines.[104] A merocyanine and di- and tetra-methinmerocyanines, in which was a thiohydantoin having a pyridyl or quinolyl substituent attached to at least one nitrogen atom, were useful sensitisers.[105] Compounds such as 3-(2-pyridyl)- and 3-(3-quinolyl)-rhodanine were used for making sensitising dyes containing these nuclei (see sections 10-A.2a, b, and c).[106]

Four methods of preparing an *N*-ethyldihydro-heterocyclic base, having a 2-acetylmethylene group,[107] depended on the formation of merocyanine salts and were applied to the preparation of a simple merocyanine with this structure. The corresponding merocyanine salt with the group ·CH:CMe(SEt) was reached by three routes (see section 7-A).[108] Two dimethinmerocyanines with a group: C(COR)(COMe) were prepared through salts of a dimethinmerocyanine with the :CS

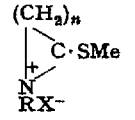
group and sensitised at a shorter wavelength than did the parent dye (see section 7-B).[109]

The *N*-alkyl group of the quaternary salt residue of dyes of the merocyanine types could be modified to an *N*-carboxyalkyl or *N*-sulphoalkyl group, and this gave the same advantage of increased solubility as when such a group was introduced into the ketomethylene residue (see sections 10-B.1, 2, 3, and 4).[110] Quaternary salts having the group *N*-CH_2CH_2OPh[111] were used in the synthesis of non-diffusing sensitisers of the merocyanine classes[112] (see sections 10-B.1, 2, and 3) (cf. X-4-A). Just as 3,4-trimethylenebenzothiazolium salts having a reactive group in the 2-position[113a] were used in the preparation of cyanines (see X-4-E), so they were used to synthesise di- and tetra-methinmerocyanines of type XX (n=1 or 2) (see sections 10-B.2 and 3).[113a]

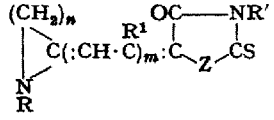


(XX)

Some of the unusual quaternary salts which were used in the preparation of cyanines (see X-5) were also used in the preparation of merocyanines. Of nuclei having one nitrogen atom, 1-ethyl-2-phenyliminoethylidenepyrrolines were, in 1952, used in the synthesis of dimethinmerocyanines, which also had a 1-alkyl-5-oxo-2-thiopyrrolidine residue (see section 10-C.2a). Subsequently the synthesis of dyes from quaternary salts of type XXI, having one nitrogen atom in the nucleus,



(XXI)

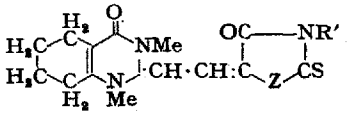


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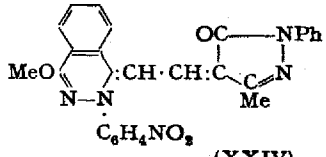
was covered in two independent patents. According to the first of these, salts of type XXI (n=3–7) gave rise to simple merocyanines which had the advantage of sensitising strongly at a wavelength shorter than that of the light emitted by the dark-room safelight.[114] Previously dimethinmerocyanines, XXII (m=1, n=3, R^1=H), of the 2*H*-pyrroline series had been synthesised.[115] According to the second patent, salts

of type XXI (n=4–6) were condensed with heterocyclic compounds, having >C:CR·Me adjacent to CO, to give β-methyl- or β-ethoxy-dimethinmerocyanines, XXII (m=1), which were sensitisers (see section 10-C.1a).[116]

Of unusual nuclei, having two nitrogen atoms as the only hetero-atoms, that were introduced into the molecules of cyanines (see X-5-B), a 4-oxohexahydroquinazoline nucleus was introduced into that of di-methinmerocyanines of type XXIII,[117] and others had a perimidine nucleus;[118,119] a phthalazine nucleus entered into the molecule of XXIV.[120] The sensitising properties of several simple merocyanines,

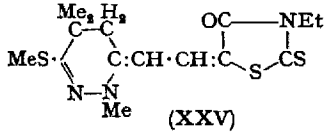


(XXIII)



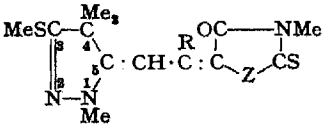
(XXIV)

and of two β-methyldimethinmerocyanines, all having a 4-SR-pyr-imidine nucleus, were described.[121] The 4,4-dimethyl-3-(methylthio)-dihydropyridazine nucleus occurred in dimethinmerocyanines, such as XXV.[122,123] The 4,4-dimethyl-3-(methylthio)pyrazolenine nucleus,

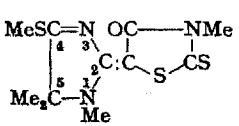


(XXV)

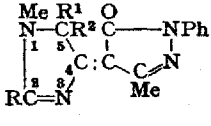
which was used in the molecules of methin- and trimethin-cyanines, and the 5,5-dimethyl-4-(methylthio)imidazolenine nucleus, which was used in that of methincyanines, also appear in the merocyanines, the former entering the molecules of dimethinmerocyanines of type XXVI, including one with a β-methyl substituent,[124] and the latter entering that of simple merocyanines, such as XXVII.[125] 4-Alkylthio-2,5,5-tri-substituted imidazoleninium salts[126] were also used in preparing dyes such as XXVIII (see section 10-C.1b).[127] 1-Methyl-1′-phenylindolo-



(XXVI)

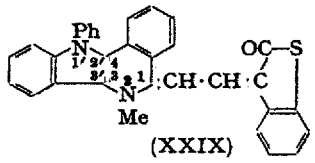


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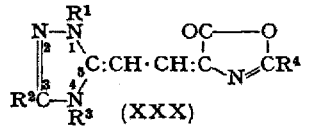
(XXVIII)

(3′,2′-3,4)isoquinoline methiodide,[128] which was used in the preparation of an azadimethincyanine (see XII-7), was also used to give the dimethinmerocyanine, XXIX. This was exceptional in having two ionic forms, in one of which the pyridine nitrogen atom, and in the second the indole nitrogen atom, takes the positive charge.[31]

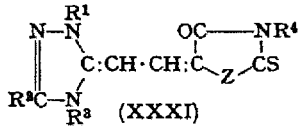


(XXIX)

Of quaternary salts having three nitrogen atoms as hetero-atoms, those of 5-methyl-1,2,4-triazole, which were used in synthesising methin- and trimethin-cyanines (see X-5-C), were also condensed with cyclic compounds having an ethoxymethylene group to give dimethinmerocyanines. Where the 4-*N*-atom became quaternary,[129] the products were of type XXX (R^3=Me),[130] but 4-aryl-1,2,4-triazoles became quaternary on the 1-*N*-atom, leading to XXXI (R^1=Me, R^3=Ar).[131]

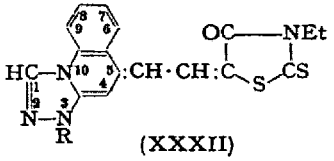


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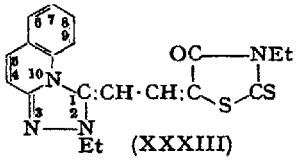


(XXXI)

Salts of s-triazolo[4,3-a]quinoline, through a reactive 5-methyl group, were used in the preparation of cyanines and also of dimethinmerocyanines such as XXXII.[132] Salts of s-triazolo[4,3-a]quinoline having a reactive 1-methyl group gave rise to XXXIII (see section 10-C.1c).[133]

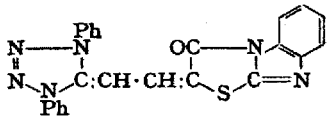


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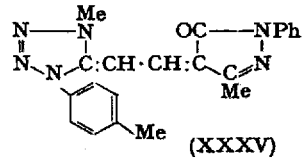


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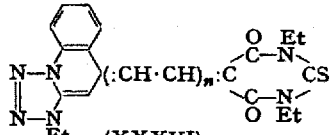
Of quaternary salts with four nitrogen atoms, 5-methyltetrazolium salts were used in the preparation of two dimethinmerocyanines, XXXIV and XXXV (cf. X-5-D).[134] Quaternary salts of 5-methyltetrazolo[a]quinoline were used to give di- and tetra-methinmerocyanines of type XXXVI (n=1 or 2).[132]



(XXXIV)



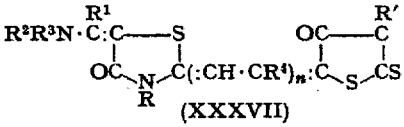
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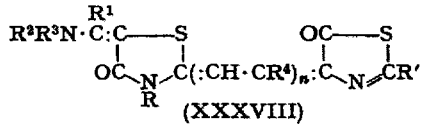
(XXXVI)

Quaternary salts, having one nitrogen and one sulphur as hetero-atoms, that were used in the preparation of dyes of the cyanine and merocyanine types, were those of 3,1,4-benzothiazine[135] and dihydro-1,3,4-thiazine,[136,137] having a reactive group, the former giving simple merocyanines and the latter mero- and dimethinmero-cyanines. In 1959 there were described dimethinmerocyanines derived from 2-methyl quaternary salts of various substituted thiazoles and benzothiazoles, including types with spirocyclic groups[138–144] (section 10-C.1e) (cf. X-5-E).

In 1955 merocyanine dyes derived from 2-alkylthio-4-oxothiazolinium salts having a substituted 5-aminomethylene group were described. The salts were synthesised by reaction of 3-alkyl-4-oxo-2-thiothiazolidines with an ethyl or methyl ortho-ester, whereby the methylene group was converted into $:CR^1(OEt)$ or $:CR^1(OMe)$, respectively, fourteen compounds of the former, and two of the latter, type being described; by heating these products with amines, the reactive group was converted into $:CR^1(NR^2R^3)$: there were nineteen examples of such 3-alkyl-5-aminomethylene-4-oxo-2-thiothiazolidines. By heating such a compound with an ester, the corresponding 2-alkylthiothiazolinium salt was formed, and was forthwith condensed with a keto-



(XXXVII)



(XXXVIII)

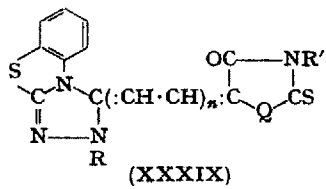
methylene compound to give a merocyanine such as XXXVII or XXXVIII (n=0), of which there were eighteen examples. Of six dimethinmerocyanines of the types XXXVII or XXXVIII (n=1),

five had a β-substituent on the chain (see section 10-C.1e); the unsubstituted one was prepared by condensation of a thiazolinium salt with a compound having an ethylidene group (see section 3-F). The dyes were particularly useful for extending the sensitivity of developing-out emulsions.[145,146]

Of salts with a nitrogen, an oxygen, and a sulphur in the nucleus (cf. X-5-F), 2-methyl derivatives of two types of dihydropyranothiazoles were used for preparing dimethinmerocyanines (section 10-C.1f).[147–149]

Amongst salts with two nitrogen atoms and one sulphur in the nucleus, those of 5-alkylthio-2-methyl-1,3,4-thiadiazole (see X-5-G) were condensed with compounds having an ethoxymethylene group, to give dimethinmerocyanines (see section 10-C.1g). An α-methyldimethinmerocyanine was prepared from a quaternary salt of 2-ethyl-5-methylthio-1,3,4-thiadiazole.[150]

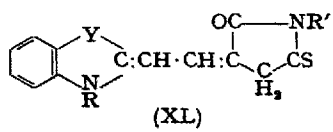
Amongst quaternary salts of complex bases having three nitrogen atoms and one sulphur, those of 1-methyl-s-triazolo[3,4-b]benzothiazole (see X-5-H) were used in the preparation of eight dimethinmerocyanines, such as XXXIX (n=1, Q=S, R=R′=Et), and of one tetramethinmerocyanine, XXXIX (n=2, Q=S, R=R′=Et) (see section 10-C.1h).[133]



(XXXIX)

Nuclei containing one nitrogen and two sulphur atoms (see X-5-I) were introduced into dimethinmerocyanines through quaternary salts of two types of 2-methylthiodihydropyranothiazoles.[148,151,152]

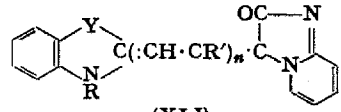
As contrasted with merocyanines prepared from unusual quaternary salts, those derived from unusual ketomethylene compounds have, of course, no counterpart amongst the cyanines. Of ketomethylene compounds with nitrogen as the one hetero-atom are substituted 5-oxo-2-thiopyrrolidines, which were converted into sensitising dimethin-



(XL)

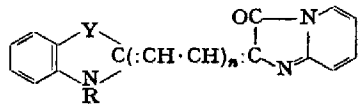
merocyanines of type XL by condensation with a dihydro-heterocyclic base having, usually, the group :CH·CH:NPh, but sometimes :CH·CHO (see section 10-C.2a).[153]

Of ketomethylene compounds with two nitrogen atoms as hetero-atoms, 3,7a-diazaindan-2-one was used in the preparation of oxonols (see XIII-4) and of merocyanines. Condensation of its hydrobromide with a 2-methylthiobenzothiazolium salt gave the hydrobromide of XLI (n=0, Y=S, R=Me, R′=H), whilst with 3-ethyl-2-formyl-methylenebenzothiazoline it gave that of XLI (n=1, Y=S, R=Et,



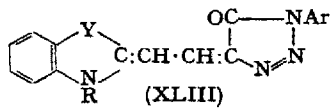
(XLI)

R′=H). A β-methyl- and a β-methylthio-dimethinmerocyanine were prepared[154] by the methods of section 8-A.2 and 8. Independently, 3,7a-diazaindan-2-one was used in the preparation of dimethinmero-cyanines and of a tetramethinmerocyanine (see section 10-B.2b).[155] These dimethinmerocyanine molecules were disrupted by compounds containing a methylene or methyl group to give oxonols, etc. The polar extreme structure was regarded as unusually important and as account-ing for the abnormal behaviour.[156] The 3,7a-diazaindan-1-one nucleus was introduced into the molecules of methinoxonols, of a *p*-dimethyl-aminobenzylidene compound (see XIII-4-B and E), and also into those of mero- and dimethinmero-cyanines, such as XLII (n=0 or 1). The absorption maxima of the isomeric substances were compared.[157]



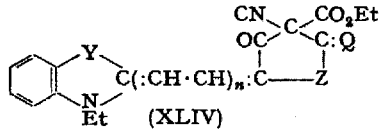
(XLII)

Of ketomethylene compounds with three nitrogen atoms, 1-aryl-5-oxo-1,2,3-triazolines, or their 4-carboxy-derivatives, gave rise to dimethinmerocyanines, XLIII, with sensitising properties (see section 10-B.2c).[158]



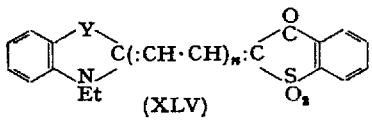
(XLIII)

Certain ketomethylene compounds with sulphur or oxygen as the one hetero-atom were used in the synthesis of various types of merocyanines (section 10-C.2d). Thus XLIV (Z=O or S, Q=S or NR), having

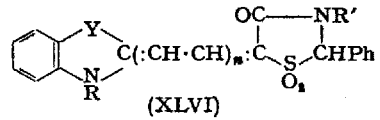


(XLIV)

a 3-carbethoxy-3-cyano-4-oxo-2-thio(or -2-:NR)tetrahydrofuran, or tetrahydrothiophene, nucleus were described as sensitisers: of the fifteen examples, eleven were dimethinmerocyanines.[159] Cyclic compounds with a sulphone group[160] were condensed with various types of quaternary salts having a reactive group to give merocyanines and di- and tetra-methinmerocyanines, including β-methyldimethinmerocyanines. Although these compounds, XLV and XLVI, were described as especially useful sensitisers, no particulars were given.[161]

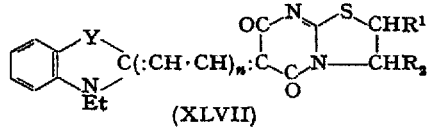


(XLV)



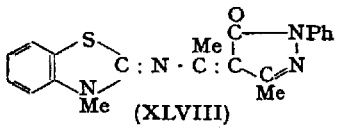
(XLVI)

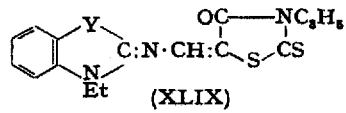
Complex ketomethylene compounds, in which a 4-oxothiazolidine had another heterocyclic nucleus fused on in the 2,3-positions, were synthesised,[162] and mero- and dimethinmero-cyanines were prepared from them.[163] Other complex ketomethylene compounds that were used in the preparation of mero- and dimethinmero-cyanines were 4,6-dioxotetrahydropyrimidine with a thiazoline, selenazoline, or thiazine nucleus fused on in the 2,3-positions. Such dimethinmerocyanines, e.g., XLVII (n=1), had sensitising properties (see section 10-C.2e).[164]



(XLVII)

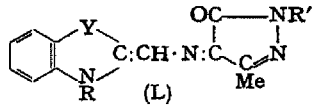
In 1940, the β-methyl derivative, XLVIII, of an α-azadimethinmerocyanine was described as resulting on heating a 2-aminobenzothiazolium salt with 4-α-ethoxyethylidene-3-methyl-1-phenyl-5-pyr-


(XLVIII)

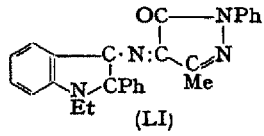

(XLIX)

azolone in pyridine.[72] Ten years later, α-azadimethinmerocyanines of type XLIX, prepared from certain 2-amino-quaternary salts by condensation with 5-acetanilidomethylene-3-allylrhodanine, proved to be sensitisers.[165] A later method of arriving at α-azadimethinmerocyanines was through quaternary salts having the group $\cdot N:C(SMe)_2$ (see section 11-A).[104]

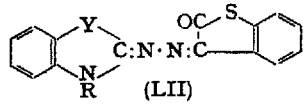
β-Azadimethinmerocyanines of type L were prepared from a quaternary salt having a reactive methyl group and a 4-isonitrosopyrazolone; many of them did not show sensitising but did show super-


(L)

sensitising properties.[166] The substance, LI, which was prepared in 1944[167] from 3-methyl-1-phenyl-5-pyrazolone and 1-ethyl-3-nitroso-2-phenylindole, may be regarded as a β-azadimethinmerocyanine, in which the

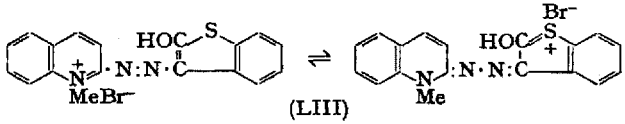

(LI)

α-carbon atom is cyclic. It was considered that the 6-ethoxy- and 6,7-benzo-derivatives of 3-oxodihydrothianaphthene gave initially compounds of the same type, but that these behaved like anils in condensing with a second molecule of ketomethylene compound, so that thioindigotins resulted (see section 11-B).[167]


(LII)

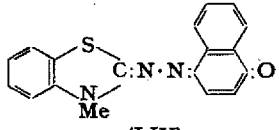
The first diazadimethinmerocyanines, LII (Y=CH:CH or S), were described in 1952,[33] being prepared through thianaphthenquinone 3-hydrazone.[30] That of the quinoline series was converted by hydrogen

bromide into a salt, to which, because of its colour, formula LIII was assigned; the salt readily regenerated the parent diazadimethinmerocyanine. The dye, LII (Y=S), of the benzothiazole series readily underwent isomerisation[83] and later it was observed that this also occurs with

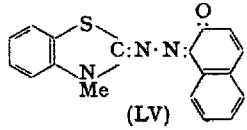


(LIII)

three other diazadimethinmerocyanines, though it was not detected with dimethinmerocyanines. The infrared spectra of the pairs of isomers were usually quite different.[168] A patent of 1954 described a different method of arriving at diazadimethinmerocyanines. It consisted in the action of an oxidising agent on the hydrazone of a heterocyclic ketone and a compound having a replaceable hydrogen. Examples of the latter were α- or β-naphthol—giving dyes LIV and LV, respectively—also phenol, barbituric acid, 3-methyl-1-phenyl-5-pyrazolone, 3-ethylrhodanine, 8-hydroxyquinoline, etc.[169]



(LIV)



(LV)

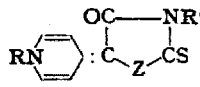
Work on colour in the merocyanine series has been considered separately in section 12, whilst section 13 deals with open-chain compounds related to the merocyanines.

2. Simple Merocyanines

A. From a Cyclic Ketomethylene Compound and a Heterocyclic Quaternary Salt Having a Reactive SR, I, CN, or SO_2R, or a Dihydro-Base Having a Reactive :NH

The simple merocyanine, II (n=0, Y=CH:CH, Q=Z=S, R=Me, R′=H), sensitised a chloride emulsion to 5700 Å, with the maximum at 5400 Å, and was prepared by condensing rhodanine with 2-iodoquinoline methiodide. Its analogue with a benzothiazole instead of a quinoline nucleus had its sensitising maximum at 4600 Å; other sensitisers

in that series were II (n=0, Y=Q=S, Z=NH, R=Me, R′=H; and n=0, Y=Z=S, Q=O, R=Me, R′=H).[1] Compounds of this kind were prepared by condensing a 2-alkylthiobenzothiazolium salt with a rhodanine, thiohydantoin, or 2,4-dioxothiazolidine. A 4-alkylthioquinolinium salt was condensed with 3-methyl-1-phenyl-5-pyrazolone;[170] also with the homocyclic 1-hydrindone, whilst 2-iodoquinoline ethiodide was condensed with 3-oxo-2,3-dihydrobenzofuran by means of sodium ethoxide in ethanol. Reaction between a 2-methylselenoquinolinium (or a 2-methylthiobenzothiazolium) salt and indan-1,3-dione was effected by heating them in pyridine.[3] An American patent on the sensitising action of merocyanines included II (n=0, Y=CH:CH, Q=Z=S, R=Et, R′=H or Ph) and the 5,6-benzo-derivative of the latter, also an analogue with a 2-linked pyridine residue.[11] They were prepared by condensing a rhodanine with 2-iodoquinoline ethiodide, or an analogue, by heating with triethylamine in ethanol.[11,16] Simple merocyanines prepared from the 2-alkylthio-, or 2-phenylthio-, quaternary salt of a heterocyclic base and a ketomethylene compound included examples with a pyridine, quinoline, benzothiazole, or benzoxazole residue, on the one hand, and a nucleus of the rhodanine, thiohydantoin, or 2-diphenylamino-4-oxothiazoline type on the other.[12,16] By heating a 4-methylthiopyridinium salt with a rhodanine and triethylamine in pyridine, the deep-yellow merocyanines, LVI (Z=S, R=Et, R′=Et,



(LVI)

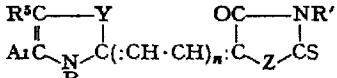
Ph or p-$C_6H_4NEt_2$; and Z=S, R=Me, R′=CH_2CO_2Et), were made. Similarly there were prepared LVI (Z=O, R=Me or Et, R′=Et; and Z=Se, R=Me, R′=Et), the last two of which sensitised at 4600 Å and 4950 Å, respectively.[171] Just as 4-cyanoquinoline methiodide could be used to prepare 4′-cyanines (see II-2-A), so it was condensed with 3-ethylrhodanine, or with 3-oxodihydrothianaphthene, by heating them with potassium carbonate in ethanol.[172,173] The merocyanine, IV (n=0, Y=S, R=Et), was prepared from 3-oxodihydrothianaphthene and 2-methylthiobenzothiazole ethotoluene-p-sulphonate.[28] Its isomer, V (n=0, Y=S, R=Et), was obtained in 90% yield by boiling 2-ethylthiobenzothiazole ethiodide and 2-oxodihydrothianaphthene with triethylamine in ethanol for six hours.[31]

Sensitising merocyanines with a 5-oxo-2-thiothiazolidine nucleus comprised representatives of the 2-linked quinoline and benzoxazole series, VI (n=0, Y=CH:CH or O, Q=Z=S, R=Me, R′=Et), and of the benzothiazole series, VI (n=0, Y=Q=Z=S, R′=Me, Et, Bu, CH_2Ph, or C_6H_{11}; and n=0, Y=Q=Z=S, R=Et, R′=Me), and the 4,5-benzo-derivative of VI (n=0, Y=Q=Z=S, R=R′=Et).[39] The compounds, VI (n=0, Y=Q=Z=S, R′=Me or Et),[37,38] were compared with the isomeric rhodanine compounds.[37]

The 4-linked quinoline analogue of VII (n=0, Y=CH:CH, Z=S, R=Et, R″=SMe), having a 2-methylthio-4-oxothiazoline nucleus, was prepared by the action of methyl toluene-p-sulphonate and potassium hydroxide on the 4-linked quinoline analogue of II (n=0, Y=CH:CH, Q=Z=S, R=Et, R′=H).[22] In the thiohydantoin series, VIII (n=0, Y=S, Z=NH, R=Et, R″=SMe), having a 2-methylthio-4-oxoimidazoline nucleus, resulted on methylation of II (n=0, Y=Q=S, Z=NH, R=Et, R′=H).[24]

Simple merocyanines, VIII (n=0, Y=CH:CH or S, Z=S, R=Me, R″=S·CH_2Ph), with a 2-benzylthio-5-oxothiazoline nucleus, had absorption maxima at 4850 Å and 4000 Å, respectively.[44] The compounds, VIII (n=0, Y=Z=S, R=Et, R″=SEt;[45] and n=0, Y=Z=S, R=Me, R″=NHCOMe)[46] were also made.

By heating a 4,5-diaryl-2-methylthio-oxazolinium salt with a 3-alkyl-4-oxo-2-thiothiazolidine and triethylamine in ethanol, there were prepared eight merocyanines, LVII (n=0, Y=O, Z=S, R=Et, Bu, or n-C_7H_{17}, Ar and R^5=usually Ph, R′=Et or CH_2CO_2H), yields varying from 28–74 %. The compounds, LVII (n=0, Y=O, Z=O or NEt, Ar=Ph, R^5=R′=Et), were described, also LVII (n=0, Y=Z=S, R=n-Bu, Ar=R^5=Ph, R′=CH_2CO_2H).[174]



(LVII)

The merocyanine, II (n=0, Y=Q=S, Z=N·COMe, R=R′=Et), with a 4-oxo-2-thio-imidazolidine nucleus, was prepared from 1-acetyl-3-ethyl-2-thiohydantoin and 2-ethylthiobenzothiazole ethotoluene-p-sulphonate by heating them with triethylamine in ethanol.[47,48] A merocyanine, VII (n=0, Y=S, Z=NPh, R=R′=Me), with a 4-oxoimidazoline nucleus, was prepared by heating 2-methyl-4-oxo-1-phenyl-

imidazoline with 2-methylthiobenzothiazole methomethylsulphate in pyridine.[49]

The merocyanine, IX (n=0, R=Me), was prepared in 58 % yield by boiling 2-phenylthioquinoline methotoluene-p-sulphonate and indan-1,3-dione with triethylamine in ethanol for 15 minutes, and recrystallising twice from methanol. Its pyridine analogue was prepared in 9 % yield by use of 2-iodopyridine methiodide. They were identical with the early products of methylation of quinophthalone and the pyridine analogue of that.[53]

By condensation of a 2-imino-3-methylbenzothiazoline with 3-methyl-1-phenyl-5-pyrazolone, by heating them in a vacuum at 150°, there were prepared the 6-methyl and 6-methoxy-derivatives of I (n=0, Y=S, R=Me, R′=Ph), in yields of 69–90 %,[175] the 6-trifluoromethylthio-derivative in 64 % yield,[96] and I (n=0, Y=S, R=R′=Ph) in 92 % yield. An analogous merocyanine from 1-ethyl-2-iminodihydropyridine resulted in 5 % yield.[175]

The simple merocyanines, II (n=0, Y=CH:CH, Z=S or O, Q=S, R=Me, R′=Et), were prepared by boiling the N-methylbetaine of quinoline-2-sulphonic acid with a ketomethylene compound and triethylamine in ethanol. Analogous compounds of the benzothiazole and 2-linked pyridine series were made, as well as the 6,7-benzo-derivatives of II (n=0, Y=Q=Z=S, R=Me, R′=CH_2CO_2H; and n=0, Y=Q=S, Z=O, R=Me or Et, R′=Et), also I (n=0, Y=S, R=Me, R′=p-$C_6H_4SO_3H$) and VII (n=0, Y=Z=S, R=Me, R″=NPh_2).[176]

3. Dimethinmerocyanines

A. From a Cyclic Ketomethylene Compound and a Heterocyclic Quaternary Salt Having the Group ·CH:CH·NR¹R², or from a Cyclic Compound with >C:CH·NR¹R² Adjacent to CO and a Quaternary Salt Having a Methyl Group

The first dimethinmerocyanines date from 1930, when a methin-hemioxonol, having a substituted pyrazolone nucleus, was condensed with a quaternary salt, having a reactive methyl group, but the products were formulated as though they contained acid.[177] Sensitising dimethinmerocyanines, described in 1933 in British patents, included dyes with a rhodanine residue linked to an N-ethyl-benzothiazoline, -benzoxazoline, or -1,2-dihydroquinoline nucleus, also hydantoin with 1,3,3-trimethylindoline, and thiohydantoin with 1,3,3-trimethylindoline or N-ethylbenzoxazoline; the first of these substances could be

TABLE I. Some Properties of Some Simple Merocyanines

Formula	Appearance of crystals	M.p. (°C) decomp.	Absorption maximum in MeOH (Å)	Sensitising (Å) Maximum	Extent	Ref.
II (n=0, Y=CH:CH, Q=Z=S, R=R′=Et)	red-brown	194–196	—	5400[a]	5700[a]	1, 16
II (n=0, Y=Q=S, Z=NCOMe, R=R′=Et)	lemon-yellow plates	243[b]	4040	—	—	47, 48
VI (n=0, Y=CH:CH, Q=Z=S, R=Me, R′=Et)	dark red	197[b]	5620[c]	—	—	37, 39
VI (n=0, Y=Q=Z=S, R=Me, R′=Et)	red needles	176	4110	4500	—	37, 38
VII (n=0, Y=S, Z=NPh, R=R″=Me)	—	257–259[b]	—	—	—	49
VIII (n=0, Y=Z=S, R=Et, R″=NHEt)	yellow prisms	170[b]	4140	—	—	47
IX (n=0, R=Me)	deep yellow needles	249–250	4520[d]	—	—	53
LVI (Z=S, R=R′=Et)	—	—	—	4850	—	171
LVII (n=0, Y=O, Z=S, Ar=R^5=Ph, R=R′=Et)	—	179	4050	—	—	174
LVII; (n=0, Y=O, Z=NEt, Ar=R^5=Ph, R=R′=Et)	needles	182	3930	—	—	174

[a] Sensitising for R=Me, R′=H. [b] Decomp. not recorded.
[c] Absorption for compound where R=Et. [d] Absorption in pyridine.

methylated to give a dimethinmerocyanine with one *N*-ethylbenzothiazoline and one 2-methylthio-4-oxothiazoline residue.[1] The dimethinmerocyanine, II (n=1, Y=Q=Z=S, R=Et, R′=H), was prepared from 2-β-acetanilidovinylbenzothiazole ethiodide and rhodanine by heating them in pyridine, or, alternatively, from 2-methylbenzothiazole ethiodide and 5-acetanilidomethylenerhodanine. Both rhodanine and 2,4-dioxothiazolidine were condensed with 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide, and thiohydantoin was condensed with 2-β-acetanilidovinylbenzoxazole ethiodide; the alternative process was applied in condensing 5-acetanilidomethylenerhodanine with quinaldine ethochloride.[2] Subsequently dimethinmerocyanines from 3-methyl(or ethyl)rhodanine were usually prepared by its reaction with a 2-β-acetanilidovinyl salt of the quinoline, benzothiazole, benzoxazole, or 3,3-dimethylindolenine series. The oxazolidine analogue of 3-ethylrhodanine was also used.[57] Other sensitisers, I (n=1, R′=Ph), were made by reaction of 3-methyl-1-phenyl-5-pyrazolone with 2-β-acetanilidovinyl derivatives of indoleninium or benzoxazolium salts.[178] The homocyclic 2-hydrindone was condensed with 2-β-acetanilidovinylbenzothiazole ethiodide by heating with pyridine in ethanol; the alternative route was used when 2-acetanilidomethylene indan-1,3-dione was heated with quinaldine ethiodide, lepidine methiodide, or 2-methylbenzothiazole ethotoluene-*p*-sulphonate in pyridine, to give IX (n=1, R=Et) and its analogues.[3]

The first American literature on dimethinmerocyanines which sensitised included II (n=1, Y=CH:CH, Q=Z=S, R=Et, R′=Et, Ph, or *p*-$C_6H_4NMe_2$), of the 2-linked quinoline series, and were prepared by heating 2-β-acetanilidovinylquinoline ethiodide and a 3-substituted rhodanine with sodium acetate in acetic anhydride; analogous 4-linked quinoline compounds having a rhodanine or 3-phenylrhodanine nucleus were similarly made. Dyes of the benzothiazole series included II (n=1, Y=Q=Z=S, R=Et, R′=H or Ph), and analogues with a barbituric acid, thiobarbituric acid, or 3-oxodihydrothianaphthene nucleus. Sensitisers of the benzoxazole series included II (n=1, Y=O, Q=Z=S, R=Et, R′=H or CH_2CO_2Et) and analogues with a barbituric acid nucleus. The 2- and 4-linked pyridine, thiazoline, benzoselenazole, and benzimidazole series were also represented.[11,14,16,17] Ten dimethinmerocyanines, described as sensitisers, and having a benzoxazole residue, were prepared by heating a 2-β-anilinovinylbenzoxazolium salt with a rhodanine or barbituric acid, and triethylamine in ethanol.[179]

β-Anilinovinyl or β-acetanilidovinyl salts of the 2- or 4-linked quinoline, benzothiazole, benzoxazole, or thiazoline series were similarly condensed with 3-oxodihydrothianaphthene, or its 2-carboxy-derivative,[18] or with a barbituric or thiobarbituric acid.[16,19] These quaternary salts, and those of the benzoselenazole series, were similarly condensed with 4-oxo-2-thio-oxazolidines.[16,21] Dimethinmerocyanines were made by condensing 2-β-acetanilidovinyl salts of the 2-linked quinoline, benzoxazole, and benzothiazole series with compounds such as 2-ethylphenylamino-4-oxothiazoline, 2,4-dioxo-3-phenylthiazolidine, and 4-oxo-3-phenyl-2-phenyliminothiazolidine.[16,22] A dimethinmerocyanine, II (n=1, Y=CH:CH, Q=S, Z=NPh, R=Et, R′=Ph), was prepared by heating 2-β-anilinovinylquinoline ethiodide and 1,3-diphenyl-2-thiohydantoin with sodium acetate and acetic anhydride. 2-β-Acetanilidovinylbenzothiazole ethiodide, by heating with 1,3-diphenyl-2-thiohydantoin and triethylamine in ethanol gave II (n=1, Y=Q=S, Z=NPh, R=Et, R′=Ph). 2-β-Acetanilidovinylbenzoxazole ethiodide was condensed with hydantoin by heating with sodium acetate in acetic anhydride, but triethylamine in ethanol was used for condensations with 2-thiohydantoin and its derivatives; this condensing agent was also used in conjunction with 2-β-anilinovinylthiazoline methiodide.[24] Subsequently various dimethinmerocyanines were prepared from 2-β-acetanilidovinyl quaternary salts and 2-thiohydantoins.[66]

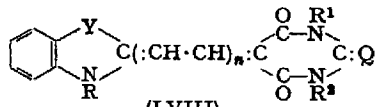
Of dimethinmerocyanines with a 4-oxo-2-thiothiazolidine (or rhodanine), or the corresponding oxazolidine, nucleus, five were made in 1949 through a β-acetanilidovinyl salt, one through a β-anilinovinyl salt, and one by the alternative route: they were II (n=1, Y=Q=S, Z=O or S, R=R′=Et), thiazoline analogues of both, the 5-chloro-derivative and the 4-linked quinoline analogue of the former, and II (n=1, Y=Q=Z=S, R=Et, R′=CH_2CO_2H). Absorption and sensitising data were given.[180] In 1951 the rhodanine dyes, II (n=1, Y=Q=Z=S, R=Et, R′=H or Me), were prepared, in yields of 70% and 64%, respectively, through the appropriate 5-acetanilidomethylenerhodanines, by heating in pyridine.[60] Also in 1951 numerous dimethinmerocyanines were described, being reached by one route or the other. They included twenty dyes in which a 3,3-dimethyl-*N*-phenyl(or-*N*-methyl)-indoline nucleus was coupled with one of ten different carbonyl-containing nuclei, including 3-ethylrhodanine. Besides this, 3-ethylrhodanine was coupled with the residue of fourteen more quaternary salts,[17] and there were other dyes too. In 1957 dimethinmerocyanines, LVII

(n=1, Y=O, Z=S), were prepared by condensation of a 2-β-anilinovinyl-4,5-diaryloxazolinium salt with a 3-alkyl-4-oxo-2-thiothiazolidine. Yields varied from 40–85 %; R was Bu, Ph, or n-C_8H_{17}, Ar and R^5 were Ph or p-C_6H_4OMe, and R′ was Et. A similar compound, LVII (n=1, Y=Z=O, R=Ar=R^5=Ph, R′=CH_2CO_2Et), with a 4-oxo-2-thio-oxazolidine nucleus was also made.[174] Again in 1957 dimethinmerocyanines were prepared from 2-ethylrhodanine by reaction with 2-β-acetanilidovinylbenzothiazole methiodide, and the corresponding salts of four substituted thiazoles,[181] whilst in 1959 3-ethylrhodanine was condensed with similarly substituted salts of 4-aminothiazole[182] and 4,5,6,7-tetrahydrobenzoxazole.[183]

Twenty dimethinmerocyanines having a 1-acyl-4-oxo-2-thioimidazolidine nucleus were prepared from 1-acyl-2-thiohydantoins by condensation with β-acetanilidovinyl quaternary salts. They were mostly of type II (n=1, Y=O or S, Q=S, Z=N·COR), of the benzoxazole or benzothiazole series, but included also representatives of the 2- and 4-linked quinoline, benzoselenazole, oxazole, and thiazoline series, and comprised useful sensitisers.[47,48] Three dyes of type LVII (n=1, Y=O, Z=NEt, R′=Et) were also made.[174]

Dimethinmerocyanines with a 5-oxo-2-thiothiazolidine nucleus comprised a representative of each of four series in VI (n=1, Y=CH:CH, Q=Z=S, R=R′=Et; and n=1, Y=S, O, or CMe_2, Q=Z=S, R=R′=Me); there were also VI (n=1, Y=O or CMe_2, Q=Z=S, R=Me, R′=Et) and the 5-methyl derivative of VI (n=1, Y=Q=Z=S, R=R′=Et).[39] Representatives of all these series, and, in addition, of the 4-linked quinoline, thiazole, and thiazoline series, besides various substituted compounds, were described elsewhere.[37,38] They included dimethinmerocyanines in which R′ was methyl, ethyl, n-heptyl, or cyclohexyl. Their absorption maxima were compared with those of their isomers having a rhodanine nucleus.[37]

To dimethinmerocyanines with a thiobarbituric acid nucleus there was added in 1951 the compound LVIII (n=1, Y=NEt, Q=S, R=R^1=R^2=Et). It was prepared by heating 3-ethyl-2-methylbenzimidazole ethiodide and 5-acetanilidomethylene-1,3-diethyl-2-thiobarbituric acid with triethylamine in pyridine.[20]



(LVIII)

Of dimethinmerocyanines with a 3-oxodihydrothianaphthene nucleus, the first, IV (n=1, Y=S, R=Et), was prepared in 1934 by use of 2-β-anilinovinylbenzothiazole ethiodide and piperidine in ethanol; derivatives of the salt were also used, besides others with a benzoxazole or substituted thiazole nucleus, and the sensitising properties of the products were noted.[27] In 1940 the alternative process was applied to the preparation of a series of dimethinmerocyanines, IV (n=1, Y=S, R=Me, Et, Pr, or Bu), by reaction of a 2-methylbenzothiazolium salt with 2-anilinomethylene-3-oxodihydrothianaphthene in pyridine containing piperidine, during 24 hours.[28] In 1944 various substituted 2-methylbenzothiazolium salts were caused to react with the same compound by heating with sodium acetate in ethanol. Hence there were prepared derivatives of IV (n=1, Y=S, R=Et), with substituents such as 6-methyl, -methoxy-, ethoxy-, -methylthio-, -chloro-, -nitro-, -dimethylamino-, -acetylamino-, 4,5-benzo-, 4,5-(2,3-naphtho-), and 6,7-(2,3-naphtho-).[184] The absorption maxima of eleven dimethinmerocyanines having a 3-oxodihydrothianaphthene nucleus were examined in chloroform and in ethanol. They were IV (n=1, Y=CH:CH, S, O, Se, CMe_2, or NMe, R=Et), also the 4-linked quinoline, 2-linked pyridine, thiazole, thiazoline, and 5-methyl-1,3,4-thiadiazole analogues.[185] Subsequently 3-oxo-2-piperidinomethylene-4,5-benzodihydrothianaphthene was condensed with lepidine methiodide in ethanol, without a catalyst.[186]

The dimethinmerocyanines, VII (n=1, Y=CH:CH or O, Z=S, R=Et, R″=SMe), having a 2-methylthio-4-oxothiazoline nucleus, were prepared by the action of methyl toluene-p-sulphonate and potassium hydroxide in methanol on II (n=1, Y=CH:CH or O, Q=Z=S, R=Et, R′=H).[22] The compound, VII (n=1, Y=Z=S, R=Et, R″=SMe), was similarly prepared in 22 % yield and was also made by use of methyl sulphate and sodium ethoxide in ethanol.[68] Dyes, VIII (n=1, Y=O, Z=NMe or NPh, R=Et, R″=SMe), having a 2-methylthio-4-oxoimidazoline nucleus, were prepared by methylation of II (n=1, Y=O, Q=S, Z=NH, R′=Me or Ph).[24]

A dimethinmerocyanine, VIII (n=1, Y=CH:CH, Z=O, R=Et, R″=Ph), with a 5-oxo-oxazoline nucleus, was prepared by heating 2-β-anilinovinylquinoline ethiodide with hippuric acid, sodium acetate, and acetic anhydride; its analogue with a 4-linked quinoline nucleus was made. 2-β-Acetanilidovinylbenzothiazole ethiodide was similarly condensed with aceturic acid and propionylglycine, respectively, to give

VIII (n=1, Y=S, Z=O, R=Et, R″=Me or Et). From 2-β-acetanilidovinylbenzoxazole ethiodide with hippuric or aceturic acid, there were prepared VIII (n=1, Y=Z=O, R=Et, R″=Ph or Me), and the benzoselenazole analogue of the former was described. 2-β-Anilinovinylthiazoline methiodide was condensed with hippuric acid by means of sodium acetate and acetic anhydride.[26] Subsequently a series of fourteen dimethinmerocyanines were prepared either by condensing 5-oxo-2-phenyloxazoline with a β-acetanilidovinyl salt, by use of triethylamine in ethanol, or through 4-ethoxymethylene-5-oxo-2-phenyloxazoline (section 3-D). The compounds, of which four were already known, were VIII (n=1, Y=CH:CH, S, O, or Se, Z=O, R=Et, R″=Ph), the 4-linked quinoline, 4-methyl- and 4-p-methoxyphenyl-thiazole analogues, VIII (n=1, Y=CMe_2, Z=O, R=Me, R″=Ph), and its thiazoline analogue, also four compounds with a benzo-substituent.[44]

By similar methods, forty dimethinmerocyanines, of which thirty-eight were new, having a 5-oxothiazoline nucleus, carrying a 2-SR-substituent, were prepared. They included VIII (n=1, Y=CH:CH, S, O, or Se, Z=S, R=Et, R″=SEt), their 4-linked quinoline, thiazoline, and 4-methyl- and 4-p-methoxyphenyl-thiazole analogues, also VIII (n=1, Y=CMe_2, Z=S, R=Me, R″=SEt), and its thiazoline analogue. Others had in the 5-oxothiazoline ring a 2-SH, -SCH_2Ph, -$SCH_2C_6H_4NO_2$(p- or m-), -SC_6H_{13}(n), -SC_7H_{15}(n), -SC_8H_{17}(n), -$SC_{10}H_{21}$(n), -$SC_{12}H_{25}$(n), or -$S(CH_2)_3Ph$ group.[44,45] 2-Acylamino-5-oxothiazolines were synthesised and their hydrobromides were used in the preparation of dimethinmerocyanines having this nucleus. The dyes included VIII (n=1, Y=CH:CH, O, S, or Se, Z=S, R=Et, R″=NHCOMe) and its 4-linked quinoline and thiazoline analogues. Two others had a 2-NHCOPr^n group and another two a 2-NHCOPh group.[44,46] A series of twenty-eight dimethinmerocyanines with a 2-OR-5-oxothiazoline nucleus included eleven of type VIII (n=1, Z=S, R″=OEt). Three others had a 2-propoxy (iso)- and another three a 2-butoxy(n)-substituent. There were also compounds in which a 3-methylthiazolidine residue was coupled with a 5-oxothiazoline nucleus carrying a 2-OC_5H_{11}(n- or tert-), -OC_6H_{13}(n), -OC_7H_{15}(n), -OC_8H_{17}(n), -$OC_{10}H_{21}$(n), -$OC_{12}H_{25}$(n), -$OC_{14}H_{29}$(n), -$OC_{16}H_{33}$(n), or -$O(CH_2)_3Ph$.[44] A set of fourteen dimethinmerocyanines in which a 5-oxothiazoline nucleus carried a substituted amino-group in the 2-position comprised nine of type VIII (n=1, Z=S, R″=NEt_2), whilst two had a 2-NEtPh, two a 2-NC_5H_{10}, and one a 2-NC_4H_8O group.[44]

A dimethinmerocyanine of the 5-oxoimidazoline series, VIII (n=1, Y=S, Z=NPh, R=Et, R″=Me), was prepared by boiling 2-methyl-5-oxo-1-phenylimidazoline with a 2-β-acetanilidovinylbenzothiazolium salt and piperidine in pyridine.[49]

The compound, IX (n=1, R=Me), which is the dimethin analogue of a substances of the Quinoline Yellow type, was prepared in 14% yield by boiling 2-β-acetanilidovinylquinoline methotoluene-p-sulphonate and indan-1,3-dione with triethylamine in ethanol and recrystallising twice from methanol.[53]

B. From a Cyclic Ketomethylene Compound and a Heterocyclic Quaternary Salt Having the Group ·CH:CH·SR or ·CH:CH·SeR

Dimethinmerocyanines were prepared by heating 2-β-ethylthiovinylbenzothiazole methotoluene-p-sulphonate with 3-ethylrhodanine or with indan-1,3-dione in pyridine; the corresponding thiazolinium salt was similarly condensed with 3-ethylrhodanine.[6] Subsequently condensation of the benzothiazolium salt with rhodanine was described, and 2-ethylthiovinyl-3,3-dimethylindolenine methiodide was condensed with 3-methyl-1-phenyl-5-pyrazolone.[7]

2-Formylmethylene-1,3,3-trimethylindoline, and its 6-methyl derivative, were converted by phosphorus pentaselenide into bases having a :CH·CH:Se group: these could be recrystallised from benzene. By heating with methyl sulphate they were converted into salts having a ·CH:CH·SeMe group. The simpler salt was condensed, by means of triethylamine in pyridine, with ketomethylene compounds to give II (n=1, Y=CMe_2, Q=S, Z=O or S, R=Me, R′=Et; n=1, Y=CMe_2, Q=S, Z=NMe, R=R′=Me; and n=1, Y=CMe_2, Q=S, Z=NPh, R=Me, R′=C_3H_5); dyes were also prepared from the salt having a 6-methyl group.[71]

C. From a Cyclic Ketomethylene Compound and a Dihydro Heterocyclic Base Having a :CH·CHO Group, or from a Cyclic Compound Having >CH·CHO Adjacent to CO and a Quaternary Salt Having a Reactive Methyl Group

Dimethinmerocyanines, II (n=1, Y=CH:CH, CMe_2, S, or Se, Q=Z=S), also of the thiazoline series, were prepared by condensing an *N*-alkyl-2-formylmethylene heterocyclic base with a rhodanine.[58] They were converted into water-soluble salts (see section 7-B). Boiling acetic anhydride was the medium in condensing 3-ethyl-2-formylmethylene-

4,5-benzobenzothiazoline with 3-ethylrhodanine, its oxazolidine analogue, and 3-methyl-1-phenyl-5-pyrazolone.[13] A dimethinmerocyanine, the 5-methyl derivative of VII (n=1, Y=S, Z=NC_6H_{11}, R=Et, R″=Me), of the 4-oxoimidazoline series, was prepared from 3-ethyl-2-formylmethylene-5-methylbenzothiazoline and 1-cyclohexyl-2-methyl-4-oxoimidazoline by stirring them in cold chloroform containing acetic anhydride. The 5,6-dimethyl derivative of the methomethylsulphate of VII (n=1, Y=S, Z=NC_6H_{11}, R=Et, R″=Me) was prepared by reaction of 3-ethyl-2-formylmethylene-5,6-dimethylbenzothiazoline and 1-cyclohexyl-2-methyl-4-oxoimidazoline methomethylsulphate, first in cold, and then in boiling, acetic anhydride, the resultant salt being converted into methiodide. The 4,5-diphenylthiazole analogue of VIII (n=1, Z=NPh, R=Et, R″=CO_2Et), having a 5-oxoimidazoline nucleus, was prepared by heating 3-ethyl-2-formylmethylene-4,5-diphenylthiazoline and 2-carbethoxy-5-oxo-1-phenylimidazoline with chloroform and acetic anhydride at 60°.[49]

For comparison with the compounds below, three substances of type IV (n=1) were prepared from the 4,5-benzo-derivative of 2-formyl-3-oxodihydrothianaphthene and one from its 6-chloro-4-methyl derivative.[31]

By condensation of 3-formyl-2-oxodihydrothianaphthene with a quaternary salt having a reactive methyl group, in the presence of a basic catalyst, or with a methylene base without a catalyst, seventeen dimethinmerocyanines of type V (n=1, Y=CH:CH, CMe_2, S, or Se) were made, including 4-linked quinoline, 2- and 4-linked pyridine, and thiazoline analogues, and compounds made from substituted salts. Other groups of five, three, and three were prepared from the 6-ethoxy-, 4,5-benzo-, and 6-chloro-4-methyl derivatives of the aldehyde.[31]

D. From a Cyclic Compound Having >C:CHOEt Adjacent to CO and a Quaternary Salt Having a Reactive Methyl Group

Heating quinaldine ethiodide with 4-ethoxymethylene-5-oxo-2-phenyloxazoline in pyridine gave VIII (n=1, Y=CH:CH, Z=O, R=Et, R″=Ph); the analogue with a 4-linked quinoline nucleus was made similarly from lepidine ethotoluene-p-sulphonate. There were also prepared VIII (n=1, Y=S, O, or Se, Z=O, R=Et, R″=Ph), VIII (n=1, Y=CMe_2, Z=O, R=Me, R″=Ph), and analogues from 2,3,4-trimethylthiazolium and 2,3-dimethylthiazolium salts. Sometimes

the condensing agent was triethylamine in ethanol.[42] Two 4-ethoxymethylene-5-oxothiazolines were synthesised and were condensed, by heating with triethylamine in ethanol, with quinaldine methiodide, to give VIII (n=1, Y=CH:CH, Z=S, R=Me, R″=S·$CH_2C_{10}H_7(\alpha)$ or SCO_2Et), and also with 2-methylbenzothiazole ethiodide. The latter ethoxymethylene compound was used in preparing VIII (n=1, Y=CMe_2, Z=S, R=Me, R″=SCO_2Et). Three 4-ethoxymethylene-5-oxo-oxazolines were synthesised and were used to give VIII (n=1, Y=CH:CH, Z=O, R=Me, R″=SPh, SC_5H_{11}(n), or SCH_2Ph), and the first two were also condensed with 2-methylbenzothiazole ethiodide.[43] Dimethinmerocyanines with a substituted 5-oxo-oxazoline or -thiazoline nucleus were prepared either from the ketomethylene compound (see section 3-A) or from its 4-ethoxymethylene derivative.[44] In preparing dimethinmerocyanines with a 5-oxothiazoline nucleus carrying a 2-SR substituent,[44] the vast majority of examples were reached through 4-ethoxymethylene derivatives.[45]

E. From a Cyclic Ketomethylene Compound, a Quaternary Salt Having a Reactive Methyl Group, and Ethyl Orthoformate, Formamide, or Diethoxymethyl Acetate

Red crystals of the dimethinmerocyanine, I (n=1, Y=CH:CH, R=Me, R′=Ph), were formed on boiling quinaldine methiodide, 3-methyl-1-phenyl-5-pyrazolone, and ethyl orthoformate, with diethylamine in ethanol; its 4-linked quinoline analogue was made by use of lepidine methiodide. The compound, I (n=1, Y=CMe_2, R=Me, R′=Ph), was made similarly, or other condensing agents could be used; analogues of this with a 1-β-naphthyl, a 3-furyl, or both these groups, in the pyrazolone nucleus were described. 2-Methylbenzothiazole alkotoluene-p-sulphonate was condensed with 3-methyl-1-phenyl-5-pyrazolone to give I (n=1, Y=S, R=Me or Et, R′=Ph), or with rhodanine to give II (n=1, Y=Q=Z=S, R′=Me or Et); there was also used, as second reactant, thiohydantoin, 3-methyl-4-oxo-2-thio-oxazolidine, or N-alkyl-2-oxoindoline. In the benzoxazole series, the condensing agent was triethylamine and there were prepared I (n=1, Y=O, R=Me or Et, R′=Ph), and also analogues of the former with a thiohydantoin or N-ethyl-2-oxoindoline nucleus. The substance, I (n=1, Y=Se, R=Et, R′=Ph), was also made.[9] The ethyl orthoformate method was used in preparing a dimethinmerocyanine having a pyrazolenine nucleus (see

section 10-C.1b), and in preparing another with a tetrazole nucleus (see section 10-C.1d).

Formamide was said to be especially useful in providing one methin group of dimethinmerocyanines, because good yields were obtained by prolonged heating and the dyes were too stable to be decomposed. The substance, I (n=1, Y=S, R=Et, R'=Ph), was obtained from 2-methylbenzothiazole ethotoluene-*p*-sulphonate and 3-methyl-1-phenyl-5-pyrazolone, by 8 hours' heating with formamide, in 85% yield, and its thiobarbituric acid analogue in 95% yield. In preparing II (n=1, Y=CH:CH or S, Q=Z=S, R=R'=Et), the yields were 14% and 52%. A 2-thio-oxazolidine analogue of the latter was made; also II (n=1, Y=S or CMe_2, Q=Z=S, R=Et, R'=Ph) and the 6,7-benzo-derivative of the former. For these three, yields varied from 15–32%.[56]

The pyridine analogue of IX (n=1, R=Me) was obtained in 17% yield by heating 2-methylpyridine methiodide, indan-1,3-dione, and diethoxymethyl acetate with piperidine at 130–140° for 30 minutes, and recrystallising twice from benzene.[53]

F. From a Cyclic Compound Having >C:CH·CH$_3$ Adjacent to CO and a Quaternary Salt Having an SR Group

The dimethinmerocyanine, I (n=1, Y=S, R=Me, R'=Ph), was prepared by heating 4-ethylidene-3-methyl-1-phenyl-5-pyrazolone with 2-methylthiobenzothiazole methotoluene-*p*-sulphonate in pyridine. Ethylidene derivatives of rhodanine, of its 3-methyl and 3-phenyl derivatives, and of thiohydantoin, were condensed with the same quaternary salt.[10] A dimethinmerocyanine, XXXVII (n=1, R=R'=CH_2CO_2Et, R^1=H, R^2R^3=C_5H_{10}), having a substituted 5-aminomethylene-4-oxothiazolidine as its quaternary salt residue, was prepared by heating 3-carbethoxymethyl-5-ethylidene-4-oxo-2-thiothiazolidine and triethylamine in ethanol with a salt prepared from 3-carbethoxymethyl-4-oxo-5-piperidinomethylene-2-thiothiazolidine. Its sensitising maximum was at 6300 Å.[145,146]

G. By Rupture of a Methinoxonol or Trimethincyanine

On heating a symmetrical methinoxonol, having pyrazolone nuclei, with a quaternary salt having a reactive methyl group, in

ethanol containing a basic condensing agent, one pyrazolone nucleus was split off, the residue condensing with the quaternary salt to give a dimethinmerocyanine. Salts used belonged to the 2-linked quinoline, benzothiazole, benzoxazole, benzoselenazole, and indolenine series. Besides oxonols derived from 3-methyl-1-phenyl-5-pyrazolone, others derived from 3-carbethoxymethyl-1-phenyl(or β-naphthyl)-5-pyrazolone, etc., were used. A β-methyldimethinmerocyanine was obtained from a *meso*-methylmethinoxonol, and the isomeric α-methyl compound by use of a 2-ethylbenzothiazolium salt.[54]

A dimethinmerocyanine, the 4-linked quinoline analogue of I (n=1, R=Et, R′=Ph), was obtained in 22 % yield when 1,1′-diethyl-4,4′-carbocyanine iodide was heated at 100° for 30 minutes with 3-methyl-1-phenyl-5-pyrazolone and piperidine in ethanol.[55]

4. Di- and Tetra-methinmerocyanines with a CS Group in Place of CO

2-β-Acetanilidovinylbenzothiazole ethiodide was condensed with 4-thiohydantoin, by heating with triethylamine in ethanol, to give III (n=1, Y=S, Q=O, Z=NH, R=Et, R′=H), in which the group adjacent to the chain was CS instead of CO.[24] A compound of a similar kind was prepared from 2-β-acetanilidovinylbenzoxazole ethiodide and 3-methyl-1-phenyl-5-thiopyrazolone[11] and 2,4-dithiothiazolidines were used in the preparation of di- and tetra-methinmerocyanines[22] (see also section 10-C.1e for simple merocyanines).

By boiling with phosphorus pentasulphide in xylene containing magnesium oxide, or in pyridine, the dimethinmerocyanines, II (n=1, Y=CH:CH, S, or O, Q=O, Z=S, R=R′=Et), were converted into their thio-analogues, III (n=1, Y=CH:CH, S, or O, Q=O, Z=S, R=R′=Et), the yields being 27%, 63%, and 75%, respectively, but the first product was accompanied by a 23 % yield of III (n=1, Y=CH:CH, Q=Z=S, R=R′=Et). Similarly III (n=1, Y=CMe_2 or Se, Q=Z=O, R=R′=Et) were prepared from their analogues with a CO group. The CO group of other nuclei, such as rhodanine or 5-oxo-2-phenyloxazoline, occurring in dimethinmerocyanines, was also converted into CS.[25]

The β-phenyl derivative of III (Y=Q=S, Z=NEt, R=Et, R′=Me) was prepared by the action of phosphorus pentasulphide and magnesium oxide in xylene on the corresponding dye with a 3-ethyl-

1-methyl-2-thiohydantoin residue. A β-(methylthio)dimethinmerocyanine with CS adjacent to the chain was prepared by the action of phosphorus pentasulphide in pyridine on XIII (n=0, R=Me, R^3=H, R^4=SMe). A β-methyldimethinmerocyanine of the thiazoline series, having a 3-ethyl-2,4-dithio-oxazolidine residue, was prepared from its analogue with a 3-ethyl-4-oxo-2-thio-oxazolidine residue.[25] (cf. XV-4-K; XV-5-B and L.)

5. Tetramethinmerocyanines

A. From a Cyclic Ketomethylene Compound and a Quaternary Salt Having the Group ·CH:CH·CH:CH·NR^1R^2, or from a Cyclic Compound Having >C:CH·CH:CH·NR^1R^2 Adjacent to CO and a Quaternary Salt Having a Methyl Group

By heating 2-(4-acetanilido-1,3-butadienyl)benzothiazole ethiodide and 3-ethyl-4-oxo-2-thio-oxazolidine with triethylamine in ethanol, there resulted green crystals of II (n=2, Y=Q=S, Z=O, R=R′=Et).[21] The same salt was also condensed with 3-ethylrhodanine.[16] By reaction with 3-phenyl-2-thiohydantoin it gave II (n=2, Y=Q=S, Z=NH, R=Et, R′=Ph), and its 4,5-benzo-derivative was condensed with 1,3-diphenyl-2-thiohydantoin, both products giving blue solutions. In the benzoxazole series, heating with sodium carbonate in ethanol was applied in the preparation of II (n=2, Y=O, Q=S, Z=NPh, R=Et, R′=Ph).[24]

By boiling a 4-anilino-1,3-butadienyl quaternary salt with 3-ethylrhodanine or 3-ethyl-1-phenyl-2-thiohydantoin and triethylamine in acetic anhydride, five tetramethinmerocyanines were made, their yields, after recrystallisation from benzene, varying from 6–17%. These dyes were II (n=2, Y=CH:CH, Z=Q=S, R=R′=Et; and n=2, Y=Q=S, Z=S or NPh, R=R′=Et), the thiazoline analogue of the rhodanine compounds, and the benzoselenazole analogue of the thiohydantoin compound.[180] 4-Acetanilido-1,3-butadienyl quaternary salts in ethanol were used in the preparation of II (n=2, Y=O or CMe_2, Q=Z=S, R=R′=Et) and LVIII (n=2, Y=CMe_2, Q=S, R=R^1=R^2=Et). By the alternative procedure 5-(3-acetanilidoallylidene)-3-ethylrhodanine was condensed by heating in ethanol with the ethiodides of bases such as lepidine, quinaldine, 2-methyl-benzoselenazole, -4,5-benzobenzothiazole, or -thiazoline, yields in five instances varying from 16–37%.[17] Subsequently II (n=2, Y=Q=Z=S, R=Me, R′=Et) was prepared

from 4-acetanilido-1,3-butadienylbenzothiazole methiodide and 3-ethylrhodanine with sodium acetate and acetic anhydride.[187] In preparing the tetramethinmerocyanines, II (n=2, Y=CH:CH, CMe_2, or S, Q=Z=S, R=R′=Et), through 5-(3-acetanilidoallylidene)-3-ethylrhodanine, trimethincyanines appeared as by-products.[188] 2-(4-Acetanilido-1,3-butadienyl)thiazole methiodides, having a 4-phenyl, 4-*p*-methoxyphenyl, 4-*p*-ethoxyphenyl, or 4-*p*-bromophenyl substituent, were condensed with 3-ethylrhodanine by heating with sodium acetate in acetic anhydride; after recrystallisation from methanol, the recorded yields of tetramethinmerocyanines were 38–44%.[187]

Tetramethinmerocyanines with a 5-oxo-2-thiothiazolidine nucleus were represented in the quinoline and benzothiazole series by VI (n=2, Y=CH:CH or S, Q=Z=S, R=Et, R′=Et, CH_2Ph, or $C_{18}H_{37}$), and there was also a compound of the thiazoline series.[39] The dyes, VI (n=2, Y=O or S, Q=Z=S, R=R′=Et), were compared with their rhodanine isomers.[37] Two others were also described.[38]

The compound, VIII (n=2, Y=Z=S, R=Et, R″=SEt), with a 2-ethylthio-5-oxothiazoline nucleus, had its absorption maximum at 6400 Å.[44,45] The compound, VIII (n=2, Y=O, Z=S, R=Et, R″=NHCOPr), prepared from 2-butyrylamino-5-oxothiazoline hydrobromide and 2-(4-acetanilido-1,3-butadienyl)benzoxazole ethiodide by boiling with triethylamine in ethanol, sensitised to 6300 Å.[46]

In the 4-oxo-2-thio-imidazolidine series, indigo-coloured needles of the tetramethinmerocyanine, II (n=2, Y=Q=S, Z=N·COMe, R=R′=Et), were prepared from 1-acetyl-3-ethyl-2-thiohydantoin. The substance had its absorption maximum at 5600 Å and sensitised to 6800 Å with maxima at 5600 Å and 6400 Å.[47,48] In the 4-oxoimidazoline series, the compound, VII (n=2, Y=S, Z=NH, R=Et, R″=Me), was prepared by heating 2-methyl-4-oxoimidazoline with 4-anilino-1,3-butadienylbenzothiazole ethiodide and diethylamine in ethanol.[49]

3-Ethyl-2-methylbenzimidazole ethiodide was condensed with 5-(3-acetanilidoallylidene)-1,3-diethyl-2-thiobarbituric acid to give LVIII (n=2, Y=NEt, Q=S, R=R^1=R^2=Et),[20] and it was also condensed with the corresponding barbituric acid derivative.[17]

The tetramethinmerocyanine, IV (n=2, Y=S, R=Et), was prepared by reaction of a 2-methylbenzothiazolium salt with 2-(3-anilinoallylidene)-3-oxodihydrothianaphthene.[28]

The tetramethinmerocyanine, V (n=2, Y=S, R=Et), was prepared by heating 3-(γ-anilinoallylidene)-2-oxodihydrothianaphthene (see

XIII-4-G.2) and 2-methylbenzothiazole ethiodide with triethylamine in pyridine.[33] It was also prepared by the alternative route.[34]

B. From a Cyclic Ketomethylene Compound and a Quaternary Salt Having the Group ·CH:CH·CH:CH·SEt or ·CH:CH·CH:CH·OMe

2-(4-Ethylthio-1,3-butadienyl)quinoline methoperchlorate was condensed, by means of sodium acetate in ethanol, with indan-1,3-dione to give the tetramethinmerocyanine, IX (n=2, R=Me); in preparing II(n=2, Y=O, Q=Z=S, R=Et, R′=Me), the condensing agent was triethylamine in ethanol.[8]

2,3,3-Trimethylindolenine phenoperchlorate was converted by heating with 1,3,3-trimethoxyprop-1-ene into the salt with the group ·CH:CH·CH:CH·OMe. This was condensed with 3-ethylrhodanine to give II (n=2, Y=CMe_2, Q=Z=S, R=Ph, R′=Et), which resulted in 16 % yield after five recrystallisations.[17]

C. From a Cyclic Compound Having >C:CH·CH:CH·CH_3 Adjacent to CO and a Quaternary Salt Having an SR Group

Condensation of 5-crotonylidene-3-phenylrhodanine with 2-methylthiobenzothiazole methotoluene-p-sulphonate, by heating them in pyridine, gave the tetramethinmerocyanine II (n=2, Y=Q=Z=S, R=Me, R′=Ph).[10] 3-Allylrhodanine was condensed with crotonaldehyde, by heating with sodium acetate in acetic anhydride; the recrystallised product (51 % yield) condensed with 2-ethylthiobenzothiazole ethotoluene-p-sulphonate, by heating with triethylamine in pyridine, to give a 57 % yield of II (n=2, Y=Q=Z=S, R=Et, R′=C_3H_5).[35]

6. Hexamethinmerocyanines

A. From a Cyclic Ketomethylene Compound and a Quaternary Salt Having the Group ·CH:CH·CH:CH·CH:CH·NR^1R^2, or from a Cyclic Compound with >C:CH·CH:CH·CH:CH·NR^1R^2 Adjacent to CO and a Quaternary Salt Having a Methyl Group

Lepidine ethiodide, 2-methyl-4-phenylthiazole ethiodide, and 2-methylbenzoselenazole ethiodide were condensed with 5-(5-acetanilido-2,4-pentadienylidene)-3-ethylrhodanine, by heating with triethylamine in ethanol, to give hexamethinmerocyanines, of which the last is II (n=3, Y=Se, Q=Z=S, R=R′=Et); excess of quaternary salt and of

condensing agent led to increased yields. The alternative route, involving 2-(6-acetanilido-1,3,5-hexatrienyl)benzothiazole ethiodide, was used in the preparation of II (n=3, Y=Q=S, Z=S or O, R=R′=Et).[16,23] The former type of reaction was applied in preparing a hexamethinmerocyanine from γ-picoline methiodide, and the latter type in preparing LVIII (n=3, Y=CMe_2, Q=S, R=R^1=R^2=Et).[17] A 44% yield of recrystallised II (n=3, Y=Q=Z=S, R=Me, R′=Et) was recorded when sodium acetate in acetic anhydride was the condensing agent and 2-(6-acetanilido-1,3,5-hexatrienyl)benzothiazole methiodide was used. Four hexamethinmerocyanines, analogous with four tetramethin compounds (see section 5-A), in yields of 44–46% after recrystallisation, resulted on heating a 2-(6-acetanilido-1,3,5-hexatrienyl)-4-arylthiazole methiodide with 3-ethylrhodanine and sodium acetate in acetic anhydride.[187] In preparing three hexamethinmerocyanines, II (n=3, Y=CH:CH, CMe_2, or S, Q=Z=S, R=R′=Et), from a 3-ethylrhodanine having a 5-:CH·CH:CH·CH:CH·NAcPh group, pentamethincyanines arose as by-products.[188]

A hexamethinmerocyanine, VI (n=3, Y=O, Q=Z=S, R=R′=Et), with a 5-oxo-2-thiothiazolidine nucleus, formed green crystals; no sensitising data were given.[39]

The known hexamethinmerocyanine, IV (n=3, Y=S, R=Et) (see section 6-B), was prepared from a 2-methylbenzothiazolium salt and 2-(5-anilino-2,4-pentadienylidene)-3-oxodihydrothianaphthene.[28]

The hexamethinmerocyanine, V (n=3, Y=S, R=Et), was prepared, in 70% yield after recrystallisation, from 2-oxodihydrothianaphthene and 2-(6-anilino-1,3,5-hexatrienyl)benzothiazole ethiodide by shaking with sodium ethoxide in ethanol for 48 hours; it could not be prepared by the alternative route (but see section 6-D). The 6-ethoxy-derivative of the ketomethylene compound was condensed with 2-(6-acetanilido-1,3,5-hexatrienyl)quinoline methiodide to give a 6-ethoxy-derivative of V (n=3, Y=CH:CH, R=Me).[33,34]

The product prepared by rupture of 2,4-dinitrophenylpyridinium chloride through 3-methyl-1-phenyl-5-pyrazolone (see XIII-4-G.3) was not only used in preparing a pentamethinoxonol (see XIII-4-D), but also, on heating with 2-methylbenzothiazole methiodide and triethylamine in pyridine, it gave the intensely blue I (n=3, Y=S, R=Me, R′=Ph).[189]

3-Ethyl-2-methylbenzimidazole ethiodide was condensed with 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid to give LVIII (n=3, Y=NEt, Q=S, R=R^1=R^2=Et).[20]

B. From a Cyclic Ketomethylene Compound and a Dihydro Heterocyclic Base Having the Group :CH·CH:CH·CH:CH·CHO

Reaction of 3-ethyl-2-(5-formyl-2,4-pentadienylidene)benzothiazoline with rhodanine in boiling acetic anhydride gave II (n=3, Y=Q=Z=S, R=Et, R′=H), whilst the corresponding benzoselenazoline and thiohydantoin gave II (n=3, Y=Se, Q=S, Z=NH, R=Et, R′=H). By boiling the benzothiazoline compound and 3-oxodihydrothianaphthene with piperidine in ethanol, there resulted IV (n=3, Y=S, R=Et).[15]

C. From a Cyclic Compound Having >C:CH·CH:CH·CH_3 Adjacent to CO and a Quaternary Salt Having a ·CH:CH·NAcPh Group

By heating 3-allyl-5-crotonylidenerhodanine and 2-β-acetanilidovinylbenzothiazole ethiodide with triethylamine in pyridine, and diluting with ethanol, the hexamethinmerocyanine, II (n=3, Y=Q=Z=S, R=Et, R′=C_3H_5), separated in 50 % yield and was recrystallised from benzene.[85]

D. From a Cyclic Ketomethylene Compound, a Quaternary Salt Having a Reactive Methyl Group, and 1-Anilino-5-anilopenta-1,3-diene

The hexamethinmerocyanine, V (n=3, Y=S, R=Et) (see section 6-A), was prepared in 23 % yield by heating 2-oxodihydrothianaphthene and 2-methylbenzothiazole ethiodide with 1-anilino-5-anilopenta-1,3-diene hydrochloride and sodium ethoxide in ethanol.[33, 34]

7. Quaternary Salts of Mero- and Dimethinmero-cyanines

A. Salts of Merocyanines

Simple merocyanines prepared by condensing a 3-methyl(or ethyl) rhodanine with the metho(or etho)toluene-p-sulphonate of an alkylthio-benzoxazole, -benzothiazole, -quinoline, or -3-methylquinazoline, could be converted into salts having a reactive alkylthio-group.[57] Merocyanines, II (n=0, Y=S or O, Q=Z=S, R=R′=Et), were converted into quaternary salts having a methylthio-group by heating with methyl toluene-p-sulphonate in nitrobenzene at 135–140° for 1·5 hours, and these sulphonates were converted into iodides; the 4,5-benzo-derivative of the latter was similarly made.[59]

The SR group of merocyanine salts could be converted to methyl by various routes involving various kinds of salts. Thus the merocyanines, II (n=0, Y=S or O, Q=Z=S, R=R′=Et), were converted into the salts, X (n=0, Y=S or O, Z=S, R=R′=Et, R″=SMe, X=I): heating these with ethyl malonate and triethylamine in ethanol gave X (n=0, Y=S or O, Z=S, R=R′=Et, R″=·CH(CO_2Et), X=I), which, by boiling hydrochloric acid, were hydrolysed to X (n=0, Y=S or O, Z=S, R=R′=Et, R″=Me, X=I). The salt, X (n=0, Y=Z=S, R=Et, R′=Pr, R″=Me, X=Cl), was made similarly.[61] Methyl sulphate was used to convert the merocyanine, II (n=0, Y=Q=Z=S, R=Me, R′=Et), into the salt, X (n=0, Y=Z=S, R=Me, R′=Et, R″=SMe, X=SO_4Me), which by reaction with ethyl acetoacetate gave the merocyanine, II (n=0, Y=Z=S, Q=:C(COMe)(CO_2Et), R=Me, R′=Et); with acetylacetanilide and malonic ester anilide, respectively, the salt gave the merocyanines, II (n=0, Y=Z=S, Q=:C(COMe)(CONHPh) or :C(CO_2Et)(CONHPh), R=Me, R′=Et). By boiling these compounds with dilute hydrochloric acid, they were converted into the salt, X (n=0, Y=Z=S, R=R″=Me, R′=Et). Action of sodium hydroxide on this gave II (n=0, Y=Z=S, Q=CH_2, R=Me, R′=Et). This was converted by phenyl isothiocyanate and carbon disulphide, respectively, into II (n=0, Y=Z=S, Q=:CH·CS(NHPh) or :CH·CS(SH), R=Me, R′=Et). A methyl ester converted the last compound into the salt, X (n=0, Y=Z=S, R=Me, R′=Et, R″=CH:C($SMe)_2$).[62] The merocyanine, II (n=0, Y=Z=S, Q=:CH·COMe, R=Me, R′=Et), was prepared by the action of acetyl chloride on the salt, X (n=0, Y=Z=S, R=Me, R′=Et, R″=SMe), or, alternatively, by converting the salt into II (n=0, Y=Z=S, Q=:C$(COMe)_2$, R=Me, R′=Et), followed by acid hydrolysis; it was better to condense the salt with R·$COCH_2CO_2$H (where R=Me or Ph), or with MeCO·CH_2·CO_2Et, as the products underwent spontaneous decarboxylation. A merocyanine salt with the group ·CH:CMe(SEt) was obtained by the action of an ester on the merocyanine having a thioacetylmethylene group, obtainable from that with an acetylmethylene group by the action of phosphorus pentasulphide; alternatively the salt could be prepared by the action of ethyl mercaptan and hydrochloric acid on the merocyanine with a :CHCOMe or :C$(COMe)_2$ group.[106]

Through a merocyanine salt, the CS group in a rhodanine nucleus could be changed into CSe. Thus the merocyanine, II (n=0, Y=Q=Z=S, R=R′=Et), was converted by methyl iodide into the salt, X

(n=0, Y=Z=S, R=R′=Et, R″=SMe, X=I), which, by the action of sodium selenide in ethanol, gave II (n=0, Y=Z=S, Q=Se, R=R′=Et).[63]

B. Salts of Dimethinmerocyanines

Dimethinmerocyanines, II (n=1, Y=CH:CH, CMe_2, S, or Se, Q=Z=S) (see section 3-C), were converted by heating with alkyl sulphates into water-soluble salts, X (n=1, Y=CH:CH, CMe_2, S, or Se, Z=S, R″=SR), as also was a thiazoline analogue.[58] The salt, X (n=1, Y=O, Z=S, R=R′=Et, R″=SEt, X=p-$SO_3 \cdot C_6H_4 \cdot$Me), was prepared by heating the dimethinmerocyanine, II (n=1, Y=O, Q=Z=S, R=R′=Et), with ethyl toluene-p-sulphonate in nitrobenzene.[59]

As in the merocyanine series, the salt, X (n=1, Y=Z=S, R=R′=Et, R″=SMe, X=I), was condensed with ethyl malonate to give its analogue, X (R″=$\cdot CH(CO_2Et)_2$), which was hydrolysed to X (R″=Me).[61] The dimethinmerocyanines, II (n=1, Y=O, Z=S, Q=:C(COMe)(CONHPh) or :C(COMe)(CO_2Et), R=R′=Et), were prepared by the action of acetylacetanilide or ethyl acetoacetate in pyridine on the methomethylsulphate of II (n=1, Y=O, Q=Z=S, R=R′=Et).[109]

In various dimethinmerocyanines, CS in the ketomethylene residue was converted to CSe through a salt. Thus the dimethinmerocyanine, II (n=1, Y=CH:CH, Q=Z=S, R=R′=Et), was converted into the salt, X (n=1, Y=CH:CH, Z=S, R=R′=Et, R″=SMe), by means of methyl iodide, and that, with aqueous sodium selenide, gave II (n=1, Y=CH:CH, Q=Se, Z=S, R=R′=Et). In the benzothiazole series, II (n=1, Y=Q=Z=S, R=R′=Et), and its 4,5-benzo-derivative, having a CS group, were converted by the action of sodium selenide on their salts, into analogues having a CSe group; methyl iodide and methyl toluene-p-sulphonate, respectively, were used for salt formation. In the benzoxazole series, a salt of II (n=1, Y=O, Q=Z=S, R=R′=Et) was made with ethyl sulphate and was used to give II (n=1, Y=O, Q=Se, Z=S, R=R′=Et); with a dye having a 3-phenylrhodanine residue, salt formation was effected with methyl toluene-p-sulphonate, and with others having a 1-ethyl-3-phenyl-, or 1,3-diphenyl-, -2-thiohydantoin nucleus, it was effected with methyl iodide, the salts being treated with sodium selenide.[63]

The salts prepared from II (n=1, Y=Q=Z=S, R=R′=Et or Ph) gave, in aqueous or alcoholic solution, decomposition products which were identified as II (n=1, Y=Z=S, Q=O, R=R′=Et or Ph): this

was proved by synthesis from 5-acetanilidomethylene-3-ethyl-2,4-dioxothiazolidine with 2-methylbenzothiazole ethoethylsulphate, and from 2,4-dioxo-3-phenylthiazolidine with 2-β-acetanilidovinylbenzothiazole pheniodide, repectively. The salt obtained by the action of methyl sulphate on 5-acetanilidomethylene-3-ethyl-4-oxo-2-thiothiazolidine was converted by alcoholic potassium hydroxide into 5-anilinomethylene-3-ethyl-2,4-dioxothiazolidine. On the other hand, alcoholic potassium hydroxide ruptured the five-membered ring of II (n=1, Y=Z=S, Q=O, R=R′=Et) and the impure product was oxidised to a disulphide.[65]

When a salt, XI (Y=S, R″=SR), having a 5-oxothiazolinium nucleus, was treated with a primary amine, dimethinmerocyanines, such as VI (n=1, Y=Z=S, Q=:NR″, R=Et; or n=1, Y=Q=S, Z=NR″, R=Et) with a substituted thiohydantoin nucleus, were amongst the products isolated; dyes of the former type isomerised to those of the latter in basic media. Unlike those salts, the salts, X (n=1, Z=:NR or S, R″=SR), reacted with primary amines to give II (n=1, Z=:NR or S, Q=NR′), in which the 2-thio-group of the parent dye had been replaced by NR′.[66] Nine examples of salts prepared from dimethinmerocyanines having a substituted 2-amino-5-oxothiazoline nucleus were mostly toluene-*p*-sulphonates and included XI (Y=O, R=Et, R′=Me, R″=NEt_2, NC_5H_{10}, or NC_4H_8O, X=$SO_3 \cdot C_6H_4Me$), and the iodide corresponding with the last, also certain analogues of the benzothiazole, benzoselenazole, and thiazoline series.[67]

8. Di-, Tetra-, and Hexa-methinmerocyanines with a Substituent on the Chain

A. β-Substituted Dimethinmerocyanines

(*1*) *β-Alkyldimethinmerocyanines from a Cyclic Ketomethylene Compound, a Quaternary Salt Having a Reactive Methyl Group, and an Acid Anhydride*

The β-methyldimethinmerocyanine, XII (n=0, Y=CH:CH, Q=Z=S, R=R′=R^4=Me, R^3=H), was prepared by heating quinaldine methotoluene-*p*-sulphonate and 3-methylrhodanine with pyridine and acetic anhydride. The 4-linked quinoline, 4-phenylthiazole, 4-phenyloxazole, 4-methylquinazoline, benzothiazole, benzoselenazole, benz-

oxazole, and 3,3-dimethylindolenine analogues were likewise made, methiodides being used in preparing the last two. Of the thirty-one examples, thirteen were of the benzothiazole series; besides the series mentioned above, the 2-linked pyridine series was also represented. Most of the ketomethylene components were rhodanines, with five examples of 3-methyl-4-oxo-2-thio-oxazolidine and one of 3-methyl-1-phenyl-5-pyrazolone. The sensitising action was described.[68] Subsequently a 2-methylthiazolinium salt was condensed with 3-methyl-, 3-ethyl-, or 3-phenyl-rhodanine, or with 3-ethyl-4-oxo-2-thio-oxazolidine, by heating with acetic anhydride and pyridine, to give β-methyldimethinmerocyanines; its condensation with the first compound, by means of propionic anhydride and pyridine, gave a β-ethyldimethinmerocyanine.[69]

(2) *β-Alkyldimethinmerocyanines from a Cyclic Ketomethylene Compound and a Quaternary Salt Having a* 2-CH:CR(SMe), *a* 2-CH:CRCl, *or a* 2-CH:CR(SeMe) *Group* (cf. section 3-B)

The β-methyldimethinmerocyanine, XII (n=0, Y=Q=Z=S, R=R′=Et, R^3=H, R^4=Me), was obtained in 48 % yield by reaction of 3-ethylrhodanine with a 3-ethylbenzothiazolium toluene-*p*-sulphonate having the 2-CH:CMe(SMe) group; the corresponding salt with the 2-CH:CMeCl group gave a 43 % yield: the medium in both instances was ethanol.[16]

A benzothiazolium salt having a β-cyclopropyl-β-(methylthio)-vinyl group was condensed with 3-ethylrhodanine, by heating with triethylamine in ethanol, to give XII (n=0, Y=Q=Z=S, R=R′=Et, R^3=H, R^4=C_3H_5); the analogue, XII (n=0, Y=Q=S, Z=O, R=R′=Et, R^3=H, R^4=C_3H_5), was also made.[190]

β-Ethyldimethinmerocyanines, the 5-methoxy-derivatives of XII (n=0, Y=Se, Q=Z=S, R=R^4=Et, R′=H, Ph, or Et, R^3=H), were prepared by condensing a 5-methoxybenzoselenazolium salt, having the group ·CH:CEt(SeMe), with various rhodanines; the 4-oxo-2-thio-oxazolidine analogue of the last dye was also made. The salt was synthesised from 3-ethyl-5-methoxy-2-propionylmethylenebenzoselenazoline by the action of phosphorus pentaselenide in pyridine at 50°, which gave the corresponding base with the group :CH·CEt:Se whence the salt was obtained by use of methyl sulphate. β-Cyclohexyldimethinmerocyanines, the 6,7-tetramethylene derivatives of XII (n=0, Y=

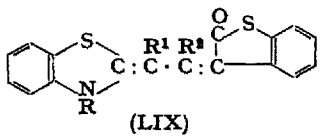
Q=Z=S, R=Et, R′=H, Ph, or Et, R^3=H, R^4=C_6H_{11}), were prepared by condensing a 6,7-tetramethylenebenzothiazolium salt, having the group ·CH:C(C_6H_{11})(SeMe), with various rhodanines; again the 4-oxo-2-thio-oxazolidine analogue of the last dye was also made.[71]

(3) *β-Alkyl- and β-CO_2R-dimethinmerocyanines from a Cyclic Ketomethylene Compound and an N-Alkylbenzothiazoline, or an N-Alkylthiazoline, Having a* 2-:CHCOR′ *Group; β-Methyldimethinmerocyanine from a Cyclic Compound Having* >CH·COMe *Adjacent to* CO *and a 2-Methylbenzothiazolium Salt* (cf. section 3-C)

In the benzothiazole series, the β-methyldimethinmerocyanine, XII (*n*=0, Y=S, Q=Z=O, R=R′=Et, R^3=H, R^4=Me), was prepared by heating 2-acetylmethylene-3-ethylbenzothiazoline and 3-ethyl-2,4-dioxo-oxazolidine in acetic anhydride.[70] The compound, XII (*n*=0, Y=Q=S, Z=O, R=R′=Et, R^3=H, R^4=Me), was made similarly, being obtained in 15 % yield.[16] So also 2-acetylmethylene-3-ethyl-4,5-benzobenzothiazoline was condensed with various rhodanines and with thiobarbituric acid. A β-ethyldimethinmerocyanine was prepared by reaction of 3-ethyl-2-propionylmethylene-4,5-benzobenzothiazoline with 3-phenylrhodanine.[70]

The β-carbethoxydimethinmerocyanine, XII (*n*=0, Y=Q=Z=S, R=Me, R′=Et, R^3=H, R^4=CO_2Et), was prepared by heating 2-(carbethoxyformyl)methylene-3-methylbenzothiazoline and 3-ethylrhodanine in acetic anhydride. In preparing the corresponding β-carboxy-compound, triethylamine in acetic anhydride was used.[191]

The β-methyldimethinmerocyanine, LIX (R=Et, R^1=H, R^2=Me), was prepared by heating 2-methylbenzothiazole ethiodide and 3-acetyl-2-oxodihydrothianaphthene with triethylamine in pyridine and gave a purple methanolic solution.[31,32]



(LIX)

The methiodides of 2-methylthiazoles, having a 4-phenyl, 4-*p*-methoxyphenyl, 4-*p*-ethoxyphenyl, 4-*p*-nitrophenyl, or 4-*p*-bromo-

phenyl substituent, were converted by acetyl chloride in pyridine into the corresponding 2-acetylmethylene-3-methylthiazolines. Condensation of these with rhodanine, or its 3-ethyl or 3-*p*-tolyl derivatives, led to nine β-methyldimethinmerocyanines, in yields of 40–52%.[192]

(*4*) *β-Alkyldimethinmerocyanines from a Cyclic Compound with* >C:CR(OEt) *Adjacent to* CO *and a Quaternary Salt Having a Reactive Methyl Group* (cf. section 3-D)

Reaction of ortho-esters with 3-methyl-1-phenyl-5-pyrazolone gave derivatives with the group 4-:CR(OEt), where R=Me, Et, or Ph. By heating the first with 2-methyl-benzoxazole or -benzothiazole metho-toluene-*p*-sulphonate in pyridine, there were prepared the β-methyl dyes, XIII (n=0, Y=O or S, R=R^4=Me, R^3=H). Use of the second gave the β-ethyl analogues, XIII (n=0, Y=O or S, R=Me, R^3=H, R^4=Et). A derivative of a 3-furyl-1-phenyl-5-pyrazolone was also prepared and used.[72]

The β-methyldimethinmerocyanine, XIV (n=0, Y=S, Z=O, R=Et, R′=Ph, R^3=H, R^4=Me), was prepared by heating 2-methylbenzothiazole ethotoluene-*p*-sulphonate with 4-α-ethoxyethylidene-5-oxo-2-phenyloxazoline in pyridine. The analogues, XIV (n=0, Y=CH:CH or O, Z=O, R=Et, R′=Ph, R^3=H, R^4=Me), also that of the 4-linked quinoline series, were made. The β-ethyl dyes, XIV (n=0, Y=S or O, Z=O, R=R^4=Et, R′=Ph, R^3=H), were also prepared. A 2,3-dimethylthiazolinium salt was used in the preparation of dimethinmerocyanines with a β-methyl or β-ethyl group.[42] Subsequently six β-methyldimethinmerocyanines with a 5-oxo-2-phenyloxazoline nucleus were made through a derivative with the :CMe(OEt) group, a quaternary salt having a reactive methyl group, and triethylamine in ethanol. They included XIV (n=0, Y=CH:CH, O, or Se, Z=O, R=Et, R′=Ph, R^3=H, R^4=Me), their 4-methylthiazole analogue, and a thiazoline analogue.[44] β-Methyldimethinmerocyanines with a 2-alkylthio-5-oxothiazoline nucleus included XIV (n=0, Y=CH:CH, S, O or Se, R=Et, R′=SEt, R^3=H, R^4=Me), also their 4-methylthiazole analogue and a thiazoline compound. In the benzoxazole series there were described XIV (n=0, Y=O, R=Et, R′=·$S(CH_2)_9Me$, R^3=H, R^4=Me or Et).[45] β-Methyldimethinmerocyanines of the benzothiazole series, having a 3-carbethoxymethylrhodanine or an indan-1,3-dione nucleus were described, also the β-ethyl analogue of the former.[146]

(5) *β-Alkyldimethinmerocyanines from a Cyclic Ketomethylene Compound, a Quaternary Salt Having a Reactive Methyl Group, and an Ortho-Ester* (cf. section 3-E)

The β-methyldimethinmerocyanines, XIII (n=0, Y=CMe_2, R=Me, R^3=H, R^4=Me or Et), were prepared by heating 2,3,3-trimethylindolenine methiodide, 3-methyl-1-phenyl-5-pyrazolone, and ethyl ortho-acetate or -propionate, with diethylamine in ethanol. Their analogues, XIII (n=0, Y=S, R=Me, R^3=H, R^4=Me or Et; and n=0, Y=O, R=R^4=Me, R^3=H), were similarly prepared by use of toluene-*p*-sulphonates. These salts of 2-methylbenzothiazole were also condensed with 3-ethylrhodanine and ethyl ortho-acetate or -propionate by heating with triethylamine in ethanol.[9]

(6) *β-Substituted Dimethinmerocyanines from a Cyclic Compound Having* >C:CR'Me *Adjacent to* CO *and a Quaternary Salt Having an* SR *Group* (cf. section 3-F)

The β-phenyldimethinmerocyanines, XIII (n=0, Y=CH:CH, S, or O, R=Me, R^3=H, R^4=Ph), were prepared by heating the appropriate 2-methylthio-heterocyclic methotoluene-*p*-sulphonates with 3-methyl-1-phenyl-4-α-phenylethylidene-5-pyrazolone in pyridine. β-Methyldimethinmerocyanines of the benzothiazole series were also made, and other 5-pyrazolones were used.[10]

The β-ethoxydimethinmerocyanine, XIII (n=0, Y=S, R=Me, R^3=H, R^4=OEt), was prepared by heating 4-α-ethoxyethylidene-3-methyl-1-phenyl-5-pyrazolone and 2-methylthiobenzothiazole methiodide with triethylamine in ethanol; the analogue, XIII (n=0, Y=CH:CH, R=Me, R^3=H, R^4=OEt), was also made. The benzoxazole series was represented and various substituted benzothiazolium salts were used. Sometimes the other reactant was 4-α-ethoxy(or methoxy)-ethylidene-3-furyl-1-phenyl-5-pyrazolone.[193] Other β-ethoxy-dyes, XII (n=0, Y=CH:CH, S, or O, Q=Z=S, R=Me, R'=Et, R^3=H, R^4=OEt), were prepared by heating 5-α-ethoxyethylidene-3-ethylrhodanine and the appropriate 2-methylthio-quaternary salt with triethylamine in pyridine.[83] β-Ethoxydimethinmerocyanines of other types, such as XIV (n=0, Y=CH:CH or S, Z=O, R=Et, R'=Ph, R^3=H, R^4=OEt), were prepared from 2-ethylthio-quaternary salts by heating with ethoxyethylidene compounds and a basic condensing agent. The cor-

responding dyes with an indan-1,3-dione nucleus were made, also others with an isoxazolone nucleus.[84,85] β-Ethoxydimethinmerocyanines derived from rhodanines were hydrolysed by strong alkali to alkali-soluble ketones.[85] Certain ethoxyethylidene compounds were converted by thiols into alkyl(or aryl)thioethylidene compounds.[146] From these, β-SR-dimethinmerocyanines, such as XII (n=0, Y=Z=Q=S, R=Et, R′=CH_2CO_2Et, R^3=H, R^4=SEt, SC_6H_4Me (*p*), or SC_8H_{17}) and a thiazoline analogue of the first were synthesised, also XIV (n=1, Y=Z=S, R=Et, R′=R^4=SEt, R^3=H). By condensing 3-substituted rhodanines with diacetyl, or with pyruvic acid in methanol, the groups :CAcMe or :CMe(CO_2Me) were introduced into the 5-position. From the products, the β-substituted dimethinmerocyanine, XII (n=0, Y=Z=Q=S, R=Et, R′=CH_2CO_2Me, R^3=H, R^4=Ac), and a thiazoline analogue of XII (n=0, Y=Z=Q=S, R=Me, R′=CH_2CO_2Me, R^3=H, R^4=CO_2Me), were prepared.[85]

(*7*) *β-Methylthiodimethinmerocyanines from a Cyclic Compound Having* >C:C(SMe)$_2$ *Adjacent to* CO *and a Quaternary Salt Having a Reactive Methyl Group*

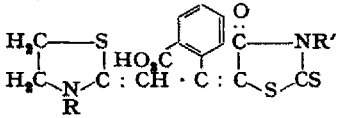
β-Methylthiodimethinmerocyanines were prepared by condensing cyclic compounds, having the group >C:C(SMe)$_2$ adjacent to CO, with quaternary salts having a reactive methyl group, by heating with triethylamine in ethanol. Examples included XII (n=0, Y=CH:CH or S, Q=Z=S, R=Et, R′=Me, R^3=H, R^4=SMe) and, in the 4-linked quinoline series, the analogue of XII (n=0, Z=O, Q=S, R=R′=Me, R^3=H, R^4=SMe). There were also prepared XII (n=0, Y=Q=Z=S, R=Et, R′=Me, R^3=H, R^4=SCH_2Ph; and n=0, Y=Q=S, Z=O, R=R′=Et, R^3=H, R^4=SMe); the 5,6-benzo-derivative of the 4-linked quinoline analogue of the last was also made.[74]

(*8*) *β-*NR^1R^2*-Dimethinmerocyanines from β-Methylthiodimethinmerocyanines and* HNR^1R^2

The β-NR^1R^2-dimethinmerocyanines, XII (n=0, Y=Q=Z=S, R=R′=Et, R^3=H, R^4=NC_4H_8, NHC_2H_4OH, or $NH(CH_2)_3Me$), were prepared by heating the β-methylthio-dye, XII (n=0, Y=Q=Z=S, R=R′=Et, R^3=H, R^4=SMe), with pyrrolidine, ethanolamine, or n-butylamine at 60° for 4 hours, sometimes with addition of triethylamine. The oxazolidine analogue of the first was also described.[75]

(9) β-o-Carboxyphenyldimethinmerocyanines from a Cyclic Ketomethylene Compound, a 2-Methylthiazolinium Salt, and Phthalic Anhydride

The β-o-carboxyphenyldimethinmerocyanines, LX (R=Me or Et, R′=Ph; and R=R′=Et), were prepared by heating a 2-methylthiazoline quaternary salt and a 3-substituted rhodanine with phthalic anhydride in pyridine. Dyes in which the o-carboxyphenyl group carried another substituent were also made.[76]



(LX)

(10) β-Methyldimethinmerocyanines from a Cyclic Ketomethylene Compound and Excess of 2-Methylthiazolinium Salt

Orange yellow dyes, formed by reaction of excess of 2-methylthiazolinium salt with a ketomethylene compound, of the 3-alkyl-4-oxo-oxazolidine, 3-alkyl-2-thiohydantoin, or 3-alkylrhodanine series, were regarded as β-methyldimethinmerocyanines: the thiazoline ring had the dual function of providing one nucleus and also the chain.[77]

B. α-Substituted Dimethinmerocyanines

(1) α-Methyldimethinmerocyanine from a Cyclic Ketomethylene Compound and a Benzothiazolium Salt Having the Group ·CMe:CH·SEt (cf. section 3-B)

The α-methyldimethinmerocyanine, XII (n=0, Y=Q=Z=S, R=R^3=Me, R′=Et, R^4=H), was prepared by condensing a benzothiazolium salt having the group ·CMe:CH·SEt with 3-ethylrhodanine.[6]

(2) α-Methyldimethinmerocyanines from a Cyclic Compound Having >CH:CHO Adjacent to CO and a 2-Ethylbenzothiazolium Salt (cf. section 3-C)

The magenta α-methyldimethinmerocyanines, LIX (R=Me or Et, R^1=Me, R^2=H), were prepared from 2-ethylbenzothiazole alkiodide and 3-formyl-2-oxodihydrothianaphthene by heating with triethylamine in pyridine.[31,32]

(3) α-Phenyldimethinmerocyanine from a Cyclic Compound Having >C:CH·CH$_2$Ph Adjacent to CO and a Quaternary Salt Having an SR Group (cf. section 3-F)

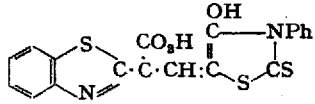
The α-phenyldimethinmerocyanine, XIII (n=0, Y=S, R=Me, R^3=Ph, R^4=H), was prepared by heating 2-methylthiobenzothiazole methotoluene-p-sulphonate with 3-methyl-1-phenyl-4-β-phenylethylidene-5-pyrazolone in pyridine.[10]

(4) α-Aryloxydimethinmerocyanines from a Cyclic Ketomethylene Compound and a Quaternary Salt Having the Group ·C(OAr):CH·NR^{1}R^2, or from a Cyclic Compound Having >C:CH·NR^{1}R^2 Adjacent to CO and a Quaternary Salt Having the Group ·CH$_2$OAr (cf. section 3-A)

In the benzothiazole series, α-aryloxydimethinmerocyanines, such as XII (n=0, Y=Q=S, Z=S or O, R=Me or Et, R′=Et, R^3=m-O·C$_6$H$_4$Me, R^4=H), were mostly prepared through benzothiazolium salts having a 2-m-tolyloxymethyl group and heterocyclic compounds with a 5-acetanilidomethylene group, though the alternative route could also be used. A dye with an α-methoxy group and a 3-phenylrhodanine residue was also made. In the benzoxazole series, the α-substituents were OPh and p-OC$_6$H$_4$Cl.[79]

(5) α-Carbethoxydimethinmerocyanine from 2-Carbethoxymethylbenzothiazole by Two Routes

The α-carbethoxydimethinmerocyanine, XII (n=0, Y=Q=Z=S, R=Me, R′=Ph, R^3=CO$_2$Et, R^4=H), was best prepared by condensing 2-carbethoxymethylbenzothiazole with 5-acetanilidomethylene-3-phenylrhodanine to give LXI, and heating the potassium salt of this



(LXI)

with methyl iodide. An alternative route involved condensation of 2-carbethoxymethylbenzothiazole methiodide with diphenylformamidine and acetylation of the product to 2-(β-acetanilido)(α-carbethoxy)vinylbenzothiazole methiodide; this was condensed with 3-phenylrhodanine by heating with potassium carbonate in pyridine, but there

were by-products and the yield was poor. The former method was also applied to the preparation of an analogue with an α-carbanilido-group.[78]

(6) α-Hydroxy- or α-Methyl-dimethinmerocyanines from a Cyclic Compound Having >C:CHOEt *Adjacent to* CO *and a Benzothiazolium Salt Having the Group* $\cdot CH_2OH$ *or* $\cdot CH_2Me$ (cf. section 3-D)

The α-hydroxydimethinmerocyanines, XII (n=0, Y=Q=Z=S, R=Me, R′=C_3H_5 or CH_2CO_2Et, R^3=OH, R^4=H), were prepared by heating 2-hydroxymethylbenzothiazole methotoluene-*p*-sulphonate and the appropriate ethoxymethylene compound with triethylamine in ethanol: both absorbed at 5600 Å in ethanol. Heating with acetic anhydride gave the α-acetoxy-dyes, which absorbed at 5300 Å and 5320 Å, respectively.[80] Similarly the α-methyl derivative of VIII (n=0, Y=Z=S, R=Et, R″=SEt), and the dye, XII (n=0, Y=Q=Z=S, R=Et, R′=CH_2CO_2Et), were prepared from 2-ethylbenzothiazole ethiodide; analogues of the thiazoline series were also made.[146]

C. αβ-Dimethyldimethinmerocyanines

(1) From a Cyclic Compound Having >CH·COMe *Adjacent to* CO *and a 2-Ethylbenzothiazolium Salt* (cf. section 3-C)

The orange-yellow αβ-dimethyldimethinmerocyanines, LIX (R=Me or Et, R^1=R^2=Me), were prepared from 2-ethylbenzothiazole alkiodide and 3-acetyl-2-oxodihydrothianaphthene.[31,32]

(2) From a Cyclic Compound Having >C:CMe(OEt) *Adjacent to* CO *and a 2-Ethylbenzothiazolium Salt* (cf. section 3-D)

The αβ-dimethyldimethinmerocyanine, XIII (n=0, Y=S, R=R^3=R^4=Me), was prepared by condensing a 2-ethylbenzothiazolium salt with 4-α-ethoxyethylidene-3-methyl-1-phenyl-5-pyrazolone.[72]

D. δ-Substituted Tetramethinmerocyanines

(1) δ-Methyltetramethinmerocyanines from a Cyclic Ketomethylene Compound and a Quaternary Salt Having the Group $\cdot CH{:}\underset{\text{Me}}{C}H\cdot CH{:}CMe(SR)$ (cf. section 5-B)

The δ-methyltetramethinmerocyanine, XII (n=1, Y=CMe_2, Q=Z=S, R=R′=R^4=Me, R^1=R^2=R^3=H), was prepared by heating

2-(4-ethylthio-1,3-pentadienyl)-3,3-dimethylindolenine methiodide with 3-methylrhodanine and sodium acetate in ethanol: its sensitising maximum was at 6900 Å. The same methiodide and indan-1,3-dione were condensed by heating with triethylamine in ethanol.[82]

(2) *δ-Methyltetramethinmerocyanine from a Cyclic Compound Having* >C:CMe_2 *Adjacent to* CO *and a Quaternary Salt Having the Group* ·CH:CH·SR

The δ-methyltetramethinmerocyanine, XIII (n=1, Y=S, R=R^4=Me, R^1=R^2=R^3=H), was prepared by condensation of 2-β-ethylthiovinylbenzothiazole methiodide with 4-isopropylidene-3-methyl-1-phenyl-5-pyrazolone.[6]

(3) *δ-Substituted Tetramethinmerocyanines from a Cyclic Compound Having* >C:CRMe *Adjacent to* CO *and a Quaternary Salt Having the Group* ·CH:CH·NAcPh (cf. section 8-A.6)

A δ-phenyltetramethinmerocyanine, XIII (n=1, Y=CMe_2, R=Me, R^1=R^2=R^3=H, R^4=Ph), was prepared by heating 2-β-acetanilidovinyl-3,3-dimethylindolenine methiodide with 3-methyl-1-phenyl-4-α-phenylethylidene-5-pyrazolone in pyridine. An analogous procedure gave the δ-methyl compound, XIII (n=1, Y=S, R=R^4=Me, R^1=R^2=R^3=H), which had its sensitising maximum at 5200 Å.[10] The 4,5-benzo-derivative of XII (n=1, Y=Q=Z=S, R=Et, R′=C_3H_5, R^1=R^2=R^3=H, R^4=Me) was prepared by means of triethylamine in pyridine, and precipitated by ethanol in 62 % yield.[85]

A δ-ethoxytetramethinmerocyanine, XII (n=1, Y=Q=Z=S, R=R′=Et, R^1=R^2=R^3=H, R^4=OEt), was prepared by heating 2-β-acetanilidovinylbenzothiazole ethiodide and 5-α-ethoxyethylidene-3-ethylrhodanine with triethylamine in ethanol.[83] The δ-ethoxytetramethinmerocyanines, XIV (n=1, Y=CH:CH, S, O or Se, Z=O, R=Et, R′=Ph, R^1=R^2=R^3=H, R^4=OEt), and their 4-linked quinoline and thiazoline analogues, also XIV (n=1, Y=CH:CH, O, or Se, Z=S, R=Et, R′=SCH_2Ph, R^1=R^2=R^3=H, R^4=OEt), were prepared, and, in both series, *N*-methyl dyes with a thiazoline or substituted indolenine nucleus, and an analogue of XIV (n=1, Y=O) with an indan-1,3-dione nucleus.[84] The δ-ethoxy- and δ-acetyl-tetramethinmerocyanines, XII (n=1, Y=Z=Q=S, R=Et, R′=CH_2CO_2Et, R^1=R^2=R^3=H, R^4=

OEt or Ac), and the 4,5-benzo-derivative of the δ-methoxy-analogue were described. The δ-ethylthiotetramethinmerocyanines, XII (n=1, Y=O or S, Q=Z=S, R=Et, R′=CH_2CO_2Et, R^1=R^2=R^3=H, R^4=SEt) and XIV (n=1, Y=Z=S, R=Et, R′=R^4=SEt, R^1=R^2=R^3=H), were also prepared, the yields of crude product varying from 39–69%.[85]

E. β-Substituted Tetramethinmerocyanines

(*1*) *β-Methyltetramethinmerocyanines from a Cyclic Compound Having* >C:CH·CH:CMe(SEt) *Adjacent to* CO *and a Quaternary Salt Having a Reactive Methyl Group*

β-Methyltetramethinmerocyanines, XII (n=1, Y=Q=Z=S, R=Et, R′=Me or Et, R^1=R^3=R^4=H, R^2=Me), the 4-linked quinoline analogue of the latter, and the 6-methyl derivative of XII (n=1, Y=CH:CH, R=R′=Et, R^1=R^3=R^4=H, R^2=Me) were prepared by heating an alkiodide, having a reactive methyl group, with a 3-alkylrhodanine having >C:CH·CH·CMe(SEt) in the 5-position, in ethanol containing diethylamine.[86]

(*2*) *β-Methylthiotetramethinmerocyanine from a Cyclic Compound Having* >C:CHNHPh *Adjacent to* CO *and a Quaternary Salt Having the Group* ·CH:CMe(SMe)

A β-methylthiotetramethinmerocyanine, XIII (n=1, R=Et, R^1=R^3=R^4=H, R^2=SMe), was prepared by condensing a benzothiazolium salt having the group ·CH:CMe(SMe) with 4-anilinomethylene-3-methyl-1-phenyl-5-pyrazolone, by heating with sodium acetate in acetic anhydride.[87]

F. ζ-Substituted Hexamethinmerocyanines

The ξ-methylhexamethinmerocyanine, XIII (n=2, Y=CH:CH, R=R^4=Me, R^1=R^2=R^3=H), was prepared by heating 2-(4-ethylthio-1,3-butadienyl)quinoline methoperchlorate with 4-isopropylidene-3-methyl-1-phenyl-5-pyrazolone and sodium acetate in ethanol. The blue crystals gave a blue benzene solution. The sensitising maximum was at 7600 Å.[8]

The ξ-ethoxyhexamethinmerocyanine, XII (n=2, Y=Z=Q=S,

R=Et, R'=CH_2CO_2Et, $R^1=R^2=R^3=H$, $R^4=OEt$), was prepared, in 44% yield, by heating 2-(4-acetanilidobuta-1,3-dienyl)benzothiazole ethiodide and 3-carbethoxymethyl-5-α-ethoxyethylidenerhodanine with triethylamine in ethanol for 2 minutes, the resultant tar being induced to crystallise by means of ethanol.[85]

9. Merocyanines in which Part of the Carbon Chain is Cyclic

A. Tetra-, Hexa-, and Octa-methinmerocyanines in which Three Carbon Atoms of the Chain are Cyclic

(*1*) *Tetramethinmerocyanines from a Cyclic Ketomethylene Compound and a Quaternary Salt Having a Substituted 2-[3-(Ethylthio)cyclohex-2-enylidene]methyl Group*

3-Ethylthio-5,5-dimethylcyclohex-2-en-1-one, prepared from a cyclohexane-1,3-dione,[194] was condensed with 2-methylbenzothiazole methotoluene-*p*-sulphonate to give an intermediate salt (cf. IX-5);[89] this was heated with 1-phenyl-3-methyl-5-pyrazolone and triethylamine in pyridine to give XV (*n*=0, Y=S, $R=R^1=R^2=Me$). The intermediate salt was also condensed with 3-methylrhodanine by means of triethylamine in ethanol.[90]

(*2*) *Tetramethinmerocyanines from a Cyclic Compound Having a Substituted 3-Methylcyclohex-2-enylidene Group Attached to the Carbon Adjacent to* CO, *and a Quaternary Salt Having an* SR *Group*

3,5,5-Trimethylcyclohex-2-en-1-one was condensed, by heating with piperidine at 135–140° for 4 hours, with ketomethylene compounds such as 3-ethylrhodanine, 1,3-diethylthiobarbituric acid, 5-oxo-3-phenyloxazoline, and 1-(2-benzothiazolyl)(or phenyl)-3-methyl-5-pyrazolone. By heating the first intermediate product with 2-methylthiobenzoxazole methotoluene-*p*-sulphonate and triethylamine in pyridine, there resulted the 3-ethylrhodanine analogue of XV (*n*=0, Y=O, $R=R^1=R^3=Me$), in 41% yield after two recrystallisations; the 6,7- and 4,5-benzo-derivatives were likewise made, also the benzoselenazole analogue of the last; analogues of the first dye, with a 3-methyl-1-phenyl-5-pyrazolone, or a 1-(2-benzothiazolyl)-3-methyl-5-

pyrazolone, nucleus were described. In the benzothiazole series there was made XVI (n=0, Y=S, R=Et, R^1=R^2=Me), which had its sensitising maximum at 6050 Å, and its 1,3-diethylthiobarbituric acid analogue.[91]

(*3*) *Hexamethinmerocyanine from a Cyclic Compound Having a Substituted 3-Methylcyclohex-2-enylidene Group Attached to the Carbon Adjacent to* CO, *and a Quaternary Salt Having the Group* ·CH:CH·NRPh

The compound, XVI (n=1, Y=S, R=Et, R^1=R^2=Me), which had its sensitising maximum at 6800 Å, was prepared by heating 2-β-acetanilidovinylbenzothiazole ethiodide and 5-oxo-3-phenyl-4-(3,5,5-trimethylcyclohex-2-enylidene)oxazoline with triethylamine in pyridine.[91]

(*4*) *Octamethinmerocyanine from a Cyclic Compound Having a Substituted 3-Methylcyclohex-2-enylidene Group Attached to the Carbon Adjacent to* CO, *and a Quaternary Salt Having the Group* ·CH:CH·CH:CH·NRPh

The compound, XVI (n=2, Y=S, R=Et, R^1=R^2=Me), for which no sensitising data were quoted, was prepared by reaction of 2-(4-acetanilido-1,3-butadienyl)benzothiazole ethiodide with the same intermediate compound.[91]

B. Di- and Tetra-methinmerocyanines in which One Carbon Atom of the Chain is Cyclic

(*1*) *Dimethinmerocyanines Having a Pyrrole Nucleus*

The methin dyes, XVIII (Q=O or S, R=Ph, R^1=R^2=H), were prepared, in yields or 97 % and 94 %, by heating 3-formyl-2,5-dimethyl-1-phenylpyrrole with barbituric or thiobarbituric acid in ethanol. Similar pyrroles, but with a benzyl, cyclohexyl, n-dodecyl, n-propyl, or n-heptyl group on the nitrogen atom, were used, also 3-formyl-1,2-dimethylindole, and, on the other hand, 1-phenyl-2-thiobarbituric acid.[92] 3-Formyl-1,2-dimethylindole was also condensed with 3-ethylrhodanine.[17]

(2) *Tetramethinmerocyanines Having a Pyrrocoline Nucleus*

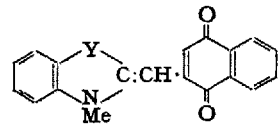
The compound, XVII (n=1), was prepared by condensing 2,3-dimethylpyrrocoline with 5-(3-acetanilidoallylidene)-1,3-diethyl-2-thiobarbituric acid, by heating them in pyridine and treating with methanol.[92]

(3) *Hexamethinmerocyanines Having a Pyrrocoline Nucleus*

The compound, XVII (n=2), was prepared from 2,3-dimethylpyrrocoline and 5-(5-acetanilido-2,4-pentadienylidene)-1,3-diethyl-2-thiobarbituric acid. An analogue with a 2-phenylpyrrocoline residue was described. Another compound had a 1-*p*-carboxyphenyl-3-pentadecyl-5-pyrazolone nucleus.[92]

(4) *Dimethinmerocyanines Prepared from a Methylene Base and a Quinone*

Reaction of a heterocyclic methylene base with a quinone at room temperature in benzene or chloroform gave a dye, with a hydroquinone as by-product. Five of the thirteen dyes were of the benzothiazole series, such as LXII (Y=S) (88 % yield), and derivatives in which one



(LXII)

or other nucleus was substituted (yields 22–44%). The dyes, LXII (Y=CH:CH or Se), were also made and other quinones, such as 1,4-benzoquinone and 1,2-naphthoquinone, were also used. Absorption data for neutral and acid solutions were given (see section 12), and hydroperchlorates of three of the dyes were isolated.[94]

C. Dimethinmerocyanines in which Both Carbon Atoms of the Chain are Cyclic

Cyclic ketomethylene compounds could be converted into cyclopentylidene derivatives by heating with cyclopentanone and piperidine

in ethanol. Such derivatives, by condensation with quaternary salts having an alkylthio-group, gave dimethinmerocyanines in which both carbon atoms of the chain were cyclic. The examples, apart from one of the benzoxazole series, were all of the benzothiazole series and comprised XIX (Y=S, Z=O or NPh, R=R'=Et; and Y=Z=S, R=Me, R'=Et), and analogues with a 3-methyl-1-phenyl-5-pyrazolone, 1,3-diethyl-barbituric or -thiobarbituric acid nucleus, etc. Several had a 6,7-benzobenzothiazoline nucleus, and, in one, the two carbon atoms of the chain entered into a cyclohexane ring.[95] The preparation and sensitising action of such compounds was independently described elsewhere.[195]

10. Variations in the Nuclei which Enter into Merocyanine Molecules

A. Introduction of Substituents

(*1*) *In the Quaternary Salt Residue*

Three dimethinmerocyanines were prepared from 2-anilinomethylene-3-oxodihydrothianaphthene, by reaction with 6-fluoro-2-methylbenzothiazole ethiodide,[96] with 2-methyl-5-trifluoromethylbenzothiazole ethiodide,[97] and with 2-methyl-6-trifluoromethylthiobenzothiazole methiodide,[98] respectively, by heating with sodium acetate in ethanol.

(*2*) *In the Ketomethylene Residue*

(*a*) *Merocyanines.* A merocyanine, I (n=0, Y=S, R=Et, R'=C_7H_4NS), with a benzothiazolyl substituent, was prepared from 2-methylthiobenzothiazole ethiodide and 1-(2-benzothiazolyl)-3-methyl-5-pyrazolone, by heating with triethylamine in ethanol.[196]

Merocyanines having a long-chain substituent were prepared by condensing 2-phenylthiobenzothiazole ethiodide with 3-n-heptylrhodanine or with 3-n-dodecyl-4-oxo-2-thio-oxazolidine, by heating with triethylamine in ethanol; their sensitising maxima were at 4700 Å and 4350 Å, respectively.[99]

A simple merocyanine, II (n=0, Y=O, Q=Z=S, R=Me, R'=$C_6H_4CO_2H$), having a carboxyphenyl group, had its sensitising maximum at 4600 Å.[100] Another, II (n=0, Y=Q=Z=S, R=Et, R'=p-$CH_{64}SO_3H$), with a sulphophenyl group, did not sensitise.[101] Mero-

cyanines, II (n=0, Y=Q=Z=S, R=Et, R′=CH_2CO_2H or $CH_2CH_2SO_3H$), with a carboxyalkyl or sulphoalkyl group, were prepared by heating the appropriate ketomethylene compound and 2-ethylthiobenzothiazole ethiodide with triethylamine in ethanol. An analogue of II (n=0, Q=Z=S, R=Bu, R′=CH_2SO_3H) with a 4-linked quinoline nucleus was made (cf. II-1) from quinoline n-butiodide and the rhodanine by heating with potassium hydroxide in ethanol.[102]

A merocyanine, II (n=0, Y=Q=S, Z=N-2-C_5H_4N, R=Me, R′=Et), having a 2-pyridyl group attached to a thiohydantoin nucleus, was made,[104] also II (n=0, Y=CH:CH or S, Q=Z=S, R=Me, R′=2-C_5H_4N) and their thiazoline analogue, in which a rhodanine nucleus carried a 2-pyridyl group.[106]

(*b*) *Dimethinmerocyanines.* Dimethinmerocyanines with a 1-(2-benzothiazolyl) group in a pyrazolone nucleus were said to sensitise in a new and useful way. The product, I (n=1, Y=CH:CH, R=Et, R′=C_7H_4NS), was prepared by heating 1-(2-benzothiazolyl)-3-methyl-5-pyrazolone, 2-β-anilinovinylquinoline ethiodide, and sodium acetate in acetic anhydride, whilst 2-β-acetanilidovinyl salts and triethylamine in ethanol were used in the preparation of I (n=1, Y=S, O, or Se, R=Et, R′=C_7H_4NS).[196]

A dimethinmerocyanine, II (n=1, Y=CH:CH, Q=S, Z=O, R=Et, R′=$C_{12}H_{25}$), with a long-chain substituent was prepared by heating 2-β-acetanilidovinylquinoline ethiodide and 3-n-dodecyl-4-oxo-2-thio-oxazolidine with triethylamine in ethanol; similarly 4-β-acetanilidovinylquinoline ethiodide was condensed with 3-n-dodecylrhodanine; both products were sensitisers. The dyes, II (n=1, Y=O, Q=S, Z=O, S, or NPh, R=Et, R′=C_7H_{15}), were made, also the benzothiazole analogue of the last. 2-β-Anilinovinylthiazoline methiodide was condensed with 3-n-heptylrhodanine and with its oxazolidine analogue.[99]

Dimethinmerocyanines, II (n=1, Y=S or O, Q=Z=S, R=Et, R′=p-$C_6H_4CO_2H$), with a p-carboxyphenyl group in a rhodanine nucleus were described, and an analogue of the former with a m-carboxy-p-hydroxyphenyl group, also I (n=1, Y=S, R=Et, R′=p-$C_6H_4CO_2H$) and its β-methyl derivative.[100]

Dimethinmerocyanines with a p-sulphophenyl group were represented by I (n=1, Y=CH:CH, R=Et, R′=p-$C_6H_4SO_3H$), its 4-linked quinoline and 4-methylthiazole analogues, also dyes of the 2-linked quinoline, benzothiazole, and benzoxazole series, in which those

nuclei were substituted, and by I (n=1, Y=CMe_2, R=Me, R'=p-$C_6H_4SO_3H$) and its thiazoline analogue; in another dye the 1-substituent in the pyrazolone nucleus was a 1,4-sulphonaphthyl group. Compounds with other ketomethylene residues were II (n=1, Y=O, Q=S, Z=O or S, R=Et, R'=p-$C_6H_4SO_3H$) and an analogue of the latter with a 2,5-disulphophenyl substituent. Various β-substituted derivatives were included.[101] Dimethinmerocyanines with a carboxyalkyl group were II (n=1, Y=CH:CH, S, or O, Q=Z=S, R=Et, R'=CH_2CO_2H; n=1, Y=Q=Z=S, R=Et, R'=$CH_2CH_2CO_2H$, $\cdot CH(CO_2H)\cdot CH_2CH_2CO_2H$, or $\cdot CHMeCO_2H$; and n=1, Y=O, Q=S, Z=$N\cdot CH_2\cdot CO_2H$, R=Et, R'=Ph). A dimethinmerocyanine of the thiazoline series, linked with a 3-carboxymethyl-4-oxo-2-thio-oxazolidine nucleus, was made. Dimethinmerocyanines with a sulphoalkyl group were II (n=1, Y=O, Q=Z=S, R=Et, R'=$CH_2CH_2SO_3H$; and n=1, Y=Z=O, Q=S, R=Et, R'=CH_2SO_3H or $\cdot CH_2CH_2SO_3H$). Some β-substituted dyes were also described.[102] Dimethinmerocyanines with a sulphoaryl group, useful for anti-halation, were I (n=1, Y=O, R=Et, R'=p-$C_6H_4SO_3H$ or α-$C_{10}H_6SO_3H$ (p)), also the sodium salt, and the 5-phenyl derivative, of the former.[103]

Examples of dyes having a pyridyl- or quinolyl-thiohydantoin nucleus comprised one simple merocyanine, thirteen dimethin-, and twenty tetramethin-merocyanines. A 2-pyridyl group occurred in twenty-seven examples, two such groups in five, and both a 2-pyridyl and 3-quinolyl group in one. The dyes belonged mostly to the benzothiazole and benzoxazole series, but the oxazole and thiazoline series were also represented.[105] Examples of dyes having a pyridyl- or quinolyl-rhodanine nucleus included three simple merocyanines, eight dimethinmerocyanines, of which one had a β-methyl substituent, and three tetramethinmerocyanines. The 2-pyridyl group was most general but 2-(6-methylpyridyl), 3-pyridyl, and 3-quinolyl also occurred. Six dyes were of the benzoxazole, four of the benzothiazole, three of the thiazoline, and one of the 2-linked quinoline series.[106]

(*c*) *Tetramethinmerocyanines.* Tetramethinmerocyanines, II (n=2, Y=Q=S, Z=O, S, or NPh, R=Et, R'=C_7H_{15}), with a long-chain group in the molecule, were prepared by condensing 2-(4-acetanilido-1,3-butadienyl)benzothiazole ethiodide, by means of triethylamine in ethanol, with a ketomethylene compound having such a substituent; the compound, II (n=2, Y=O, Q=Z=S, R=Et, R'=$C_{12}H_{25}$), was made similarly.[99]

The tetramethinmerocyanines, II (n=2, Y=O, Q=Z=S, R=Et, R′=p-$C_6H_4CO_2H$)[100] and I (n=2, Y=S, R=Et, R′=p-$C_6H_4SO_3H$)[101], were described as sensitisers, as also were II (n=2, Y=O, Q=Z=S, R=Et, R′=CH_2CO_2H or $CH_2CH_2SO_3H$).[102]

Of tetramethinmerocyanines with a pyridyl or quinolyl substituent in a thiohydantoin[105] or in a rhodanine nucleus,[105] there were twenty examples of the former and three examples of the latter kind (see section 10-A-2b).

B. Variations in the Group Attached to the Nitrogen Atom of the Quaternary Salt Residue

(*1*) *Merocyanines*

The two merocyanines, II (n=0, Y=Q=Z=S, R=$CH_2CH_2CO_2H$ or CH_2CH_2OPh, R′=Et), with an *N*-β-carboxyethyl and *N*-β-phenoxyethyl group, respectively, were prepared through 2-phenylthiobenzothiazole β-carboxyethiodide[110] and 2-methylthiobenzothiazole β-phenoxyethotoluene-*p*-sulphonate.[112]

(*2*) *Dimethinmerocyanines*

Of dimethinmerocyanines with an *N*-β-carboxyethyl group, II (n=2, Y=S or O, Q=Z=S, R=$CH_2CH_2CO_2H$, R′=Et), and their thiazoline analogue, sensitised, as also did II (n=2, Y=O, Q=Z=S, R=CH_2CO_2H, R′=Et) and its 4-linked quinoline analogue, but I (n=2, Y=CMe_2, R=$CH_2CH_2CO_2H$, R′=Ph) did not. Examples of β-substituted dyes were included.[110] Dimethinmerocyanines, II (n=1, Y=Q=Z=S, R=CH_2CH_2OPh, R′=C_3H_5; and n=1, Y=Q=S, Z=O, R=CH_2CH_2OPh, R′=Et), with an *N*-β-phenoxyethyl group were prepared, the former by reaction of 5-acetanilidomethylene-3-allylrhodanine, 2-methylbenzothiazole β-phenoxyethotoluene-*p*-sulphonate, and triethylamine in isopropanol, and the latter similarly.[112]

The dimethinmerocyanines, XX (n=1, Z=S or NPh, R′=Et), having a 3,4-trimethylenebenzothiazole residue, were prepared by condensing 2-β-acetanilidovinyl-3,4-trimethylenebenzothiazolium iodide with 3-ethylrhodanine and with 3-ethyl-1-phenyl-2-thiohydantoin. The iodide was also condensed with 3-methyl-1-phenyl-5-pyrazolone and with thiobarbituric acid.[113b]

(3) *Tetramethinmerocyanines*

A tetramethinmerocyanine with an *N*-β-carboxyethyl group, the 5-chloro-derivative of II (*n*=2, Y=Q=Z=S, R=$CH_2CH_2CO_2H$, R′=H), did not sensitise, nor did a benzoxazole analogue having a 1,3-diethylbarbituric acid residue.[110] Three tetramethinmerocyanines with an *N*-β-phenoxyethyl group were prepared, each by reaction of a 2-methyl quaternary salt with a heterocyclic compound having a γ-acetanilidoallylidene group: they were II (*n*=2, Y=Q=S, Z=NPh, R=CH_2CH_2OPh, R′=Et), I (*n*=2, Y=S, R=CH_2CH_2OPh, R′=Ph), and the 6-methoxy-derivative of II (*n*=2, Y=Se, Q=Z=S, R=CH_2CH_2OPh, R′=Et).[112]

A tetramethinmerocyanine, XX (*n*=2, Z=NPh, R′=Et), having a 3,4-trimethylenebenzothiazole residue, was prepared by heating 2-(4-anilino-1,3-butadienyl)-3,4-trimethylenebenzothiazolium iodide and 3-ethyl-1-phenyl-2-thiohydantoin in pyridine; its sensitising maximum was at 6750 Å.[113b]

(4) *Hexamethinmerocyanines*

A hexamethinmerocyanine, the 1,3-diphenyl-2-thiobarbituric acid analogue of I or II (*n*=2, Y=O, R=$CH_2CH_2CO_2H$), having an *N*-β-carboxyethyl group, did not sensitise.[110]

C. Use of Unusual Nuclei

(1) *In the Quaternary Salt Residue*

(*a*) *Nuclei with Nitrogen as the One Hetero-Atom.* The simple merocyanine, XXII (*m*=0, *n*=4, Z=S, R=Me, R′=Et), was synthesised in the stages 2-piperidone → 2-thiopiperidone → 2-methylthio-3,4,5,6-tetrahydropyridine → its methomethylsulphate, which was condensed with 3-ethylrhodanine. Its analogues, XXII (*m*=0, *n*=5 or 7, Z=S, R=Me, R′=Et), were made similarly. The three dyes had sensitising maxima at 4340 Å, 4340 Å, and 4370 Å, respectively, and increased the sensitivity six or seven times. Merocyanines, XXII (*m*=0, *n*=3, Z=S, R=Ph, Bu, or $(CH_2)_3SO_3H$, R′=Et), were synthesised similarly, also the 5-spirocyclohexyl derivative of XXII (*m*=0, *n*=3, Z=S, R=Me, R′=Et). Whereas XXII (*m*=0, *n*=3, Z=Se, R=Bu, R′=Et) gave a 10-fold increase of sensitivity, the 3-cyclohexyl derivative of XXII (*m*=0, *n*=3, Z=Se, R=Me, R′=Ph) gave a 7- or 8-fold increase.[114]

Dimethinmerocyanines, XXII (m=1, n=3, Z=O, S, or Se, R=R′=Et, R¹=H), of the 2*H*-pyrroline series were prepared by heating 1-ethyl-2-formylmethylenepyrrolidine and the appropriate ketomethylene compound with pyridine and acetic anhydride; 2-formylmethylene-1-methylpyrrolidine was condensed with thiohydantoins.[115]

The β-methyldimethinmerocyanine, XXII (m=1, n=4, Z=S, R=R¹=Me, R′=Et), was prepared by reaction of 2-methylthio-3,4,5,6-tetrahydropyridine methiodide with 3-ethyl-5-isopropylidenerhodanine and triethylamine in acetone. Its sensitising maximum was at 5300 Å and the corresponding dyes in which n=5 and 6 had their maxima at 5400 Å and 5500 Å, respectively. β-Methyldimethinmerocyanines of type XXII (m=1, n=4,5, or 6, R¹=Me), but with a 3-methyl-1-phenyl-5-pyrazolone residue, melted at 173–174°, 195–196°, and 175–176°, respectively; the first two sensitised at 4600 Å. An analogue of XXII (m=1, n=5), with a 7-methyl substituent in the 1-azacycloheptane ring, was described. By means of 5-α-ethoxyethylidene-3-ethylrhodanine there were prepared the β-ethoxydimethinmerocyanines, XXII (m=1, n=5 or 6, Z=S, R=Me, R′=Et, R¹=OEt)[116] (see also section 10-C.2a).

(*b*) *Nuclei, Including Complex Nuclei, with Two Nitrogen Atoms as the Only Hetero-Atoms.* The dimethinmerocyanine, XXIII (Z=S, R′=Me), was prepared by heating the methotoluene-*p*-sulphonate of 2,3-dimethyl-4-oxo-3,4,5,6,7,8-hexahydroquinazoline and 5-acetanilidomethylene-3-methyl-rhodanine with triethylamine in ethanol. The analogues, XXIII (Z=O, R′=Et; and Z=NMe, R′=Me), were also made. The sensitising maxima of the three substances were at 5630 Å, 5180 Å, and 5430 Å, respectively.[117]

The dimethinmerocyanine, XXIV, was prepared by condensation of 1-methoxy-4-methylene-3-*p*-nitrophenyl-3,4-dihydrophthalazine with 4-anilinomethylene-3-methyl-1-phenyl-5-pyrazolone.[120]

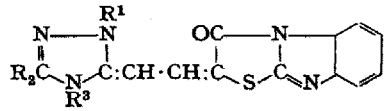
Condensation of 4,4,6-trimethyl-3-methylthiopyridazine methiodide with 5-ethoxymethylene-3-ethylrhodanine gave XXV, which had its sensitising maximum at 5800 Å. Analogues with a 5-oxo-2-phenyloxazoline, a 1,3-dimethyl-2-thiohydantoin or a 3-methyl-1-phenyl-5-pyrazolone residue were made similarly; a dimethinmerocyanine with a β-methyl group was also described.[122]

The dimethinmerocyanines, XXVI (R=H, Z=S or NMe), bearing a 4,4-dimethyl-3-methylthiopyrazolenine nucleus, had their sensitising maxima at 6000 Å and 5500 Å, respectively. The former was prepared from the 5-methylpyrazoleninium salt, 3-methylrhodanine, and ethyl

orthoformate in pyridine. A dye with a complex nucleus was also made.[124]

The simple merocyanine, XXVII, which was a sensitiser, was prepared by use of 5,5-dimethyl-2,4-di(methylthio)imidazolenine metho-toluene-*p*-sulphonate; its analogue with a 3-methyl-1-phenyl-5-pyrazolone residue, and one with a complex nucleus, were also made. The condensing agent was pyridine, or sodium acetate in ethanol.[125] By reaction of 4-methylthio-2,5,5-trisubstituted-imidazolenine methiodides with 3-methyl-1-phenyl-5-pyrazolone, dyes such as XXVIII (R=Me or Ph, R^1=R^2=Me; and R=R^1=Me, R^2=Et) were prepared. An analogue with a 3-methylrhodanine nucleus sensitised. Another with a complex nucleus was described.[127]

(*c*) *Nuclei with Three Nitrogen Atoms as Hetero-Atoms.* The dimethin-merocyanines, XXX (R^1=R^4=Ph, R^2=Me or SMe, R^3=Me), were prepared by heating the appropriate 5-methyl-1,2,4-triazole quaternary salt with 4-ethoxymethylene-5-oxo-2-phenyloxazoline and triethylamine in pyridine. More complex substances, LXIII (R^1=Ph, R^2=Me



(LXIII)

or SMe, R^3=Me) (cf. section 10-C.2e), were made similarly.[130] With 4-aryl-5-methyl-1,2,4-triazoles, salt formation occurred at the 1-*N*-atom. Such salts, by reaction with ethoxymethylene compounds, gave XXXI (Z=S, R^1=R^2=Me, R^3=*p*-C_6H_4OMe or *p*-C_6H_4Cl, R^4=Et; Z=S, R^1=Me, R^2=SEt, R^3=Ph, R^4=Et; and Z=NMe, R^1=R^2=R^4=Me, R^3=*o*-C_6H_4Me).[131]

By heating 5-methyl-s-triazolo(4,3a)quinoline alkotoluene-*p*-sulphonate and 5-acetanilidomethylene-3-ethylrhodanine with triethylamine in pyridine, there were prepared XXXII (R=Me or Et), in yields of 4% and 5%, respectively.[132] Similarly, from 1-methyl-s-triazolo(4,3-a)quinoline ethiodide, XXXIII was obtained in 16% yield after two recrystallisations.[133]

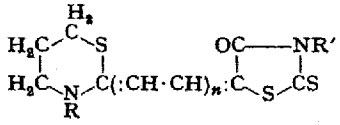
(*d*) *Nuclei with Four Nitrogen Atoms as Hetero-Atoms.* By condensation of 4,5-dimethyl-1-phenyltetrazolium iodide with the appropriate complex ethoxymethylene compound (cf. section 10-C.2e), by heatiug with triethylamine in pyridine, XXXIV was prepared. 4,5-Dimethyl-1-*p*-

tolyltetrazolium iodide and 3-methyl-1-phenyl-5-pyrazolone were heated with ethyl orthoformate and triethylamine in pyridine, to give XXXV, which had its sensitising maximum at 4400 Å.[134]

The dimethinmerocyanine, XXXVI (n=1), was prepared from 5-methyltetrazolo[a]quinoline ethotoluene-*p*-sulphonate, 5-acetanilidomethylene-1,3-diethylthiobarbituric acid and triethylamine in pyridine; there were also prepared analogues with a 3-ethyl-4-oxo-2-thiooxazolidine or a 5-oxo-3-phenylisoxazoline nucleus, the yields varying from 21–58%. The condensing agent was triethylamine in pyridine or ethanol. The tetramethinmerocyanine, XXXVI (n=2), was prepared in 20% yield by heating 5-methyltetrazolo[a]quinoline ethotoluene-*p*-sulphonate and 5-acetanilidoallylidene-1,3-diethyl-2-thiobarbituric acid with triethylamine in pyridine. The ethoethylsulphate was used similarly to give a 2% yield of an analogue with a 5-oxo-3-phenylisoxazoline nucleus.[132]

(*e*) *Nuclei with One Nitrogen and One Sulphur as Hetero-Atoms.* Merocyanines with a 3,1,4-benzothiazine nucleus were prepared by condensing a 2-alkylthio-3,1,4-benzothiazinium salt with 3-ethylrhodanine, its thio-oxazolidine analogue, or with 3-ethyl-4-thiorhodanine (cf. section 4).[135]

By boiling 2-(ethylthio)dihydro-1,3,4-thiazine methiodide and 3-ethylrhodanine with triethylamine in ethanol, the merocyanine, LXIV (n=0, R=Me, R′=Et), was obtained, in 60% yield after two recrystallisations. The dimethinmerocyanine, LXIV (n=1, R=Me, R′=Et),

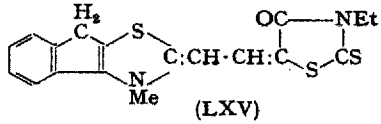


(LXIV)

was prepared by boiling 2-*β*-acetanilidovinyldihydro-1,3,4-thiazine methiodide and 3-ethylrhodanine with triethylamine in ethanol; after recrystallising from pyridine, the yield was 13%, whereas an analogue with a thiazoline nucleus was obtained in 52% yield. Both LXIV (n=0 or 1, R=Me, R′=Et) were sensitisers. The absorption maximum of the latter lay at a longer wavelength by 830 Å than that of the former.[136,137] Two dimethinmerocyanines, LXIV (n=1, R=Ph, R′=Ph or Et), had absorption maxima at 4950 Å and 4920 Å, respectively, in acetone; the analogue of the former with a 3-methyl-1-phenyl-5-pyrazolone nucleus

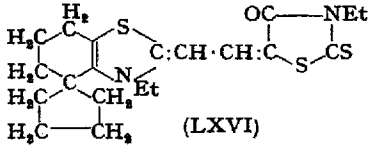
was also made. Such dimethinmerocyanines, having a 1-phenyldihydro-1,3,4-thiazine nucleus, sensitised at a slightly longer wavelength than those having a thiazoline nucleus.[197]

Quaternary salts of 2-methylthiazoles with various carbocyclic substituents were condensed with 5-acetanilidomethylene-3-ethylrhodanine to give dimethinmerocyanines. Such were quaternary salts of 2-methyl-4,5-tri(or penta)methylenethiazole,[138,143] of 4,5,6,7-tetrahydro-4-isopropyl-2,7-dimethylbenzothiazole,[139] and of 6,7-dihydro-2-methyl-4,5-benzobenzothiazole.[141] The salt of a 2-methylindenothiazole gave LXV[142] and quaternary salts of 2-methylthiazoles having spiro-

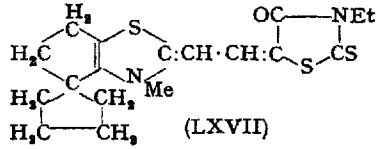


(LXV)

cyclic substituents gave LXVI[140] and LXVII.[144] The absorption maxima of methanolic solutions of these seven dimethinmerocyanines lay within the limits 5500–5560 Å.[138–144]



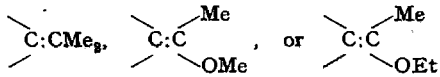
(LXVI)



(LXVII)

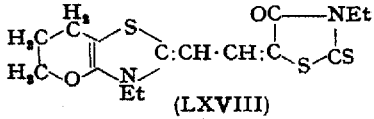
2-Alkylthio-4-oxothiazolinium salts having a substituted 5-aminomethylene group were synthesised from 3-alkyl (or aryl)-4-oxo-2-thiothiazolidines. The first step consisted in reaction of such a substance with an ortho-ester, which attacked the methylene group; four derivatives with a :CH·OEt and ten with a :CR^1·OEt group, where R^1=Me or Et, were described, also two with the group :CMe·OMe. By heating with an amine, HNR^2R^3, such as aniline, diethylamine, piperidine, or morpholine, there resulted analogues with the group :$CR^1(NR^2R^3)$ in the 5-position. Thirteen compounds with the group :CH·NR^2R^3 comprised examples where R^2=H, R^3=H, CH_2CO_2H, Ph, CH_2Ph, C_8H_{17}, or C_6H_{11}, another where R^2=Me, R^3=Ph, and others where R^2=R^3=Et, CH_2Ph, or C_6H_{11}, also R^2R^3=C_5H_{10} or C_4H_7O. Five other aminomethylene compounds included types where R^1=Me, R^2=H, R^3=Et or Ph, and R^1=R^3=Et, R^2=H, also a substance where the chain

:CH·NH·CH_2·CH_2·NH·CH: linked two heterocyclic nuclei. The quoted yields of merocyanines varied from 28–79%. The compound, XXXVII (n=0, R=R′=CH_2CO_2Et, R^1=H, R^2R^3=C_5H_{10}), was prepared by converting 3-carbethoxymethyl-4-oxo-5-piperidinomethylene-2-thiothiazolidine into a quaternary salt by heating with methyl toluene-p-sulphonate and boiling that salt with 3-carbethoxymethyl-4-oxo-2-thiothiazolidine and triethylamine in ethanol for 2 minutes. Fifteen more merocyanines were of type XXXVII (n=0), with various groups, R, R′, R^1, R^2, and R^3, whilst another two were of type XXXVIII (n=0). β-Substituted dimethinmerocyanines included XXXVII (n=1, R=R′=CH_2CO_2Et, R^1=H, R^2R^3=C_5H_{10}, R^4=Me or OMe; n=1, R=R′=C_3H_5, R^1=R^2=H, R^3=n-C_8H_{17}, R^4=Me or OEt), and XXXVIII (n=1, R=C_3H_5, R′=SEt, R^1=H, R^2R^3=C_4H_8O), which were prepared through cyclic compounds having one of the groups

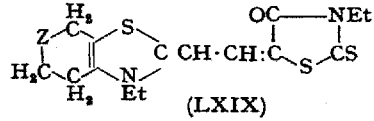


adjacent to CO.[145,146]

(*f*) *Nuclei with a Nitrogen, an Oxygen, and a Sulphur as Hetero-Atoms.* From 2-methyl salts of thiazoles with a fused-on dihydropyrano-nucleus there were prepared LXVIII, with its absorption maximum at 5560 Å,[147] and LXIX (Z=O), with its absorption maximum at 5440 Å.[148,149]

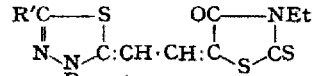


(LXVIII)



(LXIX)

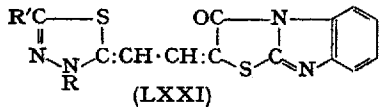
(*g*) *Nuclei with Two Nitrogen Atoms and One Sulphur as Hetero-Atoms.* 2,3-Dimethyl-5-methylthio-1,3,4-thiadiazolium iodide was condensed with 5-ethoxymethylene-3-ethylrhodanine, by means of triethylamine in ethanol, to give LXX (R=Me, R′=SMe), which sensitised; so did an



(LXX)

α-methyldimethinmerocyanine with the same quaternary salt residue. The 4-ethoxymethylene derivatives of 3-methyl-1-phenyl-5-pyrazolone

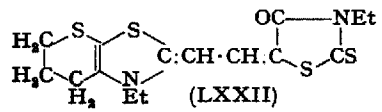
and of 5-oxo-2-phenyloxazoline were used similarly, and LXXI (R′= SMe or SCH_2Ph) (cf. section 10-C.2e) were also made.[150]



(LXXI)

(*h*) *Complex Nuclei with Three Nitrogen Atoms and One Sulphur as Hetero-Atoms.* The di- and tetra-methinmerocyanines, XXXIX (n=1 or 2, Q=S, R=R′=Et), sensitised to 6200 Å and 6800 Å, respectively. Analogues of the former with a 3-phenylrhodanine, a 1,3-diethyl-2-thiobarbituric acid, or a 3-methyl-1-*p*-sulphophenyl-5-pyrazolone nucleus, were also described, besides others of its analogues having a substituent in the benzene ring of the complex nucleus, and XXXIX (n=1, Q=S or O, R=Me, R′=Et).[133]

(*i*) *Nuclei with One Nitrogen and Two Sulphur Atoms as Hetero-Atoms.* From 2-methyl salts of thiazoles with a fused-on dihydrothiopyrano-nucleus there was prepared LXIX (Z=S), with its absorption maximum at 5440 Å,[148,151] which is the same as that of the dihydropyrano-analogue, and LXXII, with its absorption maximum at 5490 Å.[152]

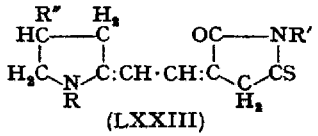


(LXXII)

(*2*) *In the Ketomethylene Residue*

(*a*) *Nuclei with Nitrogen as the One Hetero-Atom.* Fifteen dimethinmerocyanines having a 5-oxo-2-thiopyrrolidine nucleus were described. 1-Ethyl-4-formylmethylenedihydroquinoline was warmed with 1-ethyl-5-oxo-2-thiopyrrolidine and piperidine in pyridine at 50–60° for 45 minutes. Formylmethylene compounds were also used in syntheses in the indolenine series, but otherwise aniloethylidene compounds were used. In the benzothiazole series, the 5,6-dimethyl derivatives of XL (Y=S, R=Et, R′=Et or CH_2Ph) were made, in the benzoxazole series the 5-methyl, 5-phenyl and 5-methoxy-derivatives of XL (Y=O, R=Et, R′=Et, C_3H_5, or CH_2Ph, respectively), in the benzoselenazole series the 5-methoxy-derivatives of XL (Y=Se, R=Et, R′=Et or CH_2Ph), and in the indolenine series the 5,6-dimethyl and the 5-methyl

derivatives of XL (Y=CMe_2, R=Me, R′=Et or C_6H_{11}, respectively). Besides this, there were two dyes of the thiazoline series and three with a second pyrroline residue, viz., LXXIII (R=R′=Et, R″=H or Ph; and R=R′=Me, R″=H).[153]



(LXXIII)

(*b*) *Nuclei with Two Nitrogen Atoms as the Only Hetero-Atoms.* Condensation of 2-β-acetanilidovinylquinoline ethiodide with 3,7a-diazaindan-2-one hydrobromide, by heating with triethylamine in ethanol, gave the hydrobromide of XLI (*n*=1, Y=CH:CH, R=Et, R′=H); this was converted by triethylamine into the dye base, which had its sensitising maximum at 5800 Å. The benzothiazole analogue was made similarly and also by use of the sodium salt of 3,7a-diazaindan-2-one. Dyes of the benzoxazole, thiazoline, and 2- and 4-linked pyridine series were also described.[155] The compounds were obtained as hydrohalide even when excess of triethylamine was used in their preparation.[156] The tetramethinmerocyanine, XLI (*n*=2, Y=O, R=Et, R′=H), was prepared by boiling 4-acetanilido-1,3-butadienylbenzoxazole ethiodide and 3,7a-diazaindan-2-one hydrochloride with triethylamine in ethanol, and treating the product with triethylamine. By means of methyl toluene-*p*-sulphonate, the tetramethinmerocyanine was converted into a quaternary salt.[155]

The merocyanines, XLII (*n*=0, Y=CH:CH or S, R=Me), were prepared, in yields of 58 % and 54%, by heating 3,7a-diazaindan-1-one hydrochloride and the 2-ethylthio-derivative of the appropriate methotoluene-*p*-sulphonate with triethylamine in pyridine, and precipitating with sodium carbonate. The dimethinmerocyanines, XLII (*n*=1, Y=CH:CH, S, or O, R=Et), were similarly prepared, in yields of 70%, 56%, and 51%, from the same hydrochloride and the 2-β-acetanilidovinyl derivative of the appropriate ethiodide. An *N*-methyl compound of the 2-linked pyridine series was also made.[157]

(*c*) *Nuclei with Three Nitrogen Atoms as Hetero-Atoms.* 1-Aryl-5-oxo-1,2,3-triazolines or their 4-carboxy-derivatives were condensed with a quaternary heterocyclic salt having a ·CH:CH·SR or ·CH:CH·NR^1R^2 group, to give dimethinmerocyanines. The thirteen examples comprised, in the quinoline series, XLIII (Y=CH:CH, R=Me, Ar=Ph

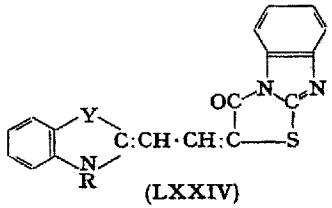
or *p*-C_6H_4Br), and in the benzothiazole and benzoxazole series, XLIII (Y=S or O, R=Et, Ar=Ph, *p*-C_6H_4Cl, or *p*-C_6H_4Br): all these were prepared through the carboxy-compounds and some of the benzothiazole dyes were also prepared through the triazoline; in the indolenine series the dyes were XLIII (Y=CMe_2, R=Me, Ar=Ph, *p*-C_6H_4Cl, or *p*-C_6H_4Br).[158]

(*d*) *Nuclei with Sulphur or Oxygen as the One Hetero-Atom.* Two merocyanines, XLIV (*n*=0, Y=Z=S, Q=S or NPh), with a tetrahydrothiophene nucleus, were described. In the benzothiazole series, there were prepared dimethinmerocyanines, XLIV (*n*=1, Y=Z=S, Q=NPh, NMe, or S), with that nucleus, and XLIV (*n*=1, Y=Q=S, Z=O) with a tetrahydrofurane nucleus, also the analogue of the last with a carboxy-, instead of a carbethoxy-, group: thiazole analogues of the first two and of XLIV (*n*=1, Y=Q=S, Z=O) were described. In the benzoxazole series, the 5-methyl, 5-phenyl, and 4,5-benzo-derivatives of XLIV (*n*=1, Y=Z=O, Q=NPh), with a tetrahydrofurane nucleus, all sensitised to 5500 Å with the maximum at 5300 Å. One preparation was carried out with a 2-*β*-ethylthiovinyl salt, but the rest with 2-*β*-acetanilidovinyl salts in pyridine. The hexamethinmerocyanine, XLIV (*n*=3, Y=Z=S, Q=NPh), sensitised from 6200–6700 Å.[159]

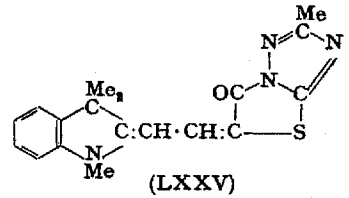
A merocyanine, XLV (*n*=0, Y=CH:CH), having a 1,3,3-trioxodihydrothianaphthene nucleus was described, also the 4,5-benzo-derivative of XLV (*n*=0, Y=S). By reaction of 2-*β*-acetanilidovinyl quaternary salts and triethylamine in ethanol with 3-methyl-4-oxo-2-phenylthiazolidine-1,1-dioxide, there were prepared the dimethinmerocyanines, XLVI (*n*=1, Y=CH:CH, S, or O, R=Et, R′=Me), also 4,5-benzo- and 5-chloro-derivatives of the compound of the benzothiazole series, and XLVI (*n*=1, Y=CMe_2, R=R′=Me), the yields varying from 28–82%. There were also made XLVI (*n*=1, Y=S or O, R=Et, R′=CH_2Ph), and the 4,5-benzo-derivative of the latter. The *β*-methyl derivative of XLV (*n*=1, Y=S) and its 6,7-benzo-derivative were described. By heating 2-(4-anilino-1,3-butadienyl)benzothiazole ethiodide and 3-methyl-4-oxo-2-phenylthiazolidine-1,1-dioxide with triethylamine in pyridine, the tetramethinmerocyanine, XLVI (*n*=2, Y=S, R=Et, R′=Me), was prepared in 45% yield; its 4,5-benzo-derivative was obtained similarly.[161]

(*e*) *Complex Nuclei.* Condensation of two complex 4-oxothiazolidines of uncertain constitution, with 2-methylthiobenzothiazole methotoluene-*p*-sulphonate gave two merocyanines. Condensation of a 4-oxo-

thiazolidine, having a fused-on nucleus in the 2,3-positions, with a 2-β-acetanilidovinylbenzothiazolium salt gave LXXIV (Y=S, R=Et); LXXIV (Y=S, O, or CMe_2, R=Me) were made similarly, also LXXV, besides two dimethinmerocyanines of undetermined structure (see also section 10-C.1c, d, and g).[163]

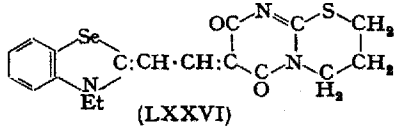


(LXXIV)



(LXXV)

A merocyanine, XLVII (n=0, Y=S, R^1=R^2=H), comprising a complex 4,6-dioxotetrahydropyrimidine nucleus, was prepared by heating 2-phenylthiobenzothiazole ethiodide and the complex ketomethylene compound with triethylamine in isopropanol. By use of the same condensing agent, 2-β-acetanilidovinylbenzothiazole ethiodide reacted with the ketomethylene compound to give the dimethinmerocyanine, XLVII (n=1, Y=S, R^1=R^2=H); a 6-methyl derivative was similarly made. XLVII (n=1, Y=S, R^1R^2=$(CH_2)_4$) was also described. In the benzoxazole series, XLVII (n=1, Y=O, R^1=Me, R^2=H) was prepared, and, in the benzoselenazole series, a 6-methoxy-derivative of LXXVI. A β-ethyl-6-methoxy-derivative of XLVII (n=1, Y=Se,



(LXXVI)

R^1=H, R^2=Ph) was prepared by reaction of a salt having a β-ethyl-β-(methylthio)vinyl group with the ketomethylene compound. The tetramethinmerocyanine, XLVII (n=2, R^1=R^2=H), was described. Spectrograms illustrated the sensitising action of the dyes (cf. XIII-4-B).[164]

11. α- and β-Aza- and αβ-Diaza-dimethinmerocyanines

A. α-Azadimethinmerocyanines, Including Those with a β-Substituent

The β-methyl-α-azadimethinmerocyanine, XLVIII, was the first representative of azadimethinmerocyanines.[72]

The α-azadimethinmerocyanine, XLIX (Y=S), which had its sensitising maximum at 5200 Å, was prepared by boiling 2-aminobenzothiazole ethiodide with 5-acetanilidomethylene-3-allylrhodanine and triethylamine in pyridine for 2 hours. Its 2-linked pyridine and quinoline, and benzoxazole analogues were described, also the 5-phenyl derivative of the last. 6-Ethoxy-, 6-methoxy-, 6-methyl, and 6,7-benzo-derivatives of XLIX (Y=S), all of them sensitisers, were prepared.[165]

A method of arriving at a β-methylthio-α-azadimethinmerocyanine consisted in converting methyl *N*-(2-pyridyl)dithiocarbamate into dimethyl *N*-(2-pyridyl)dithioisocyanate; the ethotoluene-*p*-sulphonate of this was condensed with 3-ethylrhodanine. An analogue with a thiazole instead of a pyridine nucleus was similarly synthesised, the yields of recrystallised dyes being 57 % and 73 %, respectively.[104]

B. β-Azadimethinmerocyanines, Including One in which Part of the Dimethin Chain is Cyclic

The β-azadimethinmerocyanine, L (Y=CMe_2, R=Me, R′=Ph), was prepared by heating 2,3,3-trimethylindolenine methiodide and 4-isonitroso-3-methyl-1-phenyl-5-pyrazolone with sodium acetate and acetic anhydride, being obtained in 11 % yield after two recrystallisations from methanol. Its thiazoline analogue was described, also L (Y=S, O, or Se, R=Et, R′=Ph), and their 4-methylthiazole analogue, as well as some derivatives. From isonitrosopyrazolones having a 1-(2-benzothiazolyl) group, there were obtained L (Y=CH:CH or S, R=Et, R′=C_7H_4NS), and the 3-methyl derivative of the former, besides L (Y=CH:CH, R=Me, R′=C_7H_4NS), and its analogues of the 4-linked quinoline, 2-linked pyridine, and 1-linked isoquinoline series.[166]

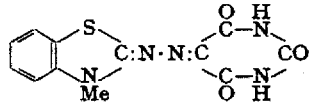
The compound, LI, was prepared by heating 1-ethyl-3-nitroso-2-phenylindole with 3-methyl-1-phenyl-5-pyrazolone and zinc chloride in coal gas at 135–140° for 2 hours, washing with water, and recrystallising from ethanol.[167]

C. αβ-Diazadimethinmerocyanines

The αβ-diazadimethinmerocyanine, LII (Y=CH:CH, R=Me), was prepared by boiling an ethanolic solution of 2-iodoquinoline methiodide and thianaphthenquinone 3-hydrazone with triethylamine for 10 minutes. The red colour changed to yellow-orange when a suspension of the compound in warm acetone was treated with 48 % aqueous

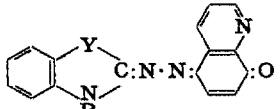
hydrobromic acid; in damp air the hydrobromide reverted to the diaza-dimethinmerocyanine. An analogous substance, LII (Y=S, R=Et), was prepared through 2-ethylthiobenzothiazole ethiodide and had m.p. 175–176°, λ_{max} 4540 Å. Under various conditions it passed into an isomer of m.p. 259–260°.[33] Such isomerisation was a common property of LII (Y=CH:CH, R=Me; and Y=S, R=Et), and of their derivatives having a 6-ethoxy-group in the thianaphthene ring.[188]

Addition of ammonia to an aqueous alcoholic solution containing 3-methyl-2-oxobenzothiazoline hydrazone, α- or β-naphthol, and an oxidising agent, such as potassium ferricyanide, copper sulphate, or silver nitrate, gave red needles of LIV and LV, respectively, in yields of 90% and 100%. The presence of substituents in the α-naphthol nucleus could induce coupling in the β-position. Addition of ammonia to a solution containing the same hydrazone, potassium ferricyanide, and barbituric acid gave LXXVII; when the last reactant was replaced by 3-ethylrhodanine or 3-methyl-1-phenyl-5-pyrazolone, the

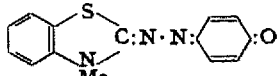


(LXXVII)

diaza-analogues of II (n=1, Y=Q=Z=S, R=Me, R'=Et) and I (n=1, Y=S, R=Me, R'=Ph) resulted. From the hydrazone of 1-ethyl-2-quinolone, an oxidising agent, and 8-hydroxyquinoline there was prepared LXXVIII (Y=CH:CH, R=Et); a derivative of LXXVIII (Y=S, R=Me), having a 6-ethoxy-group in the benzothiazole nucleus, was also made. From 3-methylbenzothiazolone and phenol there was prepared LXXIX. In the pyridine series, condensation was effected between a 2-hydrazone and β-naphthol, and between a 4-hydrazone with *o*-cresol or *m*-diethylaminophenol.[189]



(LXXVIII)



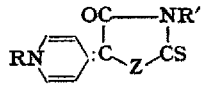
(LXXIX)

12. The Colour of Merocyanine Dyes

Solutions of dyes of the merocyanine groups varied from colourless to greenish blue.[16] Certain complex merocyanines (see XV-6-M) had

their absorption maxima in the infrared but such absorption was believed to be unique for non-ionised dyes.[85] The positions of the sensitising and absorption maxima of merocyanines were related, as in the cyanines (see XVII-2-C), but whereas the sensitising maxima of cyanines in a silver bromide emulsion usually lay at a longer wavelength by 250 to 450 Å than the corresponding absorption maxima in ethanol, the shift for certain di-, tetra- and hexa-methinmerocyanines, having a 3-ethylrhodanine nucleus, was greater, lying between 320 to 1890 Å. The vinylene shifts of absorption maxima on passing from di- to tetra-, and from tetra- to hexa-methinmerocyanines were, on the average, 820 Å and 300 Å, respectively, but for sensitising maxima the average shift was 1100 Å for each.[188]

With regard to sensitising, simple merocyanines of type LXXX, having a 4-linked pyridine nucleus, were in 1944 claimed as better



(LXXX)

than their isomers with a 2-linked pyridine nucleus.[171] In 1952 twenty-eight dimethinmerocyanines having various heterocyclic nuclei coupled with rhodanine or 3-ethylrhodanine were prepared (section 3-A), and were all sensitisers, those from 3-ethylrhodanine being the better, as well as the more soluble. Those with a thiazole, thiazoline, or 2-linked pyridine residue were good sensitisers but one with 4-linked quinoline was inferior and caused fogging.[198]

A comparison in 1940 of the absorption maxima of four dyes, IV (m=0, 1, 2, or 3, Y=S, R=Et), with a 3-oxodihydrothianaphthene nucleus, showed that each vinylene increment caused a bathochromic shift of 820–900 Å.[28] Introduction of various substituents into the benzothiazole nucleus of the dimethinmerocyanine, IV (n=1, Y=S, R=Et), usually produced a bathochromic shift of absorption.[184] Subsequently dimethinmerocyanines in which a 3-oxodihydrothianaphthene nucleus was coupled with each of eleven different heterocyclic nuclei, which were also introduced into trimethincyanines (see XVI-2), were examined. As the basicity of the variable nucleus increased, the hypsochromic shift of absorption maximum first diminished and then increased.[185]

Merocyanine dyes were formulated as resonance hybrids between

an uncharged and a dipolar structure, in which an additional double bond entered each of the two rings (see section 1). The two forms were not equivalent energetically, the polar form having higher energy than the non-polar form.[17] In 1940 light measurements were made on the tetramethinmerocyanine, II (n=2, Y=CMe_2, Q=Z=S, R=R'=Et), having a 3-ethylrhodanine nucleus, on its analogue with a 1,3-diethylthiobarbituric acid nucleus, and on a tetramethinmerocyanine with one 1,3-diethylbenzimidazoline and one 1,3-diethylbarbituric acid nucleus: these three dyes had, respectively, one, two, and four polar structures. The large dipole moments, which were measured in benzene or dioxane, increased with increase in the number of contributing polar structures.[199]

A comprehensive study of the absorption of the merocyanines was published in 1951, with tables of preparative details, optical data, and various figures.[17] The absorption maximum of a methanolic solution of each dye was compared with the arithmetic mean of those of the related pair of symmetrical dyes, and the deviation was calculated. Depending on the nuclei paired in each dye, the resonance stabilisation acquired might be low, high, or intermediate. If it was low, the dye had low intrinsic polarity and showed large λ_{max} deviations in all solvents. In a figure dealing with six dimethinmerocyanines derived from 3-ethylrhodanine, with various heterocyclic nuclei, the deviations varied from 30 to 455 Å. Another figure comprised nine di- and nine tetra-methinmerocyanines, derived from 3-ethylrhodanine: here the deviations varied from 25 to 455 Å for the former type and from —30 to 855 Å for the latter type. The order of decreasing deviation for dyes of a given chain-length would be the order of increasing basicity of the variable nuclei. So also, a series of ten ketomethylene compounds were arranged in order of acidity by comparing the deviations of dimethinmerocyanines containing each in conjunction with a 3,3-dimethyl-1-phenylindoline nucleus: the deviations varied from 45 to 575 Å. In a series of ten with the slightly more basic 1,3,3-trimethylindoline nucleus, the deviations were, with one exception, somewhat smaller. Both sets of deviations established the order of increasing deviation as that of decreasing acidity of the ketomethylene nucleus. It was noted that in merocyanines with low intrinsic polarity λ_{max} tended to shift to longer wavelengths with increasing polarity of the solvent, especially for the dyes of longer chain-length. Dyes of high intrinsic polarity exhibited shifts of λ_{max} to shorter wavelengths with increasing polarity of the

TABLE II. Properties of Some Merocyanines and of the Related Di-, Tetra-, and Hexa-methinmerocyanines

Formula	Appearance of crystals	M.p. (°C) decomp.	Absorption maximum (Å) in MeOH	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
I (n=0, Y=S, R=Me, R′=Ph)	yellow needles[a]	177[a,b]	—	—	—	175
I (n=1, Y=CMe_2, R=Me, R′=Ph)	red needles	183[b]	4760	—	—	7, 17
I (n=3, Y=S, R=Me, R′=Ph)	blue	—	—	—	—	189
II (n=0, Y=Q=Z=S, R=R′=Et)	yellow; blue reflex	246–248	4320[c]	—	—	16, 17
II (n=1, Y=Q=Z=S, R=R′=Et)	red	265	5280[c]	5800	—	17,180
II (n=2, Y=Q=Z=S, R=R′=Et)	greyish blue	238[b]	6050[c]	6900	7300	17,180
II (n=3, Y=Q=Z=S, R=R′=Et)	emerald green	231–233	6350[c]	8000[d]	8800[d]	16, 17, 23
IV (n=0, Y=S, R=Et)	yellow needles	214–216[b]	4470	—	—	28
IV (n=1, Y=S, R=Et)	violet needles	210–211	5580	—	—	28
IV (n=2, Y=S, R=Et)	green needles	219–220	6400	—	—	28
IV (n=3, Y=S, R=Et)	blue-green needles	177–178[b]	—	—	—	28

(Table continued)

TABLE II. *continued*

Formula	Appearance of crystals	M.p. (°C) decomp.	Absorption maximum (Å) in MeOH	Sensitising (Å) Maximum	Extent	Ref.
V (n=0, Y=S, R=Et)	yellow-brown	175–176[b]	4180	—	—	31, 33
V (n=1, Y=S, R=Et)	brown	230–231[b]	5310	5800[e]	—	31, 32
V (n=2, Y=S, R=Et)	blue	173–174[b]	6190	6850	—	33
V (n=3, Y=S, R=Et)	blue	172[b]	6440	7800	—	33
LVIII (n=1, Y=CMe_2, Q=S, R=Me, R^1=R^3=Et)	bright orange	275–276[b]	4950[c]	—	—	17
LVIII (n=2, Y=CMe_2, Q=S, R=R^1=R^3=Et)	dark; blue reflex	302–303	5950[c]	—	—	17
LVIII (n=3, Y=CMe_2, Q=S, R=R^1=R^3=Et)	bluish; blue reflex	190–192[b]	6975[c]	—	—	17
LVIII (n=1, Y=NEt, Q=S, R=R^1=R^3=Et)	yellow needles	311–312	—	4800	5100	20
LVIII (n=2, Y=NEt, Q=S, R=R^1=R^3=Et)	red needles	279–280	—	5600	6100	20
LVIII (n=3, Y=NEt, Q=S, R=R^1=R^3=Et)	purple needles	270–272	—	5400, 6500	7100	20

[a] For 6-MeO-derivative. [b] Decomp. not recorded. [c] Absorption in pyridine.
[d] Sensitising data for compound where Y=Se. [e] Sensitising maximum for 6-EtO-derivative.

solvent.[17] The absorption maxima of four pairs of dimethinmerocyanines with a 3,7a-diazaindan-1-one, or a 3,7a-diazaindan-2-one nucleus, compared in three different solvents, with one exception showed a hypsochromic shift with increasing polarity of the solvent.[157]

Twenty-eight dimethinmerocyanines having a rhodanine or 3-ethylrhodanine nucleus were mostly sparingly soluble in ethanol. Their colours, unlike those of the compounds having a 3-oxodihydrothianaphthene nucleus, were scarcely affected by dilute mineral acids. Their absorption maxima lay at a shorter wavelength than the arithmetic means of the related trimethincyanines and methinoxonols.[198] Through 3-ethylrhodanines having a $:CH(\cdot CH:CH)_{0-2}NAcPh$ group in the 5-position, there were synthesised three types of merocyanines in which a 3-ethylrhodanine nucleus was coupled with others of varying basicity. The absorption maxima of three di-, three tetra-, and three hexa-methinmerocyanines, II (n=1, 2, or 3, Y=CH:CH, CMe_2, or S, Q=Z=S, R=R′=Et), were compared with those of the related pairs of symmetrical dyes. Absorption data were also given for eight dimethinmerocyanines of type II (n=1, Q=Z=S, R=R′=Et) in methanol, ethanol, propanol, butanol, chloroform, benzene, carbon tetrachloride, and hexahydrobenzene.[200] Other dimethinmerocyanines, having a 3-ethylrhodanine nucleus, for which absorption data were given, were II (n=1, Y=S, O, or Se, Q=Z=S, R=R′=Et), and analogues of the 4-phenylthiazole or thiazoline series, also for the 6-dimethylamino- and 4,5-benzo-derivatives of the dye of the benzothiazole series.[201] Absorption maxima of twelve dimethinmerocyanines with a 3-diacetylaminorhodanine nucleus were compared with those of the corresponding twelve with a rhodanine nucleus and of two with a 3-aminorhodanine nucleus. Those with a 3-diacetylaminorhodanine nucleus were very soluble. One dimethinmerocyanine, II (n=1, Y=Q=Z=S, R=Et, R′=NAc_2), was arrived at by three routes but the eleven analogues were prepared by one or other of the methods of section 3-A. They included compounds with 2- and 4-linked quinoline, benzoxazole, benzoselenazole, indolenine, and thiadiazole nuclei.[202] Absorption maxima were recorded for four dimethinmerocyanines of the oxazole or benzoxazole series, having 3-phenylrhodanine as the other nucleus.[66]

In the 3-ethylrhodanine and the 3-ethyl-4-oxo-2-thio-oxazolidine series, fluorescence was studied. Thus the fluorescence was examined for three sets of merocyanines: II (n=0, 1, 2, or 3, Y=Q=Z=S,

R=R′=Et; and n=0, 1, or 2, Y=O, Q=Z=S, R=R′=Et), and the 4-linked quinoline analogues of II (n=0 or 1, Q=S, R=R′=Et) (cf. XVII-2-E). The first members of the first two series did not fluoresce. The maxima progressively shifted to a longer wavelength as the dielectric constant of the solvent increased, but change in dielectric constant did not cause a non-fluorescent dye to fluoresce or vice versa.[303]

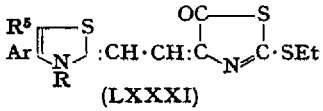
Absorption data and other physical properties were given for twelve dimethinmerocyanines of type II (n=1, Q=S, Z=NMe), prepared from 2-β-acetanilidovinyl quaternary salts and 2-thiohydantoins (section 3-A). Nuclei of the benzothiazole, benzoxazole, thiazoline, bisbenzothiazole, or bisthiazoline series were used, and the group R′ comprised Me, Et, Ph, n-C_7H_{15}, cyclo-C_6H_{11} and $\cdot CH_2 \cdot CH_2 \cdot$.[66]

Absorption maxima of solutions, in benzene, methanol, and aqueous methanol, of a merocyanine, fifteen dimethinmerocyanines, and two tetramethinmerocyanines of type VI (Z=S), comprising a 5-oxo-2-thiothiazolidine nucleus, were compared with those of their isomers of type II (Q=Z=S). Those with a 5-oxo-group absorbed at longer wavelengths than those with a 4-oxo-group. The nature of R in the NR group did not affect the absorption maximum except that methyl caused a hypsochromic shift.[37]

Absorption maxima of fourteen dimethinmerocyanines with a 5-oxo-2-phenyloxazoline nucleus varied from 4740 Å to 6200 Å. Those of forty dimethinmerocyanines with a 5-oxo-2-SR-thiazoline varied from 4630 Å to 5930 Å;[44] they were photographic sensitisers.[45] The absorption maxima of ten dimethinmerocyanines with a 2-acylamino-5-oxothiazoline nucleus varied from 4800 Å to 5930 Å. Absorption maxima were recorded for twenty-eight dimethinmerocyanines having a 2-OR-5-oxothiazoline nucleus; in eleven of these with a 2-ethoxy-group the maxima varied from 4450 Å to 5680 Å. Absorption maxima of fourteen dimethinmerocyanines with a 2-NR^1R^2-5-oxothiazoline nucleus varied from 4690 Å to 5880 Å. In all these instances, it was the dye derived from a thiazoline salt that had its absorption at the shortest wavelength whilst that derived from a 4-linked quinoline salt absorbed at the longest wavelength.[44]

The absorption of merocyanines prepared from certain special quaternary salts was studied. Salts of 4-aryl-5-aryloxy(or -5-arylthio)-2-methylthiazoles, which were used in the preparation of methin- and trimethin-cyanines (see II-4-M and V-7-C) were also used in preparing thirteen dimethinmerocyanines of type LVII (n=1, Y=Z=S, R′=Et),

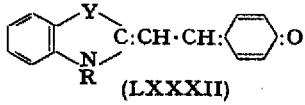
and nine of type LXXXI, by the methods of sections 3-A and 3-D. Introduction of substituents into the 4-aryl group, or replacement of 4-phenyl by 4-β-naphthyl, had little effect on the absorption maximum.



(LXXXI)

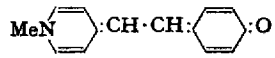
Replacement of 5-phenyl by 5-aryloxy-, or by 5-*p*-tolylthio-, caused a bathochromic shift of 50–100 Å.[204] Quaternary salts of 2-methyl-4-(or -4,5-di-)substituted oxazoles, which were used in the preparation of methin- and trimethin-cyanines (see II-4-F and V-7-B and C), were also used in the preparation of ten dimethinmerocyanines, of type LVII (n=1, Y=Z=O), of ten in which the oxazole residue was coupled with 3-alkyl-1-phenyl-2-thiohydantoin, and of ten, LVII (n=1, Y=O, Z=S), in which it was coupled with 3-alkyl-4(or 5-)oxo-2-thiothiazolidine; eleven others had a substituted oxazole coupled with various types of nuclei. Substituents in the aryl ring of the oxazole did not affect the absorption: this was explained by the hypothesis that this nucleus lay outside the resonance system.[205] 4,5-Diaryl-2-thio-oxazolines and -thiazolines were synthesised from 1,2-diaryl-2-oxoethylamines (desylamines), and their salts were used in the preparation of eight merocyanines of type LVII (n=0, Y=O, Z=S), etc. (see section 2), of which absorption maxima varied from 4040–4200 Å. Other dyes of this type were described, including dimethinmerocyanines, LVII (n=1, Y=O, Z=S), with absorption maxima varying from 4910–4950 Å (see section 3-A). Many of the dyes with short resonance paths were fluorescent and almost colourless.[174]

The styryl dyes obtained by condensing *o*- and *p*-hydroxybenzaldehyde with quaternary salts having a reactive methyl group (see XIII-1-A, B, E, and K) were converted by alkali into quinonoid dyes, of which the colour varied greatly according to the nature of the solvent, the absorption maximum lying at a longer wavelength in chloroform than in water, but the compound from 2-*p*-hydroxystyrylquinoline ethiodide was exceptional in not being intensely coloured. It was suggested in 1940 that the coloured compounds approached the



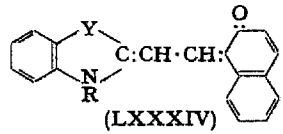
(LXXXII)

uncharged structure, e.g., of type LXXXII in a non-polar solvent, and in a polar solvent, the dipolar resonance structure.[206,207] The importance of the basicity of the nitrogen-containing nucleus was later recognised.[208] Subsequently such dimethinmerocyanines were obtained by treating *p*-hydroxystyryl salts (see XIII 1-A, D, E, and J) with aqueous ammonia. The dimethinmerocyanine, LXXXIII, and its analogues with



(LXXXIII)

an *N*-methyl-benzothiazoline, -tetrahydrobenzothiazoline, or -3,3-dimethylindoline nucleus were made, also others with a 5-chloro-3-ethylbenzothiazoline, 3-benzyl-5-chlorobenzothiazoline, or 3,3-dimethyl-1-phenylindoline nucleus. Their polarity was studied by means of pyridine/water mixtures. It was concluded that no single structural formula could account for the absorption of these dyes and that the energy relationship of the contributing structures could be varied by change of solvent. The extremely polar dye, LXXXIII, and also another, showed such large hypsochromic shifts, when water was added to their pyridine solutions, that they could be used for the colorimetric determination of one solvent in the other.[209] Solutions of certain condensation products of 2-hydroxy-1-naphthaldehyde, such as LXXXIV (Y=CH:CH, R=Me; and Y=S, R=Et), showed a hypsochromic shift on

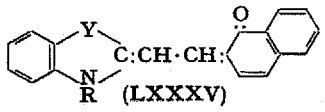


(LXXXIV)

addition of water.[210] A study of the pyridine/water mixtures of each dye led to the conclusion that this also is solvatochromism.[209] Subsequently, however, various solvents were tried, whence it appeared that there was no simple correlation between the absorption and the dielectric constants of the solvents. Thus the spectra in chloroform, pyridine, acetone, and nitrobenzene were similar, although the dielectric constant varied from 5 to 35; the spectra in formamide and in ethanol were similar, yet the dielectric constants were 109 and 28, respectively. On the other hand, the order of seven spectra was the same as the order of the sizes of the solvent molecules. The spectra fell into two groups, in one of which the solvent molecule had hydrogen-bonding

properties, and this may be a factor in spectral displacement.[211]

The abnormality of IX (n=0, R=Me), the N-methyl derivative of Quinoline Yellow, in absorbing at a longer wavelength in chloroform than in water[52] occurred also with its dimethin analogue and with that of the 2-linked pyridine compound and this was noted in 1951 as characteristic of strongly polar merocyanines,[53] such as those having a benz- or naphth-imidazoline in conjunction with a thiobarbituric acid nucleus.[20] Whereas IX (n=0, R=Me) had its absorption maximum at 4250 Å, the compound LXXXV (R=Me), which was synthesised



(LXXXV)

from 2-acetyl-1-naphthol and o-methylaminobenzaldehyde, absorbed at 5760 Å. This bathochromic shift was attributed to the increase in the number of limiting structures, due to the replacement of CO by CH:CH.[212]

Colour changes were recorded when solutions of dimethinmerocyanines, such as LXXXIII, were cooled to 110° K, the band at the longer wavelength becoming less intense and that at the shorter wavelength more intense. Absorption curves at 20°, —40°, —65°, —90°, and —150° were plotted for LXXXIII and for the 2-linked pyridine analogue of the N-ethyl compound, also for LXXXV (Y=CH:CH, R=Me). The energy difference between the two modifications was measured.[213]

The absorption curves for chloroform or ethanolic solutions of dyes, such as LXII (Y=S, Se, or CH:CH) and ten analogues, derived by reaction of methylene bases and quinones (see section 9-B.4) were broad, without sharp maxima. There were hypsochromic shifts on transition to a solvent of lower dielectric constant and on acidification. The more polar the molecules the longer the wavelength of absorption.[94]

The influence of factors such as temperature, degree of dilution, and partial replacement of ethanol by water was studied, for a series of dimethinmerocyanines, derived from eight different types of quaternary salts and eight different types of ketomethylene compounds. The varied behaviour was attributed to differences in polarity. The most highly polar dyes had two absorption bands, of which that at the shorter wavelength was attributed to a quaternary cation formed between dye and solvent.[214]

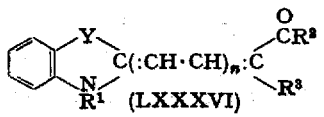
Some observations on the colours of dimethinmerocyanines with a substituent on the chain have been noted. It was observed in 1950 that a β-carboxy- and a β-carbethoxy-dimethinmerocyanine (see section 8-A.3) had much the same absorption as the unsubstituted parent dye.[191] In the 2-oxodihydrothianaphthene series, an α- and a β-methyl- and an αβ-dimethyl-dimethinmerocyanine (see sections 8-B.2, A.3, and C.1) were, respectively, magenta, purple-red, and orange.[31,82] Two α-hydroxydimethinmerocyanines (see section 8-B.6) were magenta in ethanolic solution (λ_{max} 5600 Å) and gave a transient blue with triethylamine before becoming colourless. They were converted into the α-acetoxy-derivatives, which had absorption maxima (at 5300 Å and 5320 Å) similar to those of the unsubstituted dyes.[80] Absorption maxima of dimethinmerocyanines of type II (n=1, Y=S=O, Q=Z=S) were compared with others having a substituent in the α-position or a methyl group in the β-position. The bathochromic shift caused by an α-methyl group diminished with increasing basicity of the nucleus and, for dyes of the 4-phenylthiazole series, the shift was hypsochromic.[201] The absorption maxima of thirteen β-substituted dimethinmerocyanines, nine δ-substituted tetramethinmerocyanines, and a ξ-substituted hexamethinmerocyanine were compared with those of the respective unsubstituted dyes. In general, introduction of OEt caused a hypsochromic shift, whilst introduction of SR always gave a strong bathochromic shift.[85]

13. Merocyanine Analogues with an Open Chain Instead of a Cyclic Ketomethylene Residue

A. Compounds with a Heterocyclic Nucleus Linked by an Even-Numbered Chain to :CR'(COR)

(1) *Linkage by an Unsubstituted Chain*

Heterocyclic quaternary salts having a β-anilino(or acetanilido)-vinyl group (cf. section 3-A) were condensed with non-cyclic ketomethylene compounds, such as benzoylacetonitrile or cyanoacetanilide, by heating with triethylamine in ethanol or sodium acetate in acetic



(LXXXVI)

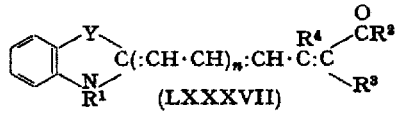
anhydride, to give photographic sensitisers, e.g., LXXXVI (n=1, Y=CH:CH or O, R^1=Et, R^2=Ph or NHPh, R^3=CN).[215] Other non-cyclic ketomethylene compounds were used similarly and the products were classed as dimethinmerocyanines,[16] but the author has thought it suitable to consider them in this separate section. The preparation of dimethinmerocyanines from quaternary salts having a ·CH:CH·SR group (section 3-B) included LXXXVI (n=1, Y=S, R^1=R^2=Me, R^3=COMe).[6] Condensation of 3-ethyl-2-formylmethylene-4,5-benzobenzothiazoline (cf. section 3-C) with acetylacetone and ethyl 2-quinolylpyruvate, respectively, gave the 4,5-benzo-derivatives of LXXXVI (n=1, Y=S, R^1=Et, R^2=Me, R^3=COMe; and n=1, Y=S, R^1=Et, R^2=CO_2Et, R^3=C_9H_6N).[13] By boiling 2-methylbenzothiazole ethiodide with ethyl (cyano)(formyl)acetate and piperidine in pyridine (cf. section 3-C), there resulted LXXXVI (n=1, Y=S, R^1=Et, R^2=OEt, R^3=CN). Similarly there were prepared LXXXVI (n=1, Y=CH:CH, R^1=Me, R^2=OEt, R^3=CN or COMe).[216] In 1953 absorption maxima were given for di- and tetra-methin compounds including the types LXXXVI (n=1 or 2, Y=CMe_2, R^1=Me, R^2=OR, R^3=CN).[217] By condensing a quaternary salt having a reactive methyl group with $(EtO_2C)(CN)C:CHOEt$ (cf. section 3-D) or with $(CN)_2C:CHOEt$ (cf. section 13-B.1), there resulted yellow to orange compounds, which were named malocyanines. Those of the former type included LXXXVI (n=1, Y=CH:CH, O, or S, R^1=Me, R^2=OEt, R^3=CN), and analogues of the 2- and 4-linked pyridine series; the 4-linked quinoline series was also represented.[218] The compound, LXXXVI (n=1, Y=S, R^1=Et, R^2=NH_2, R^3=CN), was prepared from 2-methylbenzothiazole ethiodide, by heating either with (cyano)(ethoxymethylene)acetamide and piperidine in pyridine (cf. section 3-D), or with cyanoacetamide and ethyl orthoformate (cf. section 3-E).[219] The benzothiazolium salt was condensed with cyanoacetanilide and formamide (cf. section 3-E) to give LXXXVI (n=1, Y=S, R^1=Et, R^2=NHPh, R^3=CN).[55]

Through salts having a 4-acetanilido-1,3-butadienyl group (cf. section 5-A), higher vinylene homologues, LXXXVI (n=2, Y=S or O, R^1=Et, R^3=CN), were made.[215] Amongst dyes having ·CH_2·CH_2OPh attached to N (section 10-B.3) was LXXXVI (n=2, Y=S, R^1=CH_2CH_2OPh, R^2=Ph, R^3=CN) and this was reached by the alternative route of heating a benzothiazolium salt having a 2-methyl group with 3-(acetanilidoallylidene)(benzoyl)acetonitrile and triethylamine in ethanol (cf. section 5-A).[112] A compound analogous with a simple merocy-

anine was prepared from 2-methylthio-3,1,4-benzothiazine methiodide (cf. section 10-C.1e) and benzoylacetonitrile, by heating them with potassium carbonate in ethanol.[135]

(2) *Linkage by a Substituted Chain*

(*a*) *Analogues of β-Substituted Dimethinmerocyanines.* The preparation of β-methyldimethinmerocyanines from an *N*-alkylbenzothiazoline, having the group :CH·COMe (section 8-A.3), included a reaction with benzoylacetonitrile in acetic anhydride.[70] Somewhat as quaternary salts having a reactive methyl group were converted into β-alkyldimethinmerocyanines by cyclic compounds having >C:CR(OEt) adjacent to CO (section 8-A.4), so were 2-methylbenzothiazolium salts brought into reaction with compounds of the type $(RO_2C)(CN)C:CR(SR')$[220] to give β-substituted products, such as LXXXVII (n=0, Y=S, R^1=Et, R^2=OEt, R^3=CN, R^4=Me or Et), described as valuable sensitisers.[221] Comparable with the condensation of quaternary salts, having an SR group, with cyclic compounds having >C:CR'Me adjacent to CO, to give β-substituted dimethinmerocyanines (section 8-A.6) was the condensation of 2-alkylthiobenzothiazolium salts with substances, $(RO_2C)(CN)C:CMe(SR')$, to give β-alkylthio-compounds, such as LXXXVII (n=0, Y=S, R^1=Me, R^2=OEt, R^3=CN, R^4=SMe);



(LXXXVII)

the alkylthio-group could also be SEt, SPr^i, or SBu^n.[222] Alkylthio-quaternary salts condensed with substances, $(RO_2C)(CN)C:CMe(OR')$, to give β-alkoxy-compounds, such as LXXXVII (n=0, Y=S, R^2=OMe or OEt, R^3=CN, R^4=OMe or OEt); these belonged mostly to the benzothiazole series but 2-linked quinoline and benzoxazole were also exemplified.[223] The salts were also condensed with substances, $(RO_2C)(CN)C:CMeR'$, to give β-methyl compounds, such as LXXXVII (n=0, Y=CH:CH, O, or S, R^1=Me, R^2=OEt, R^3=CN, R^4=Me). Substituents such as β-phenyl or β-2-thienyl were also introduced. Again the examples belonged mostly to the benzothiazole series but 2-linked quinoline, benzoxazole, and indolenine also occurred.[224] A β-methyl compound was prepared from 2-methylthio-1-azacycloheptane meth-

iodide (cf. section 10-C.1a) and $(EtO_2C)(CN)C:CMe_2$ by heating them with triethylamine in acetone.[116] β-Substituted compounds, of the benzothiazole series, were sensitisers. β-Substituents were *p*-tolyl, styryl, *p*-methoxystyryl, and β-naphthyl (cf. section 13-A.2b).[225] Quaternary salts having a reactive methyl group were condensed not only with cyclic compounds having $>C:C(SMe)_2$ adjacent to CO (section 8-A.7), but also with $(EtO_2C)(CN)C:C(SMe)_2$. Thus by boiling *p*-toluquinaldine methotoluene-*p*-sulphonate with this substance[226] in pyridine, there resulted the 6-methyl derivative of the β-methylthio-compound, LXXXVII (n=0, Y=CH:CH, R^1=Me, R^2=OEt, R^3=CN, R^4=SMe). Other such sensitisers, LXXXVII (n=0, Y=O, S, or Se, R^1=Me, R^2=OEt, R^3=CN, R^4=SMe), and their thiazoline analogue, were prepared similarly.[227] By means of $(EtO_2C)(CN)C:C(SEt)_2$ and $(EtO_2C)(CN)C:C(SCH_2Ph)_2$,[226] a β-ethylthio- or a β-benzylthio-group could be introduced.[227] An alternative procedure was to convert an *N*-alkyldihydro-heterocyclic base having a :CH·CS(SMe) group[228] into a quaternary salt with the group ·CH:C(SMe)$_2$, which salt could be condensed with substances, $ROC·CH_2CN$, to give β-methylthio-compounds, such as LXXXVII (n=0, Y=S, R^1=Me, R^2=NH_2 or NHPh, R^3=CN, R^4=SMe). The examples were mostly of the benzothiazole series but 2-linked quinoline also occurred.[229] Just as β-methylthiodimethinmerocyanines could be converted by amines, HNR^1R^2, into analogues with a β-NR^1R^2 group (section 8-A.8), so, similarly, were open-chain compounds with a β-SR or β-OR group converted by H_2NR into others with a β-NHR group.[75,230]

(*b*) *Analogues of δ-Substituted Tetramethinmerocyanines.* Comparable with the preparation of δ-methyltetramethinmerocyanines from a quaternary salt having a ·CH:CH·SR group and a cyclic compound having $>C:CMe_2$ adjacent to CO (section 8-D.2) is the reaction of quaternary salts, although these had the group ·CH:CH·NAcPh, with substances, $(RO_2C)(CN)C:CMe_2$, by heating with triethylamine in ethanol, to give sensitisers: such were LXXXVII (n=1, Y=S, R^1=Et, R^2=OEt, R^3=CN, R^4=Me) and its *N*-methyl analogues of the 4-linked quinoline and benzoxazole series.[224] Both types of salts were condensed (cf. section 8-D.3) with substances $(RO_2C)(CN)C:CR'Me$ to give δ-substituted sensitising dyes of type LXXXVII (n=1). The δ-substituents were *p*-methoxyphenyl and styryl, and the series represented were benzothiazole, benzoxazole, and thiazoline.[225] The salts were also condensed with substances, $(RO_2C)(CN)C:CMe(SR')$, to give δ-alkylthio-

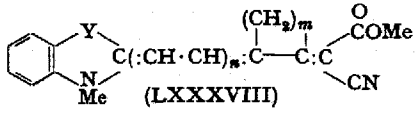
compounds of type LXXXVII (n=1, Y=S, R^1=Me, R^2=OEt, R^3=CN, R^4=SR); the δ-alkylthio-group was usually SEt, but other compounds had SMe, SPr^i, SBu^n, or SCH_2Ph; besides the benzothiazole series, benzoxazole and thiazoline were represented.[231] The salts were also condensed with substances, $(EtO_2C)(CN)C{:}CMe(OR)$,[232] to give δ-alkoxytetramethin compounds, which included derivatives of the 2-linked quinoline, benzoxazole, benzothiazole, and indolenine series.[233] By the action of amines, H_2NR, the δ-alkylthio- or δ-alkoxy-group was converted to δ-NHR.[230]

(*c*) *Analogues of β-Substituted Tetramethinmerocyanines.* Somewhat resembling the condensation of a quaternary salt having the group ·CH:CMe(SMe) with a cyclic compound having >C:CH·NHPh adjacent to CO (section 8-E.2) is the reaction of this type of benzothiazolium salt with a substance, $(RO_2C)(CN)C{:}CHOR'$, to give β-methylthio- or β-ethylthio-compounds. The benzothiazolium salt could alternatively have the group ·CH:CMe(OR), whence there resulted β-methoxy- or β-ethoxy-compounds.[234]

(*d*) *Analogue of a ζ-Substituted Hexamethinmerocyanine.* The ζ-substituted compound, LXXXVII (n=2, Y=S, R^1=Et, R^2=OEt, R^3=CN, R^4=*p*-C_6H_4OMe), prepared by condensation of a salt, having the group $(\cdot CH{:}CH)_2\cdot NAcPh$, with $(EtO_2C)(CN)C{:}CR^4\cdot Me$ (cf. section 13-A.2a and b) sensitised from 5800 Å to 7000 Å.[225]

(*3*) *Compounds in which Part of the Chain Enters into a Ring*

Analogous with substances such as XIX was LXXXVIII (n=0, m=3, Y=S), where both members of a dimethin chain are cyclic. It resulted on prolonged reaction of 2-methylthiobenzothiazole methomethylsulphate, methyl cyclopentylidenecyanoacetate, and triethyl-



(LXXXVIII)

amine in pyridine. The 2-quinoline analogue was also made. In preparing LXXXVIII (n=0, m=4, Y=S or CH:CH), the appropriate quaternary salt was heated with methyl cyclohexylidenecyanoacetate and triethylamine in isopropanol. The compound, LXXXVIII (n=1,

m=3, Y=CMe_2), in which two members of a tetramethin chain are cyclic, was prepared by heating 2-formylmethylene-1,3,3-trimethylindoline and methyl cyclopentylidenecyanoacetate with acetic anhydride and pyridine at 60°.[195] Absorption data for two similar com-

TABLE III. Some Properties of Open Chain Analogues of Di- and Tetramethinmerocyanines of the Benzothiazole Series (Y=S in formulae)

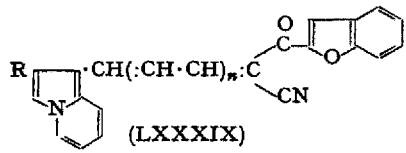
Formula	Appearance of crystals	M.p. (°C)	Sensitising (Å) Maximum	Extent	Ref.
Compounds with Substituent on Chain					
LXXXVII (n=0, R^1=R^4=Et, R^2=OEt, R^3=CN)	orange	129	4800	5200	221
LXXXVII (n=0, R^1=Et, R^2=OEt, R^3=CN, R^4=·CH:CHPh)	bright red	207	—	5000	225
LXXXVII (n=0, R^1=Me, R^2=OEt, R^3=CN, R^4=SEt)	yellow-red needles	128	5300	5500	222
LXXXVII (n=0, R^1=Et, R^2=R^4=OEt, R^3=CN)	yellow	159	4000	4600	223
LXXXVII (n=0, R^1=Me, R^2=OEt, R^3=CN, R^4=NHEt)	yellow	152	3900	4400	230
LXXXVII (n=1, R^1=Et, R^2=OEt, R^3=CN, R^4=Me)	dark blue	199	5400[a] 5900[a]	6400	224
LXXXVII (n=1, R^1=Et, R^2=OEt, R^3=CN, R^4=·CH:CHPh)	blue	211–212	6400	6900	225
LXXXVII (n=1, R^1=Et, R^2=OEt, R^3=CN, R^4=SEt)	mauve needles	151	6800	7000	231
LXXXVII (n=1, R^1=Et, R^2=R^4=OEt, R^3=CN)	bluish	136	5800	6300	233
β-Substituted analogue of preceding compound	dark red	231	5400	5800	234
LXXXVII (n=1, R^1=Me, R^2=OEt, R^3=CN, R^4=NHEt)	orange-yellow	152	5100	5500	230
Compounds in which Chain Enters Carbocyclic Ring					
LXXXVIII (n=0, m=3)	orange-yellow[b]	184	—	—	195
Analogue of XCII (R^1=R^2=R^3=Me, with :C(CO_2Et)(CN) in place of :C$(CN)_2$)	—	179–180[c]	6000	6300	235

[a] Indefinite maxima. [b] Colour of methanolic solution.
[c] With decomp.

pounds of the indolenine series, one of them comprising a cyclohexane ring, were recorded.[217] Together with compounds in which three members of a tetramethin chain, linking a heterocyclic nucleus to $:C(CN)_2$, formed part of a carbocyclic ring (see section 13-B.2), was one in which the end group was $:C(CO_2Et)(CN)$.[235]

Table III gives some properties of a series of open-chain analogues of di- and tetra-methinmerocyanines with a substituted chain, or in which the chain enters into a carbocyclic ring, compounds with an unsubstituted chain being perforce omitted because of the paucity of information.

The pyrrocoline nucleus was introduced, not only into the molecule of XVII (n=1 or 2) (cf. section 1 and section 9-B.2 and 3), but also gave such compounds as LXXXIX (n=1 or 2, R=Ph). The former was



(LXXXIX)

prepared by heating 2-phenylpyrrocoline and triethylamine in ethanol with 2-(3-acetanilidoallylidene)cyanoacetylbenzofuran, whilst, for the latter, the higher vinylene homologue of the benzofuran compound was used.[92]

(4) *Analogue of a Diazadimethinmerocyanine*

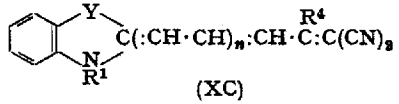
Just as a hydrazone of the benzothiazole series reacted with a heterocyclic ketone in the presence of an oxidising agent (cf. section 1 and section 11-C), so it reacted with acetylacetone to give the diaza-analogue of LXXXVI (n=0, Y=S, R^1=R^2=Me, R^3=COMe).[169]

B. Compounds with a Heterocyclic Nucleus Linked by an Even-Numbered Chain, or Directly Linked, to $:C(CN)_2$

(1) *Substances with an Open Chain*

In 1947 dicyano-compounds of the type $(CN)_2C:(SR)_2$ were made and were condensed with quaternary salts having a reactive methyl group, by heating in pyridine, or with triethylamine in ethanol, to give β-alkylthio-dimethin compounds of the type XC (n=0, R^4=SMe

or SEt) (cf. section 13-A.2a). Compounds of the benzoxazole, benzothiazole, 4-linked quinoline, and thiazoline series were made. Use of a 2-ethylbenzothiazolium salt led to an α-methyl-β-methylthio-compound.[236] Quaternary salts having the group ·CH:C $(SR)_2$ were condensed, not only with a substance, ROC·CH_2CN (section 13-A.2a), but



(XC)

also with malonitrile by heating with triethylamine in ethanol, to give compounds such as XC (n=0, Y=S or CH:CH, R^1=Me, R^4=SMe).[229] Not only were quaternary benzothiazolium salts, possessing the group ·CH:CMe(SMe) or ·CH:CMe(OR), condensed with substances, $(RO_2C)(CN)C:CHOR'$, to give β-SMe- or β-OR-tetramethin compounds (section 13-A.2c), but they were also condensed with ethoxymethylenemalonitrile.[234] Analogous with various substituted compounds prepared by use of $(RO_2C)(CN)C:CR'Me$ (section 13-A.2a, b, and d) were β-alkyl(or benzyl)dimethin compounds and a δ-benzyl tetramethin compound, prepared through $(CN)_2C:CRMe$.[237] In the indolenine series, absorption data were recorded for four tetramethin compounds of this kind, of which two had a δ-alkyl, one a γ-ethyl, and one δ-ethyl-γ-methyl substituents.[217] The sensitising action of various such compounds was patented. The dimethin compounds all belonged to the benzothiazole series but, in the tetramethin group, the indolenine and thiazoline series were also represented. Amongst the substituents on the chain were phenyl, styryl, isopropyl, and t-butyl.[225] Comparable with the preceding diazadimethin compound (section 13-A.4) was one prepared by use of malonitrile.[169]

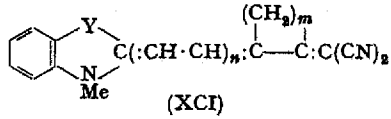
The absorption of di- and tetra-methin compounds, XC (n=0 or 1, Y=CMe_2, R^1=Me, R^4=H), with unsubstituted chains, was recorded.[217] The preparation of dimethin compounds of the type XC (n=0, R^4=H), through ethoxymethylenemalonitrile, has already been mentioned (section 13-A.1). Those which were described included XC (n=0, Y=CH:CH, O, S, or Se, R^1=Me, R^4=H), and their analogues of the 2- and 4-linked pyridine series. In five such series, the colour of an ethanolic solution of a compound having a dimethin chain linked to :$C(CN)_2$ was the same as that of the compound with the same nucleus but in which the chain was linked to :$C(CO_2Et)(CN)$. Higher vinylene

homologues could be obtained by an analogous method, but preferably by condensing a quaternary salt, having a reactive methyl group, with an aldehyde, $OCH(\cdot CH:CH)_{1-2}\cdot NMePh$, and by treating the resultant quaternary salt, possessing the group $(\cdot CH:CH)_{2-3}\cdot NMePh$, with malonitrile.[218] The sensitising action of the dimethin compound, XC (n=0, Y=NMe, R^1=Me, R^4=H), was especially powerful.[238] Such compounds were also applied in a supersensitising combination with other dicyano-compounds,[239] whilst tetra- and hexa-methin compounds, XC (n=1 or 2, R^4=H), of various series were patented as sensitisers.[240]

Although *N*-methyl-4-oxo-1,4-dihydroquinoline does not show normal ketonic properties, *N*-methyl(or phenyl)-4-oxo-1,2,3,4-tetrahydroquinoline, on the contrary, condensed with malonitrile to give red compounds, in which $:C(CN_2)$ was directly linked to the heterocyclic nucleus. Likewise substances such as 1,6-dioxojulolidine (cf. IX-1; XIII-4-A and F) condensed with one or two mols. of nitrile to give, respectively, deep red or purple products. It was remarkable that, in all these compounds, the sensitising maximum lay at a shorter wavelength than the absorption maximum.[241]

(2) *Substances in which Two or Three Members of the Chain Enter into a Ring*

Absorption data were given for XCI (n=0, m=3 or 4, Y=CMe_2), in which two members of a tetramethin chain enter into a carbocyclic ring.[217] The compound, XCI (n=0, m=3, Y=S), was prepared from

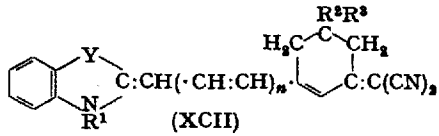


(XCI)

2-methylthiobenzothiazole methomethylsulphate and cyclopentylidenemalonitrile by heating them with triethylamine in ethanol, whilst XCI (n=0, m=4, Y=S) was similarly obtained by use of cyclohexylidenemalonitrile. The latter nitrile was condensed with 2-formylmethylene-1,3,3-trimethylindoline, by heating them with pyridine and acetic anhydride, to give XCI (n=1, m=4, Y=CMe_2)[195] (cf. section 13-A.3).

Various compounds in which three members of the chain, linking a heterocyclic nucleus to $:C(CN)_2$, entered into a carbocyclic ring were

sensitisers. Substances of this type, XCII (n=0 or 1), may be regarded as chain-substituted tetra- or hexa-methin compounds. The series exemplified were benzoxazole, benzothiazole, benzimidazole, 2- and



(XCII)

4-linked quinoline, and thiazoline. Most of the substances were prepared through 3-dicyanomethylene-1-methylcyclohex-1-ene or 3-dicyanomethylene-1,5,5-trimethylcyclohex-1-ene, giving XCII (R^2=R^3= H or Me).[235]

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CHAPTER XV

Trinuclear and Polynuclear Cyanines

1. Introduction

In earlier chapters there occur a few instances of dyes in which a third heterocyclic nucleus is present as substituent in one of the two nuclei or on the chain. Chapter IX includes certain cyanines which are tri(or tetra)-nuclear, because of the participation of a carbocyclic nucleus (or nuclei) in the structure of the chain. A tetranuclear pentamethinoxonol in which two heterocyclic nuclei enter into the chain has also been mentioned (XIII-4-A and E). The subject of the present chapter is those compounds containing more than one cyanine, or merocyanine, structure, each of which could make its contribution to resonance. The subject is complex and there is more than one way of formulating each dye. Each of the following sections (except the last two) begins with a table of the types of compounds to be found therein, with one formulation for the characteristic chain, information being given as to the number of nuclei, and whether they are quaternary salt residues or ketomethylene residues. The methods are considered in the order in which they originated, each being followed to its conclusion.

The first section (section 2) which dates from 1920, is on dyes having a central quaternary salt residue, with two positions of linking, and with two chains. The various dyes of this type contain two cyanine structures, the term being used in its widest sense to include merocyanines also. In the earliest of these trinuclear dyes, all three nuclei were quaternary salt residues and the product, like the original quaternary salt, was mono-ionic. Although in the first compounds the two chains were of equal length, subsequently two-stage processes made possible the synthesis of dyes where the two odd-numbered chains were unequal in length (section 2-A). Recent syntheses with quaternary salts of an indenothiazole, which had a reactive methyl and a reactive methylene group, led to mono-ionic trinuclear dyes with one

odd- and one even-numbered chain (section 2-B). Another development was the use of a quaternary salt having a reactive amino- and a reactive methyl group, whereby the pair of odd-numbered chains could be ·N: and CH:, ·CH:CH·N: and ·CH:CH·CH:, or ·CH:CH·CH:CH·N: and ·CH:CH·CH:CH·CH: (section 2-C).

Certain quaternary salts having two alkylthio-groups were converted, by a two-stage process, into non-ionic trinuclear dyes, in which the central nucleus was attached to another quaternary salt residue by a methin group, and to a ketomethylene residue either directly or by a dimethin chain (section 2-D).

Through a diquaternary salt there resulted trinuclear di-ionic compounds with three quaternary salt residues and two methin or two trimethin chains (section 2-E). From the reactive diquaternary salts of bis-heterocycles, there were synthesised symmetrical di-ionic tetranuclear compounds, with a pair of methin, trimethin, or pentamethin chains (section 2-F). These diquaternary salts also led to symmetrical non-ionic tetranuclear products, with two dimethin chains (section 2-G).

Neocyanine, or Allocyanine as it was called in Germany, was described as a sensitiser for the infrared in 1926. It had arisen as a by-product accompanying 4,4′-carbocyanine. Although it was recognised as trinuclear in 1928, its exact constitution was only established twenty years later. It and related dyes, all having three cyanine structures, in which a branched chain was attached to a quaternary salt residue, form the subject of the next section (section 3). Neocyanine itself, and closely analogous compounds, are di-ionic and comprise two trimethin structures and one pentamethin. Whereas in those dyes that arose as by-products, the three nuclei were identical, the synthetic neocyanines could have one dissimilar and two similar nuclei, or even three dissimilar nuclei (section 3-A). A synthesis of neocyanines, which involved the conversion of a trimethincyanine into a diquaternary salt, having an α-alkylthiomethylene group, was also applied to pentamethincyanines, whence di-ionic dyes with the chain $:C\langle^{CH:CH\cdot}_{CH:CH\cdot CH:CH\cdot}$ were obtained (section 3-B).

From α-anilomethyltrimethincyanines by condensation with ketomethylene compounds, or, alternatively, from α-anilomethyldimethinmerocyanines by condensation with quaternary salts having a reactive methyl group, there were synthesised mono-ionic dyes with the chain $:C\langle^{CH:CH\cdot}_{CH:}$. They were also made by condensing diquaternary salts having an α-ethylthiomethylene group with ketomethylene com-

pounds (section 3-C). Such a diquaternary salt, having a pentamethin instead of a trimethin chain, led to a mono-ionic dye with the chain $:C\langle^{CH:CH\cdot CH:CH\cdot}_{CH:}$ (section 3-D).

Trinuclear dyes, which were originally described as non-ionic, with the chain $:C\langle^{CH:}_{CH:}$, were subsequently reached by a different route, and, on account of their absorption, were regarded as *meso*-ionic trimethinoxonols, with the chain $\cdot C\langle^{CH:}_{CH:}$ (section 3-E).

The next section deals with trinuclear dyes, again having three cyanine structures, but with a chain branching from a carbon atom in the β-position to a quaternary salt residue. The important observation of the reactivity of the *meso*-methyl group in *meso*-methylthiacarbocyanine was demonstrated in 1936 by its condensation with *p*-dimethylaminobenzaldehyde (see VI-1 and 10) and, following upon this, trinuclear cyanines were prepared by condensation of *meso*-methylcarbocyanines with heterocyclic salts having a suitable reactive group, to give mono-ionic trinuclear dyes with the chain $\cdot CH:C\langle^{CH:}_{CH:}$. They were also synthesised from a quaternary salt possessing the group $\cdot CH:C(SMe)_2$ or $\cdot CH:CMe_2$ (section 4-A). Condensation of a *meso*-methylthiacarbocyanine with a salt having a 2-β-acetanilidovinyl group gave a mono-ionic dye with the chain $\cdot CH:C\langle^{CH:}_{CH:CH\cdot CH:}$ (section 4-B). Condensation of salts having the group $\cdot CH:C(SMe)_2$ with others having a cyclohexane group gave trinuclear dyes with the chain $\cdot CH:C\langle^{CH:CH\cdot CH:}_{CH:CH\cdot CH:}$ but comprising two carbocyclic rings (section 4-C). Dimethincyanines having a pyrryl, indolyl, or pyrrocolyl nucleus (see X-5-A), if they had a methyl group in the α-position to it, showed the same reactivity as did *meso*-methyltrimethincyanines. Their condensation with heterocyclic salts having an alkylthio- or iodo-substituent gave mono-ionic dyes with the chain $\cdot CH:\dot{C}\cdot CH:$ (section 4-D), and with salts having a β-acetanilidovinyl group gave others with the chain $\cdot CH:\dot{C}\cdot CH:CH\cdot CH:$ (section 4-E), corresponding with those of sections 4-A and B, respectively. α-Azatrimethincyanines having a *meso*-methyl substituent were condensed with quaternary salts having an alkylthio-group to give mono-ionic dyes with the chain $\cdot N:C\langle^{CH:}_{CH:}$ (section 4-F) and with salts having a β-acetanilidovinyl group to give analogues with the chain $\cdot N:C\langle^{CH:}_{CH:CH\cdot CH:}$ (section 4-G). A benzothiazolium salt with the group $\cdot CH:C(SMe)_2$ was condensed with one having an amino-group to give a dye with the chain $\cdot CH:C\langle^{N:}_{N:}$ (section 4-H). A different kind of reaction consisted in the conversion of β-methyldimethinmerocyanines having a pyrazolone residue (XIV-8-A.4)

into quaternary salts, which reacted, through the β-methyl group, with salts having a methylthio-group, to give mono-ionic dyes with the chain ·CH:Ċ·CH: (section 4-I), whilst with salts having a β-acetanilidovinyl group they gave mono-ionic dyes with the chain ·CH:Ċ·CH:CH·CH: (section 4-J). These two groups have the same types of chain as in Chapter XV (sections 4-D and E, respectively) but differ from them in having a ketomethylene residue which, however, takes part in salt formation.

Non-ionic trinuclear dyes were synthesised from *meso*-substituted carbocyanines with a cyclic ketomethylene compound, or suitable derivative (sections 4-K, L, and M). Alternatively they were obtained from β-methyldimethinmerocyanines by reaction with a quaternary salt having an alkylthio- or β-acetanilidovinyl group (sections 4-K and M). From one trinuclear dye there were prepared various tetranuclear derivatives (section 4-K). Dimethinmerocyanines having a pyrryl or indolyl nucleus, and a methyl group in the α-position to it, were not only condensed with heterocyclic salts having a reactive group (sections 4-D and E), but also with cyclic compounds, having an acetanilidomethylene substituent on the carbon adjacent to CO, to give non-ionic trinuclear dyes with the chain :CH·Ċ:CH·CH: (section 4-N).

Dyes of the next type with the chain :CH·Ċ: were reached by two methods, and are mono-ionic in that they comprise the structure of a methinoxonol (section 4-O), whilst an analogue with the chain $:CH\cdot C\leqslant^{CH:CH:}_{CH\cdot CH:}$ comprises that of a pentamethinoxonol (section 4-P).

The conversion of merocyanine dyes containing the structure $\overset{|}{\underset{R}{N}}\!-\!C:S$ into reactive salts having an alkylthio-group has already been discussed (XIV-1 and 7). Such dye salts were used in the preparation of numerous types of trinuclear derivatives, having a central ketomethylene residue, linked by chains of various lengths, and are mostly considered in the next section (section 5), although a few instances of the method, when it led to tetra- or penta-nuclear derivatives of certain trinuclear dyes, have already been mentioned (sections 4-I, K, and O). The first patent, in 1936, covered compounds in which the chain carried a substituent. The dyes are however grouped here according to chain-lengths, irrespective of whether the chains are substituted. The methods are adaptations of those which have been applied to simpler dyes and which have already been considered in earlier chapters. Mono-ionic trinuclear dyes with a central ketomethylene residue, linked by a methin

group to one quaternary salt residue, and directly to another such, are considered first (section 5-A), followed by analogues with the same types of nuclei but with one methin and one dimethin linkage (section 5-B), and by others with one methin and one tetramethin linkage. Dyes of the last class in which the tetramethin chain carried a β-alkyl group were prepared in 1942 by an alternative process involving a rhodanine with a 5-(γ-alkyl)(γ-alkylthio)allylidene group (section 5-C). An alternative method of preparing a trinuclear dye with one direct linkage and one methin chain consisted in converting a simple merocyanine having a 3-methyl-1-phenyl-5-pyrazolone residue into a quaternary salt, which through the reactive methyl group in the ketomethylene residue, underwent condensation with a salt having a 2-alkylthio-group (section 5-A) (cf. section 5-H). It was reported in 1949 that certain trinuclear cyanines having two identical quaternary salt residues, a methin and a dimethin chain, could be prepared by reaction of a 2-methyl quaternary salt, a rhodanine, and ethyl orthoformate (section 5-B). Another simplified method of arriving at trinuclear dyes, which had previously been reached through the quaternary salts of merocyanines, consisted in the condensation of a methincyanine, in which one quaternary salt residue was of the 4-oxothiazoline series (i.e., it was a ketomethylene residue) with various other types of quaternary salts. There resulted thereby products having one methin linkage, the other being direct, or through a di-, tetra-, or hexa-methin chain (sections 5-A, B, C, and D). Moreover the 5-methylene group in methincyanines having a 4-oxothiazoline residue was converted into other reactive groups, and these products were condensed with quaternary salts to give trinuclear dyes (sections 5-B, C, and D). Trinuclear dyes with an azamethin linkage, the other being direct or a dimethin chain, were prepared by reaction of the quaternary salt of a suitable mero- or dimethinmero-cyanine with a salt having a 2-amino-group. They also could be obtained from azamethincyanines of the 4-oxothiazoline series (sections 5-E and F). In 1952 there were described various trinuclear dyes with a central 3-substituted rhodanine residue attached by a dimethin linkage in the 5- and a methin linkage in the 2-position to quaternary salt residues, one or both of which belonged to substituted thiazole series (section 5-B). Instead of the central residue being a rhodanine, it might be the isomeric 5-thiazolidone (sections 5-B and C). By converting various types of merocyanines into quaternary salts having an alkylthio-group and condensing these with salts having the group ·CH:CMe(OR) (cf. VI-15),

there were prepared trinuclear dyes having one β-alkoxytrimethin chain, and one direct linkage or even-numbered chain (sections 5-G, H, and I). A dimethinmerocyanine having a 1-cyclohexyl-2-methyl-4-oxoimidazoline residue was converted into a quaternary salt, which condensed, through the reactive methyl group in the ketomethylene residue, with a salt having a β-acetanilidovinyl group (section 5-H) (cf. section 5-A). Certain simple and di- and tetra-methinmerocyanines having a 2-methyl-4-oxothiazoline residue, were converted into quaternary salts, which underwent condensations through the reactive methyl group (sections 5-G, H, and J).

Non-ionic trinuclear dyes were prepared by the condensation of salts of certain simple or dimethin-merocyanines, through an alkylthio-group, with ketomethylene compounds (sections 5-K and L). Besides numerous types of trinuclear compound in which the central ketomethylene nucleus was directly linked to the other such nucleus, and by a dimethin chain to the quaternary salt residue, others were synthesised in which the dimethin linking was to the second ketomethylene residue, the quaternary salt residue being directly linked (section 5-L). Dimethinmerocyanines having a 4- or 5-thiazolidone residue were condensed with rhodanines having a 5-:CRMe group to give trinuclear dyes with two dimethin chains (section 5-M), and analogues with one di- and one tetra-methin chain were also described (section 5-N). Simple merocyanines in which the quaternary salt residue was a substituted 5-aminomethylene-4-oxothiazoline (cf. XIV-1 and 10-C.1e) led to trinuclear dyes which were abnormal in that the quaternary salt residue was a ketomethylene residue (section 5-K).

Dyes of the final group in this section have the character of a methincyanine and also of a compound of the oxonol class and may therefore be written as di-ionic (section 5-O).

There have been described in the patent literature certain dimethinmerocyanines with a thioketomethylene in place of a ketomethylene residue (XIV-1 and 4). Trinuclear dyes prepared from these have been included with their analogues having a ketomethylene residue (sections 5-B and L).

In the section on tetranuclear dyes, the compounds that are considered first are quite unlike all the rest, having been formulated as di-ionic, with four quaternary salt residues, and the structure of double pentamethincyanines (section 6-A). All the other groups have at least two ketomethylene residues.

Methods which were used for preparing symmetrical methincyanines from quaternary salts were applied to similar salts derived from mero- and dimethinmero-cyanines, to give symmetrical tetranuclear mono-ionic dyes (sections 6-B and C). Symmetrical tetranuclear dyes with a central azamethin linkage (section 6-D), or trimethin linkage (sections 6-E and F), were likewise made by an extension of methods which had been used in preparing dinuclear cyanines. Both symmetrical and unsymmetrical mono-ionic tetranuclear derivatives were synthesised from the quaternary salts of trinuclear dyes, in which the terminal ketomethylene residue was 3-ethylrhodanine (section 6-G).

Symmetrical non-ionic tetranuclear compounds, having a central diazadimethin linkage, were reached by condensation of hydrazine with the quaternary salts of mero- and dimethinmero-cyanines having a 3-ethylrhodanine residue (sections 6-H and I). From the quaternary salts of non-ionic trinuclear dyes, in which the terminal nucleus was a 3-substituted rhodanine, non-ionic tetranuclear derivatives were synthesised (sections 6-J, K, L, and M), including one with the anomaly that the quaternary salt residue was also a ketomethylene residue (section 6-J). Some of these dyes, possessing the structure of complex merocyanines, were remarkable, as such, in having their absorption maxima in the infrared (sections 6-L and M).

As the compounds of the final group in this section are not only diquaternary salts but also have the character of oxonols, they are regarded as tri-ionic. They include both symmetrical and unsymmetrical substances. One method of preparation was based on the use of dialkylthio-quaternary salts prepared from symmetrical methinoxonols having 3-alkylrhodanine residues. A more comprehensive one involved reactions of methincyanines, having a 4-oxothiazoline residue, and derivatives in which that residue had a substituent of one kind or another (cf. section 5). Some of the tetranuclear dyes were sensitisers for infrared light (section 6-N).

The preparation in 1947 of quaternary salts in which two heterocyclic nuclei, each having a reactive methyl group, were linked, through their nitrogen atoms, by a chain $(CH_2)_n$, led to bis-cyanines, in which the two dye units were thus linked. Condensation of two bis-quaternary salts of this kind might give rise to polymers of greater complexity. The sensitising maxima quoted for the polymers were not remote from those of the simpler dyes. Polymeric *p*-dimethylaminostyryl dyes with a linking *N*-$(CH_2)_n$-*N* were made, also various types of non-ionic merocyanine dyes (section 7).

The nomenclature of the complex dyes of this chapter is itself complex. Apart from two independent names for the neocyanines section 3-A), one based on a tri-, the other on a penta-methincyanine, there has been little attempt at simplification. For the rest, various lengthy names have been put forward, but there seems no need to record these here.

2. Dyes with Two Cyanine Structures: Trinuclear Cyanines Having a Central Quaternary Salt Residue with Two Positions of Linking: Symmetrical Tetranuclear Cyanines with Two Central Quaternary Salt Residues

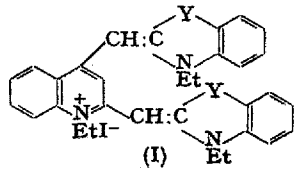
Ref.	Chain	No. of quaternary salt residues	No. of ketomethylene residues	Type
2-A	Two ·CH:, or ·CH: and ·CH:CH·CH:	3	0	trinuclear, mono-ionic
2-B	·CH:CR·CH: and :CH·CH:, or ·CH: and direct linkage	3	0	trinuclear, mono-ionic
2-C	·(CH:CH·)$_n$N: and ·(CH:CH·)$_n$CH: (where n=0–2)	3	0	trinuclear, mono-ionic
2-D	·CH: and direct linkage, or ·CH: and :CH·CH:	2	1	trinuclear, non-ionic
2-E	Two ·CH:CR·CH:, or Two ·CH	3	0	trinuclear, di-ionic
2-F	Two ·(CH:CH·)$_n$CH: (where n=0–2)	4	0	tetranuclear, di-ionic
2-G	Two :CH·CH:	2	2	tetranuclear, non-ionic

A. Mono-Ionic Trinuclear Dyes with Two Cyanine Structures, Three Quaternary Salt Residues, and Two ·CH: Chains, or with ·CH: and ·CH:CH·CH:

It was noted forty years ago that the 2,4′-cyanine prepared from quinaldine alkiodide still had a reactive methyl group, since its colour changed from red to blue on condensation with benzaldehyde.[1] Similarly a 2,2′-carbocyanine having 4,4′-dimethyl groups changed from blue to green on reaction with benzaldehyde.[1,2] A 2,2′- or a 2,4′-carbocyanine with a reactive methyl group underwent condensation with *p*-dimethylaminobenzaldehyde.[3] Thirty years ago, 2,4-dimethylquinoline ethiodide

was used in the preparation of a bis-*p*-dimethylaminostyryl salt and of the corresponding dianil (see XIII-1-R and 2-B-5).[4]

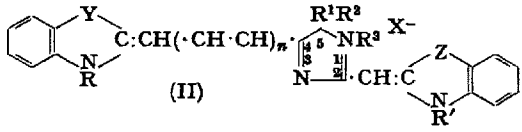
It was recorded in 1937 that both non-ionic iodine atoms of 2,4-di-iodoquinoline ethiodide could condense with a salt having a reactive methyl group to give a trinuclear dye. The resultant compound, I (Y = CH:CH), was alternatively prepared from 2,4-dimethylquinoline



(I)

ethiodide. It was also reached in two stages by condensation of 2-iodo-quinoline ethiodide with 1,1'-diethyl-2'-methyl-2,4'-cyanine iodide. Condensation of 2,4-di-iodoquinoline ethiodide with a 2-methylbenzo-thiazolium salt gave I (Y=S). Other resonance extremes of the first dye, in which a different nitrogen atom carried the positive charge, were written. The absorption curve of each of the two dyes consisted of two distinct bands.[5] The sensitising action of the compounds, I (Y=O, S, or Se), was patented.[6]

Many years later it was found that quaternary salts of 2,4-di(alkyl-thio)-5,5-di-substituted imidazolenines[7] could, in virtue of the two alkylthio-groups, undergo condensations with two molecules of quater-nary salt, having a reactive methyl group, to give trinuclear dyes of type II (n=0, Y=Z), which were sensitisers. A usual procedure was to heat



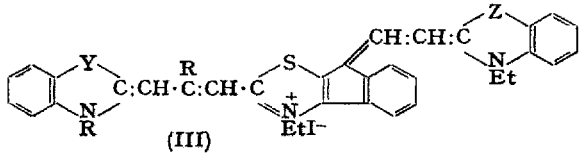
(II)

together the two bases and alkyl toluene-*p*-sulphonate, then heat further with triethylamine in pyridine, and convert into iodide or perchlorate. Amongst the numerous examples, the series represented were 2- and 4-linked quinoline, benzothiazole, and benzoxazole. The 5,5-substituents were generally dimethyl but there were also examples with 5,5-diethyl, 5,5-cyclopentamethylene, and 5-benzyl-5-methyl substituents.[8] Alternatively the condensation could be carried out in

two stages, in which a methincyanine having a 4-alkylthio-5,5-disubstituted imidazolenine residue[7] was condensed with a quaternary salt having a reactive methyl group: products such as II (n=0, Y=CH:CH or O, Z=S) were described, also an analogue in which the first nucleus was of the 4-linked quinoline series.[8] Instead of a quaternary salt of a 2,4-di(alkylthio)-5,5-disubstituted imidazolenine, the base itself could be condensed with two mols. of heterocyclic salt having a reactive methyl group, to give acid dyes of type II (n=0, Y=Z, R^3=H). Most of the examples were of the benzothiazole series, but there was also one of each of the series 2- and 4-linked quinoline, benzoxazole, benzoselenazole, and indolenine. Two of these acid dyes of the benzothiazole series were converted by alkali hydroxide into the corresponding bases.[9] A *meso*-methylmethincyanine and a trimethincyanine, each characterised by having a 4-alkylthio-5,5-dimethylimidazolenine residue,[10] were condensed with a quaternary salt having a reactive methyl group, the latter giving II (n=1, Y=CMe_2, Z=S, R=R^1=R^2=R^3=Me, R'=Et, X=ClO_4).[11] Methincyanines having a 2,5,5-trimethylimidazolenine residue[12] were condensed with quaternary salts having an alkylthio-group to give trinuclear dyes such as II (n=0, Y=Z=S or CH:CH, R^1=R^2=Me, X=ClO_4), an analogue having two 4-linked quinoline nuclei, and another with two such nuclei and, in the imidazolenine nucleus, the 5,5-cyclopentamethylene substituent; on the other hand, condensation with quaternary salts having a β-acetanilidovinyl group gave II (n=1, Y=CMe_2 or S, Z=S, X=ClO_4), and an analogue with a 4-linked quinoline nucleus attached to the trimethin chain[13] (cf. section 2-D).

B. Mono-Ionic Trinuclear Dyes with Two Cyanine Structures, Three Quaternary Salt Residues, the Pair of Chains ·CH:CR·CH: and :CH·CH:, or ·CH: and a Direct Linkage

2-Methyl-(2,1d)indenothiazole ethiodide (cf. X-5-E; XIV-10-C.1e) had a reactive methylene as well as a reactive methyl group, in virtue of which it could be condensed with 2-β-acetanilidovinylbenzoxazole ethiodide to give III (Y=Z=O, R=H); an analogue with two thiazol-

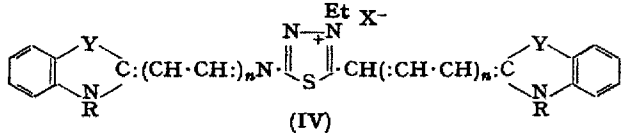


(III)

ine residues was also described. 2-β-Acetanilidovinylbenzoxazole ethiodide was also condensed with a *meso*-methyltrimethincyanine, having one benzothiazole and one indenothiazole residue, to give III (Y=S, Z=O, R=Me). In other examples the indenothiazole residue was linked to one nucleus by a methin chain and to the other directly.[14]

C. Mono-Ionic Trinuclear Dyes with Two Cyanine Structures, Three Quaternary Salt Residues, and a Pair of Chains ·N: and ·CH:, ·CH:CH·N: and ·CH:CH·CH:, or ·CH:CH·CH:CH·N: and ·CH:CH·CH:CH·CH:

The two reactive groups in 2-amino-5-methyl-1,3,4-thiadiazole ethiodide could be used to make this the central nucleus of a trinuclear cyanine. Thus by heating this salt with 2-β-acetanilidovinylbenzothiazole ethiodide and triethylamine in pyridine there was produced IV (*n*= 1, Y=S, R=Et), which was a sensitiser. Sixteen examples of this type



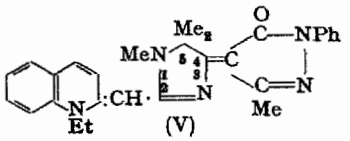
(IV)

included representatives of the benzothiazole, benzoxazole, benzoselenazole, indolenine, thiazole, and thiazoline series. Five other dyes, with the chains ·N: and ·CH: belonged to the 2-linked quinoline, benzothiazole, benzoselenazole, or thiazole series. There was one compound IV (*n*=2, Y=S, R=Et, X=I). In an additional dye of the benzothiazole series, having the chains ·N:CH·CH: and ·CH:CH·CH:, the central nucleus was a 1,3,4-oxadiazole residue. The sensitising action of such compounds was patented.[15]

D. Non-Ionic Trinuclear Dyes with Two Cyanine Structures, Two Quaternary Salt Residues, One Ketomethylene Residue, and a Pair of Linkages, ·CH: and Direct, or ·CH: and :CH·CH:

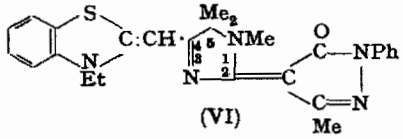
Methincyanines having a 4-alkylthio-5,5-dimethylimidazolenine residue were not only condensed with quaternary salts having a reactive methyl group (see section 2-A) but also with ketomethylene compounds, to give trinuclear dyes, of which V was one.[8] An analogue of the benzothiazole series was also described.[11] A type in which the methin linking was to the 4- and the direct linking to the 2-position of the central

nucleus resulted on condensing a simple merocyanine having a 4-alkylthio-5,5-dimethylimidazolenine residue[7] (see XIV-10-C.1b)[8] with a

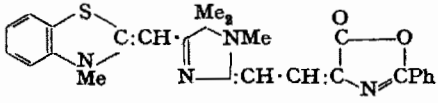


(V)

quaternary salt having a reactive methyl group: one example was VI.[8] A methincyanine having a 2,5,5-trimethylimidazolenine residue was condensed with 4-ethoxymethylene-5-oxo-2-phenyloxazoline to give VII, for which no sensitising data were given.[13]



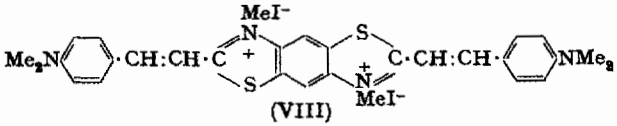
(VI)



(VII)

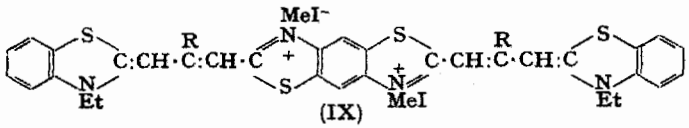
E. Di-Ionic Trinuclear Dyes with Two Cyanine Structures, Three Quaternary Salt Residues, and Two ·CH: or Two ·CH:CR·CH: Chains

In 1923 the dimethiodide of a dimethylbenzobisthiazole was converted into a bis-(*p*-dimethylaminostyryl) derivative VIII.[16] Subsequently true cyanines with a central nucleus of this kind, attached to

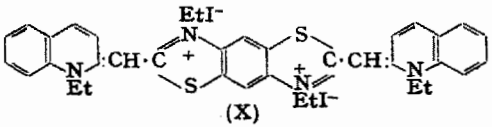


(VIII)

two similar nuclei, were prepared, and their sensitising action was patented. The examples included double trimethincyanines, such as IX (R=H or Et), and the methincyanine, X.[17]



(IX)



(X)

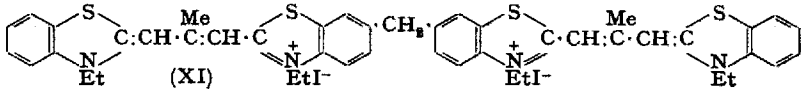
TABLE I. Properties of Some Trinuclear Cyanines Having a Central Quaternary Salt Residue with Two Positions of Linking

Group	Particulars	Appearance	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
	Mono-Ionic Dyes						
2-A	I (Y=CH:CH)	dull bronze	291–292	4800, 6150	5550, 6200	6700[a]	5
2-A	I (Y=S)	brownish; greenish reflex	274–276	4515, 5475	4650, 5550	6250	5, 6
2-A	II (n=0, Y=Z=CH:CH, R=R′=R^1=R^2=R^3=Me, X=I)	red needles; green reflex	284	—	5500	5750	8
2-A	II (n=0, Y=Z=S, R=R′=R^1=R^2=R^3=Me, X=I)	orange needles; blue reflex	324	—	5800	5900	8
2-A	II (n=1, Y=Z=CH:CH, R=R′=Et, R^1=R^2=R^3=Me, X=ClO_4)	green leaflets	309	—	5500	5850	13
2-A	II (n=1, Y=Z=S, R=R′=Et, R^1=R^2=R^3=Me, X=ClO_4)	blue plates	278	—	5800	6350	13
2-B	III (Y=Z=O, R=H)	bronze needles	288	4580, 4600	—	—	14
2-B	III (Y=S, Z=O, R=Me)	blue	236–238	4740, 6500	—	—	14
	Di-Ionic Dye						
2-E	IX (R=H)	—	263–264[b]	—	6000	6400	17

[a] Some reduction of blue-sensitivity. [b] Decomp. not recorded.

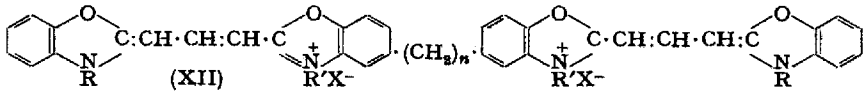
F. Symmetrical Di-Ionic Tetranuclear Dyes with Two Cyanine Structures, Four Quaternary Salt Residues, and Two ·CH:, Two ·CH:CH·CH:, or Two ·CH:CH·CH:CH·CH: Chains, from the Diquaternary Salts of Bis-Heterocycles

By the reaction of a diquaternary salt of a bis-6-(2-methylbenzothiazolyl)methane with a benzothiazolium salt having the group 2-CH:CMe(SMe), there was prepared the tetranuclear dye, XI. By reaction of a diquaternary salt of a bis-5-(2-methylbenzoxazolyl)methane



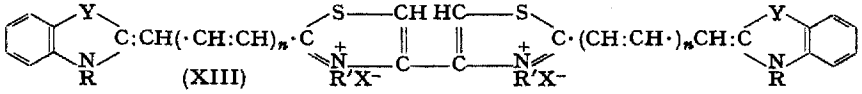
(XI)

with a benzoxazolium salt having a 2-β-acetanilidovinyl group, there resulted XII (n=1, R=CH_2Ph, R′=Me, X=Br). By reaction of a diquaternary salt of a bis-5-(2-methylbenzoxazole) with a 2-methylbenzoxazolium salt and ethyl orthoformate in acetic anhydride, there resulted XII (n=0, R=R′=Me, X=SO_4Me)[17] (cf. XIII-1-R).



(XII)

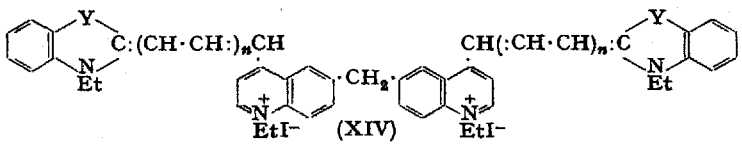
From bis-4-(2-methylthiazole) diquaternary salts, by condensation with two mols. of other quaternary salts having a reactive group, there were synthesised symmetrical tetranuclear dyes which were sensitisers. Six of the examples had trimethin chains, which might be *meso*-substituted, and they were usually of the benzothiazole series, XIII (n=1,



(XIII)

Y=S), but benzoxazole and benzoselenazole were also represented. One dye of the 2-linked quinoline series, with two methin chains, was described, and another, XIII (n=2, Y=O, R=Et, R′=$(CH_2)_2OPh$, X=I), of the benzoxazole series, with two pentamethin chains.[18]

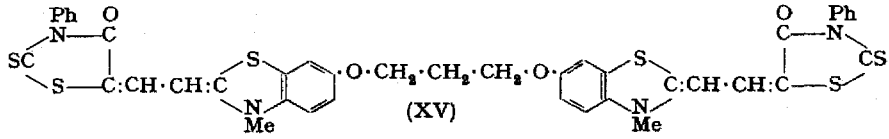
(Bis-6-lepidyl)methane was synthesised and its diquaternary salts were condensed with others having a 2-β-acetanilidovinyl group to give XIV (n=1, Y=S or O), and with 2-iodoquinoline ethiodide to give XIV (n=0, Y=CH:CH).[19]



(XIV)

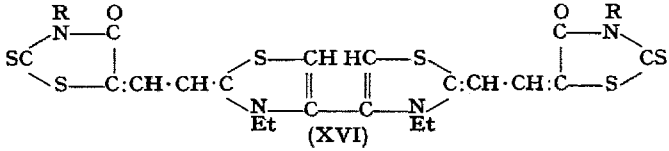
G. Symmetrical Non-Ionic Tetranuclear Dyes with Two Cyanine Structures, Two Central Quaternary Salt Residues, Two Ketomethylene Residues, and Two :CH·CH: Chains, from the Diquaternary Salts of Bis-Heterocycles

From the diquaternary salt of a base having two 2-methylbenzothiazole nuclei, linked in their 6-positions by the chain $\cdot O \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot O \cdot$, by condensation with 5-acetanilidomethylene-3-phenylrhodanine, there was prepared XV.[17]



(XV)

Similarly, from bis-4-(2-methylthiazole) diquaternary salts there were prepared XVI (R=Et, C_3H_5, or Ph), which were sensitisers.[20]



(XVI)

3. Trinuclear Dyes with Three Cyanine Structures and a Chain Branching from the Carbon Attached to a Quaternary Salt Residue: Neocyanine and Related Dyes

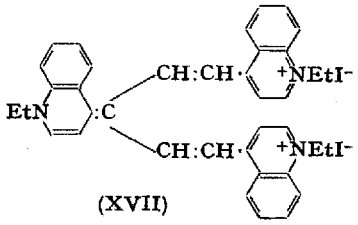
Ref.	Chain	No. of quaternary salt residues	No. of ketomethylene residues	Type
3-A	:C<CH:CH· CH:CH·	3	0	Di-ionic
3-B	:C<CH:CH· CH:CH·CH:CH·	3	0	Di-ionic
3-C	:C<CH:CH· CH:	2	1	Mono-ionic
3-D	:C<CH:CH·CH:CH· CH:	2	1	Mono-ionic
3-E	:C<CH: CH:	1	2	Non-ionic or *meso*-ionic

A. Neocyanines: Di-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain $:C\langle^{CH:CH\cdot}_{CH:CH\cdot}$ with One Penta-, and Two Tri-methin Segments

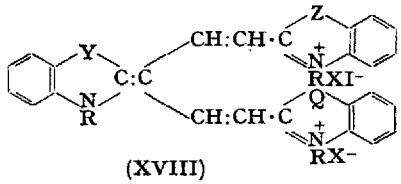
Although in 1926 neocyanine was said to sensitise more powerfully beyond 8000 Å than any dye then known,[21] its promise was unfulfilled, partly owing to the discovery of the di- and tri-carbocyanines (see chapters VII and VIII). The compound had been obtained, together with 4,4′-carbocyanine, by interaction of lepidine alkyl halide and iodoform in the presence of a strong base (IV-3-B).[22] It also occurred as a by-product in preparing the 4,4′-carbocyanine by the pyridine and ethyl orthoformate method (IV-6-C),[23] Analysis showed that neocyanine was formed from 3 mols. of lepidine alkyl halide with elimination of one mol. of acid, and that either one or two additional carbon atoms had entered the molecule. It was (incorrectly) formulated as a β-substituted 4,4′-trimethincyanine.[24] This type of formula was applied to other trinuclear dyes, which were made by condensation of the alkiodides of various heterocyclic bases with orthoformic ester or with diphenylformamidine, and which comprised representatives of the 2-linked quinoline and 2-linked pyridine series, and of the benzothiazole, thiazole, and benzimidazole series.[25] In patents on trinuclear cyanines which accompanied thiazolocarbocyanines prepared by the pyridine and ethyl orthoformate method (IV-6-G), an alternative type of formula was proposed for the di-ionic trinuclear dye, in which the chain was $\cdot CH:C\langle^{CH:}_{CH:CH\cdot}$; it had an advantage over the earlier one in explaining the stability of neocyanines to alkali.[26] The correct formula appeared in 1935, when neocyanine was represented as having an unbranched pentamethin chain with three similar nuclei symmetrically attached, so that two trimethin chains were also present.[27]

The synthesis of neocyanines was described in 1947. From various heterocyclic methylene bases and their anilomethyl derivatives[28] by heating them with ethylisoformanilide and zinc chloride, there were obtained the *N*-alkyldihydro-derivatives of heterocyclic bases having a reactive dianiloisopropylidene group. Their condensation with quaternary ammonium salts, having the same nucleus, but a reactive methyl group, resulted in neocyanines, identical with those which had been obtained empirically in the 4-linked quinoline, thiazole, and benzothiazole series; neocyanines of substituted benzothiazole series, and of the benzoselenazole and thiazoline series, were also made. Neocyanine

itself was represented by formula XVII, and other neocyanines, also with dicyclic nuclei, were of types XVIII (Y=Z=Q=S or Se). The dyes had well-defined narrow absorption bands, the maxima for seven such substances being intermediate between those of the related tri- and penta-methincyanines. The bathochromic shifts on passing from



(XVII)



(XVIII)

trimethincyanine to neocyanine varied from 375–710 Å, and those on passing from neocyanine to pentamethincyanine varied from 350–520 Å.[29]

Dyes of the neocyanine type, occurring as by-products in the preparation of trimethincyanines, and having three similar nuclei, were also recorded in other series. Such were the 1,3,4-thiadiazole,[30] tetrahydrobenzothiazole, tetrahydrobenzoselenazole,[31] oxazole, benzoxazole, and 4-linked pyridine series; these last three, and other known types, were prepared by use of diethoxymethyl acetate instead of ethyl orthoformate (cf. IV-13).[32] Together with other dyes having a 4,5-trimethylenethiazole nucleus (X-5-E; XIII-1-M.5; XIV-10-C.1e), there was included a neocyanine.[33]

The preceding synthesis of neocyanines was extended. Thus *N*-alkyldihydro-bases having a dianiloisopropylidene group were condensed with two molecular proportions of a 2-methyl quaternary salt of a different series to give trinuclear dyes of type XVIII (Z=Q), having two similar nuclei and one dissimilar, the two similar nuclei being at the ends of the pentamethin chain. Absorption maxima of twenty neocyanines of this kind were compared with those of the related tri- and penta-methincyanines. Besides this, the dianils were condensed with one mol. of quaternary salt to give dinuclear intermediate salts having the chain $:C\langle^{CH:CH\cdot}_{CH:NPh}$. These are in fact α-anilomethylcarbocyanines. Their absorption maxima were compared with those of the related carbocyanines, aniloethylidene compounds, and anilobutenylidene compounds, the data for these last two types being recorded under both basic and acidic conditions. The intermediate salts

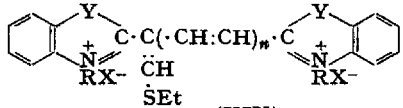
were used in the synthesis of six neocyanines, such as XVIII (Y=Z), having two similar nuclei at the ends of a trimethin chain and a dissimilar one at the other end of the pentamethin chain. The salts were also used in the preparation of four neocyanines in which all three nuclei were dissimilar. The absorption maxima of both types were compared with those of the related tri- and pentamethincyanines.[34]

Independently, at about the same date, the problem of the constitution of neocyanine was approached from a different angle, when the production of such dyes from a trimethincyanine, a quaternary salt having a reactive methyl group, and ethyl trithio-orthoformate, by heating them together in a minimum amount of acetic anhydride, was patented. In fourteen of the examples, the trimethincyanine was symmetrical and then there was no doubt that the product was of type XVIII (Y=Z), but in seven instances, where an unsymmetrical trimethincyanine was used, alternative formulae had to be written, although sometimes the point of attachment of the new chain could be deduced from a different synthesis.[35,36] The predominant formation of only one neocyanine from an unsymmetrical trimethincyanine was remarkable.[36] Intermediate di-ionic salts, such as XIX (n=1, Y=S), having an α-ethylthiomethylene group, were prepared by heating a 2-methylbenzothiazolium salt with toluene-p-sulphonic acid, ethyl trithio-orthoformate, and acetic anhydride[37] (cf. section 3-B). Such salts were condensed with others, having a reactive methyl group, by boiling them in pyridine, or, for adding a substituted indolenine nucleus, they were condensed with the methylene base in acetic anhydride, to give neocyanines. The nine examples comprised the types XVIII (Y=Z=S, Q=CH:CH, S, O, or CMe_2; and Y=Z=Q=CH:CH or Se).[38]

It was recorded subsequently that a carbocyanine having two 4-methylthiazole nuclei was converted, by boiling with 2-β-anilinovinyl-4-methylthiazole methiodide, potassium acetate, and acetic anhydride, into the neocyanine with three 4-methylthiazole residues. The trinuclear dye was also obtained by boiling the carbocyanine with ethyl orthoformate in acetic anhydride;[39] neocyanine itself resulted on boiling the 4,4'-carbocyanine with ethyl orthoformate in acetic anhydride.[40] A later synthesis of neocyanines consisted in the condensation of α-formylcarbocyanines with quaternary salts having a reactive methyl group.[41]

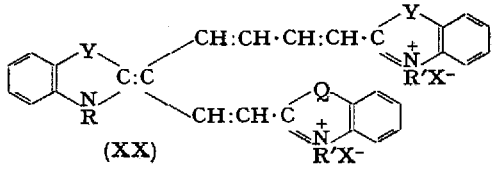
B. Di-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain $:C\begin{smallmatrix}CH:CH\cdot\\CH:CH\cdot CH:CH\cdot\end{smallmatrix}$ with Tri-, Penta-, and Hepta-methin Segments

Not only tri- but also penta-methincyanines were condensed with ethyl trithio-orthoformate, in the presence of toluene-*p*-sulphonic acid and acetic anhydride, to give diquaternary salts. The three examples belonged to the benzothiazole and indolenine series, i.e., XIX (n=2, Y = S or CMe_2) (cf. section 3-A).[37] By condensing such salts with others having a reactive methyl group, in the presence of pyridine (or acetic



(XIX)

anhydride for the indolenine series), there were obtained trinuclear compounds, of which the ten examples belonged to the types XX (Y= CMe_2, Q=CH:CH, CMe_2 or S; and Y=S, Q=CH:CH, S, O, or CMe_2).[38]



(XX)

C. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain $:C\begin{smallmatrix}CH:CH\cdot\\CH:\end{smallmatrix}$ with Di-, Tri-, and Tetra-methin Segments

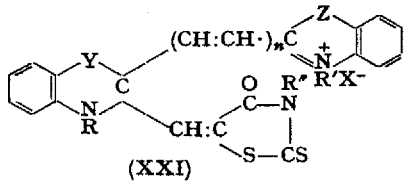
The *N*-alkyldihydro-derivatives of heterocyclic bases having a dianiloisopropylidene group[29] could be condensed with equimolecular amounts of cyclic ketomethylene compounds to give dimethinmerocyanines having an α-anilomethyl group, i.e., with the chain $:C\begin{smallmatrix}CH:NPh\\CH:\end{smallmatrix}$. The absorption maxima of fourteen such compounds were compared with those of the related aniloethylidene compounds, having the chain ·CH:CH:NPh, under both acid and basic conditions, and with those of the related anilinoallylidene compounds, having the chain :CH·CH:CH·NHPh. The α-anilomethyldimethinmerocyanines could be condensed with quaternary salts having a reactive methyl group to

TABLE II. Some Properties of Di-Ionic Trinuclear Dyes Having Three Similar Quaternary Salt Residues

Group	Particulars	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum in MeOH (Å)	Sensitising (Å) Maximum	Extent	Ref.
3-A	XVIII (Y=Z=Q=CH:CH, R=Et, X=I)	green; gold reflex	205[a]	6560	—	—	32
3-A	XVII (neocyanine)	brassy	280	7750	8300	9000	21, 29
3-A	XVIII (Y=Z=Q=S, R=Et, X=I)	dark green	243	6015	6450	7000	29
3-A	XVIII (Y=Z=Q=O, R=Me, X=I)	red	265[a]	5550, 5950	—	—	32
3-A	XVIII (Y=Z=Q=Se, R=Et, X=I)	dull green	226	6200	desensitiser		29
3-A	Analogue of XVIII (R=Me, X=I), of 2-linked pyridine series	green	236[a]	5970	—	—	32
3-A	Analogue of XVIII (R=Me, X=I), of 4-linked pyridine series	—	267[a]	6450	—	—	32
3-A	Analogue of XVIII (R=Et, X=I), of 4-Me-thiazole series	dark blue	206	5875	6300	7100	29
3-A	Analogue of XVIII (R=Et, X=ClO_4), of thiazoline series	brick-red	230	5060	—	5700	29
3-B	XX (Y=Q=S, R=Et, X=I[b])	dark blue	213	—	—	—	38
3-B	XX (Y=Q=CMe_2, R=Me, X=I)	brown; red reflex	238	—	—	—	38

[a] Decomp. not recorded. [b] 5-Me substituent in each nucleus.

give trinuclear dyes, such as XXI ($n=1$), with the chain $:C<^{CH:CH\cdot}_{CH:}$. Such compounds were alternatively prepared by the condensation of α-anilomethyltrimethincyanines (cf. section 3-A) with ketomethylene compounds. Altogether nine such dyes were synthesised and their absorption maxima were compared with those of the related simpler dyes.

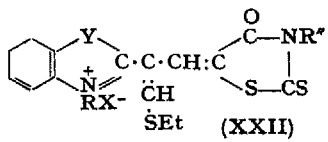


(XXI)

In every instance there was a bathochromic shift (120–480 Å) on passing from trimethincyanine to trinuclear dye and, in eight instances, a bathochromic shift (360–780 Å) on passing from dimethinmerocyanine to trinuclear dye, with one hypsochromic shift (30 Å), but on passing from tetramethinmerocyanine to trinuclear dye the shift was hypsochromic (−150 to −495 Å) in five instances, and bathochromic (115 Å and 230 Å) in two.[42]

Not only were intermediate salts, such as XIX ($n=1$), condensed with quaternary salts having a reactive methyl group (section 3-A), but they could also be condensed with 3-alkylrhodanines to give trinuclear dyes, such as XXI ($n=1$, Y=Z=CH:CH, S, or Se), or with 3-methyl-1-phenyl-5-pyrazolone, or, in one example out of the nineteen, with 3-ethyl-4-oxo-2-thio-oxazolidine.[38]

Not only was ethyl trithio-orthoformate in the presence of acid used to introduce an α-ethylthiomethylene group into the chain of tri- and penta-methincyanines, giving di-ionic salts (see sections 3-A and B), but it was also used to introduce such a group into the chain of dimethinmerocyanines giving, for instance, mono-ionic salts, such as XXII (Y=CH:CH, S, O, or CMe_2).[43] Condensation of such a salt with



(XXII)

another having a reactive methyl group could give dyes such as XXI ($n=1$). The original dimethinmerocyanines belonged to various series,

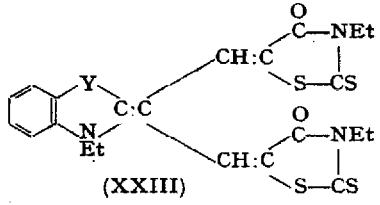
giving dyes, XXI (n=1, Y=CH:CH, O, or CMe_2). Other quaternary salts were used at the second stage, giving XXI (n=1, Z=S or CH:CH).[44]

D. Mono-Ionic Trinuclear Dye Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain :C<CH:CH·CH:CH· / CH: with Di-, Penta-, and Hexa-methin Segments

By condensation of the diquaternary salt, XIX (n=2, Y=CMe_2, R=Me), with 3-methylrhodanine, by heating them in acetic anhydride, there was obtained XXI (n=2, Y=Z=CMe_2, R=R′=R″=Me, X=I).[38]

E. Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues, and the Chain :C<CH: / CH: with One Tri- and Two Di-methin Segments

N-Alkyldihydro-derivatives of heterocyclic bases having a dianiloisopropylidene group[29] were condensed with two molecular proportions of certain ketomethylene compounds to give non-ionic dyes with the chain :C(·CH:)$_2$. The absorption maxima of eleven such, e.g., of XXIII (Y=S or Se), and of analogues of the 4-linked quinoline,

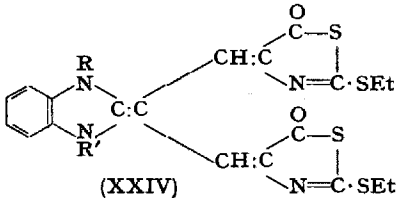


(XXIII)

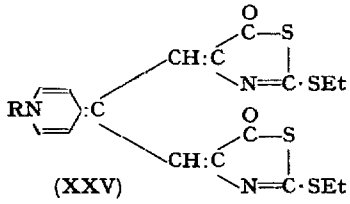
4-methylthiazole, and thiazoline series, were compared with those of the related dimethinmerocyanines and, in five instances, of the related trimethinoxonol. By condensation of an α-anilomethyldimethinmerocyanine (see section 3-C) with a ketomethylene compound, it was possible to arrive at trinuclear dyes in which the two ketomethylene nuclei were dissimilar. The absorption maxima of three of these were compared with those of the appropriate pair of dimethinmerocyanines.[42]

On the other hand, condensation of the crude salt, XXII (Y=CH:CH, R=R″=Et, X=*p*-SO_3·C_6H_4Me), with 3-ethylrhodanine gave XXIII (Y=CH:CH).[44]

An abnormal condensation, between quaternary salts of 2-methylperimidine and cyclic compounds having an ethoxymethylene group on the carbon adjacent to CO, gave not only orange dimethinmerocyanines (see XIV-1), but also magenta trinuclear dyes. Such pairs of dyes were prepared by use of 3-alkyl-5-ethoxymethylenerhodanines and also of 4-ethoxymethylene-2-ethylthio-5-oxothiazoline. The trinuclear dyes might be formulated as having the chain $:C(\cdot CH:)_2$. Attempts to condense an ethoxymethylene compound with other quaternary salts was successful with one of 2-methylbenzimidazole, giving a dye of type XXIV, and with one of γ-picoline, giving one of type XXV, but not

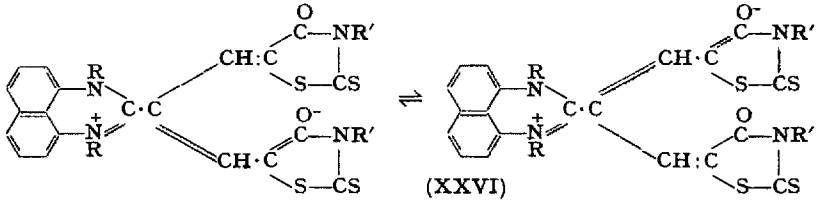


(XXIV)



(XXV)

with salts of more basic nuclei. The dyes showed powerful absorption and were sensitisers. They were regarded as *meso*-ionic oxonols, e.g., XXVI, with the chain $\cdot C\lessgtr^{CH:}_{CH:}$. Models indicated that the third nucleus was forced out of the plane of resonance.[45] Further trinuclear



(XXVI)

dyes of this type, possessing two 5-oxo-2-phenyloxazoline, two 5-oxo-3-phenylisoxazoline, or two 1,3-diethyl-2-thiobarbituric acid residues, were also made. It seemed that steric factors sometimes prevented the formation of the trinuclear compound. A dye of type XXIV was also prepared by the dianil method. Absorption data were given for ten trinuclear dyes and comparison was made with the related dimethinmerocyanines and trimethinoxonols. The absorption of the trinuclear compounds lay at a longer wavelength than that of the related dimethinmerocyanines, except when a quinoline nucleus was present.[46]

4. Trinuclear Dyes with Three Cyanine Structures and a Chain Branching from a Carbon in the β-Position to a Quaternary Salt Residue: Some Tetra- and Penta-Nuclear Derivatives

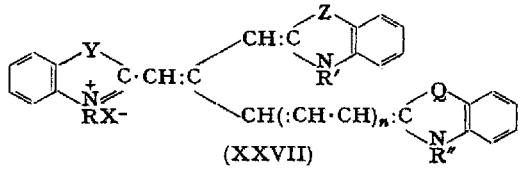
Ref.	Chain	No. of quaternary salt residues	No. of ketomethylene residues	Type
4-A	·CH:C<(CH:)(CH:)	3	0	mono-ionic
4-B	·CH:C<(CH:)(CH:CH·CH:)	3	0	mono-ionic
4-C	·CH:C<(CH:CH·CH:)(CH:CH·CH:)	3	0	mono-ionic
4-D	·CH:C<(CH:)	3	0	mono-ionic
4-E	·CH:C<(CH:CH·CH:)	3	0	mono-ionic
4-F	·N:C<(CH:)(CH:)	3	0	mono-ionic
4-G	·N:C<(CH:)(CH:CH·CH:)	3	0	mono-ionic
4-H	·CH:C<(N:)(N:)	3	0	mono-ionic
4-I	·CH:C<(CH:)	2	1	mono-ionic
4-J	·CH:C<(CH:CH·CH:)	2	1	mono-ionic
4-K	:CH·C(=)·CH:	2	1[a]	non-ionic
4-L	:CH·C(=)(CH·CH:)(CH:)	2	1	non-ionic
4-M	:CH·C(=)·CH:CH·CH:	2	1	non-ionic
4-N	:CH·C<(=)(CH·CH:)	2	1	non-ionic
4-O	:CH·C<(=)(=)	1	2	mono-ionic
4-P	:CH·C<(=)(CH:CH·CH·CH:)	1	2	mono-ionic

[a] Including dyes with a thioketomethylene residue.

A. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain ·CH:C<(CH:)(CH:) with Three Trimethin Segments

Following on the condensation of *meso*-methylthiacarbocyanines with *p*-dimethylaminobenzaldehyde,[47] they were also condensed with

heterocyclic quaternary salts, preferably toluene-*p*-sulphonates, having an alkylthio-, arylthio-, or iodo-substituent, to give trinuclear dyes of the type XXVII (n=0, Y=Z=S, Q=S or CH:CH). The reaction



(XXVII)

was also applied to a *meso*-methyl-oxa- and -selena-carbocyanine, giving XXVII (n=0, Y=Z=O or Se, Q=S), and to three *meso*-methyloxathiacarbocyanines, giving compounds of the type XXVII (n=0, Y=O, Z=S, Q=S or CH:CH).[48] When cyanines having a phenanthroline nucleus were described (see X-5-B), the condensation of the quaternary salt of a methylthiophenanthroline with an oxathia- and with a thiacarbocyanine, each having a *meso*-methyl group, was patented.[49]

An alternative method of arriving at dyes with the chain $\cdot CH:C(\cdot CH:)_2$ and with three similar quaternary salt residues, consisted in the condensation of a quaternary salt, having a reactive methyl group, with dialkyl trithiocarbonate, $S:C(SR)_2$. The examples were of the general formula, XXVII (n=0, Y=Z=Q=CH:CH, S, O, or Se, X=I), and included several with substituted benzothiazole nuclei. The usual procedure was fusion of the base with alkyl toluene-*p*-sulphonate and dimethyl trithiocarbonate, followed by boiling with pyridine and treatment with potassium iodide.[50] A modification of the procedure consisted in the conversion of *N*-alkyldihydro-heterocyclic bases, having the group $:CH\cdot CS(SR)$,[51,52] into quaternary salts having a (di-*β*-alkylthio)vinyl group, and by reaction of these with other salts having a methyl group, e.g., by heating with triethylamine in ethanol. The thirteen examples comprised one of type XXVII (n=0, Y=Z=Q=S), with three identical benzothiazole nuclei; seven others had three benzothiazole nuclei but, owing to the presence of substituents, two of these nuclei were similar and one dissimilar; two were of the type XXVII (n=0, Y=S, Z=Q=CH:CH), and there was an analogue with two 4-linked, instead of two 2-linked, quinoline nuclei; other types were XXVII (n=0, Y=CH:CH, Z=Q=S; and n=0, Y=S, Z=Q=O).[53] Subsequently a phenanthroline quaternary salt having a (di-*β*-methylthio)vinyl group was condensed with one having a methyl group, to give a dye with three phenanthroline residues; or it was condensed

with a salt of the quinaldinium or 2-methylthiazolium series to give trinuclear dyes with one phenanthroline and two quinoline or two thiazole residues; from a benzothiazolium salt with a 2-(di-β-methylthio)vinyl substituent, there was prepared a trinuclear dye with one benzothiazole and two phenanthroline nuclei.[54]

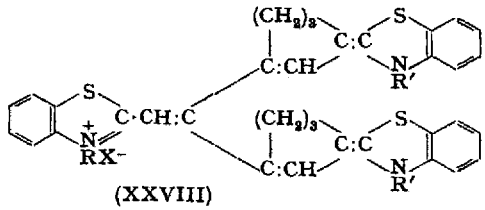
In addition to the syntheses of XXVII (n=0, Y=Z=Q=S) starting from a *meso*-methylthiacarbocyanine, or from a benzothiazolium salt having a 2-(di-β-methylthio)vinyl group, a third method consisted in the reaction of a benzothiazolium salt having a 2-methylthio-group with one having the group ·CH:CMe_2, all these condensations being carried out by heating with triethylamine in pyridine. The absorption maximum, 5550 Å, of the trinuclear dye was so close to that of the unsubstituted thiacarbocyanine, 5600 Å, that it was concluded that the third nucleus lay in a different plane from the other two.[55]

B. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain ·CH:C<CH:
CH:CH·CH: with One Tri- and Two Penta-methin Segments

Not only did *meso*-methylcarbocyanines give rise to dyes with the chain ·CH:C(·CH:)$_2$ (see section 4-A), but a *meso*-methylthiacarbocyanine was also condensed with a salt having a 2-β-acetanilidovinyl group, whence there was obtained XXVII (n=1, Y=Z=Q=S, R=R′=R″=Et, X=I).[48]

C. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain :CH:C<CH:CH·CH:
CH:CH·CH: with One Hepta- and Two Penta-methin Segments but Comprising Two Carbocyclic Rings

Not only could benzothiazolium salts having a 2-(di-β-methylthio)vinyl group be condensed with others having a 2-methyl group (see section 4-A) but they were also condensed with benzothiazolium salts having a 2-cyclohexane substituent: two dyes of type XXVIII,

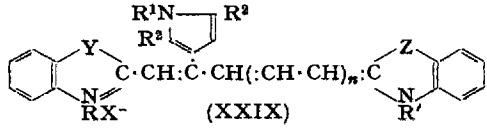


(XXVIII)

in which two portions of the chain $\cdot CH:C(\cdot CH:CH\cdot CH:)_2$ were cyclic, were formulated.[53]

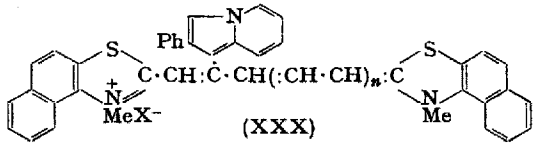
D. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain $\cdot CH:\dot{C}\cdot CH:$ with One Tri- and Two Di-methin Segments

Dimethincyanines having a pyrrole nucleus, with a methyl group in the α-position to it, were condensed with heterocyclic salts having an alkylthio- or iodo-substituent to give trinuclear compounds, which are analogous to those of section 4-A but have one carbon atom of the



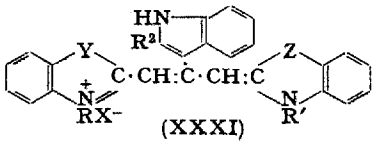
(XXIX)

chain included in the pyrrole nucleus. Regarded as *meso*-pyrrylcarbocyanines, the series represented in the seven examples were of the thia- (XXIX; $n=0$, Y=Z=S), thia-2'- (XXIX; $n=0$, Y=S, Z=CH:CH), and thia-4'-carbocyanine types. There was also a dye, XXX ($n=0$,

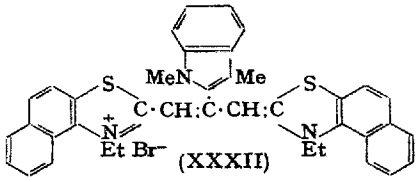


(XXX)

X=*p*-$SO_3C_6H_4Me$), with a pyrrocolyl substituent and three examples with a 3-indolyl substituent, of type XXXI, representing the thia-, oxa-, and selenathia-carbocyanine series; another, XXXII, had a 2-indolyl substituent.[56]



(XXXI)



(XXXII)

E. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain $\cdot CH:\dot{C}\cdot CH:CH\cdot CH:$ with One Di-, One Tetra-, and One Pentamethin Segment

Condensation of a dimethinmerocyanine having a pyrrole nucleus, and a methyl group in the α-position to it, with 2-β-acetanilidovinyl-

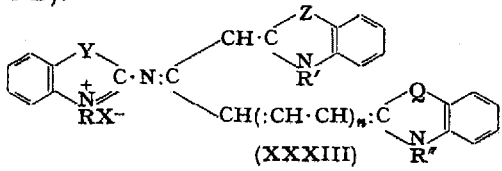
benzothiazole ethiodide gave rise to XXIX (n=1, Y=Z=S, R=R′=R^1=Et, R^2=Me, X=ClO_4).[56] Examples of type XXX (n=1), but with a 3-linked indolyl nucleus, were also described.[57]

F. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain ·N:C<CH:/CH:> with One Trimethin and Two α-Azatrimethin Segments

Condensation of α-azatrimethincyanines having a *meso*-methyl group[58] (see XII-1 and 4) with quaternary salts having an alkylthio-group gave rise to trinuclear dyes, XXXIII (n=0), which were α-aza-analogues of XXVII (n=0) (section 4-A), and which were sensitisers. Most of them were prepared from *meso*-methyl-α-azathiacarbocyanines, to give compounds of type XXXIII (n=0, Y=Z=S), but a *meso*-methyl-α-azaoxathiacarbocyanine was used to synthesise a compound of the type XXXIII (n=0, Y=O, Z=Q=S). The third nucleus usually belonged to the benzothiazole, but sometimes to the benzoxazole or thiazoline series, whilst use of a *meso*-ethylcarbocyanine gave a trinuclear dye with the substituted chain ·N:C<CH:/C(Me):>.[59]

G. Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues and the Chain ·N:C<CH:/CH:CH·CH:> with One α-Azatrimethin, One Pentamethin, and One α-Azapentamethin Segment

An α-azathiacarbocyanine having a *meso*-methyl group was condensed with quaternary salts, having a β-acetanilidovinyl group, by heating in pyridine, to give dyes, XXXIII (n=1, Y=Z=S, Q=S or CMe_2),[59] which were the α-aza-analogues of those of type XXVII (n=1) (section 4-B).



(XXXIII)

H. Mono-Ionic Trinuclear Dye Having Three Quaternary Salt Residues and the Chain ·CH:C<N:/N:> with One αγ-Diazatrimethin and Two α-Azatrimethin Segments

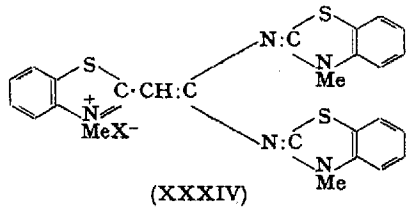
By heating *N*-methylbenzothiazoline, having the 2-substituent :CH·CS(SMe), with 2-aminobenzothiazole and methyl toluene-*p*-

TABLE III. Some Properties of Mono-Ionic Trinuclear Dyes Having Three Quaternary Salt Residues

	Group Particulars	Appearance of crystals	M.p. (°C) (decomp.)	Sensitising (Å) Maximum	Extent	Ref.
4-A	XXVII (n=0, Y=Z=Q=S, R=R′=R″=Et, X=I)	green	204[a]	6200	6600	53
4-A	XXVII (n=0, Y=Z=Q=Se, R=R′=R″=Et, X=I)	brownish	220[a]	—	—	50
4-A	XXVII (n=0, Y=S, Z=Q=O, R=R′=R″=Et, X=ClO_4)	brownish	230[a]	5500	6300	53
4-A	XXVII (n=0, Y=S, Z=Q=O, R=Me, R′=R″=Et, X=I)	orange needles; green reflex	234–235	5450	5800	48
4-A	XXVII (n=0, Y=CH:CH, Z=Q=S, R=R′=R″=Et, X=I)	bronze-green	275–276	5900	6500	48
4-A	XXVII (n=0, Y=S, Z=Q=Se, R=R′=R″=Et, X=Br)	reddish purple needles	213–215	5450, 6000	6500	48
4-B	XXVII (n=0, Y=Z=Q=S, R=R′=R″=Et, X=I)	coppery	209–211	7200	7500	48
4-D	XXIX (n=0, Y=Z=S, R=R′=R^3=Me, R^1=Et, X=I)	—	169–170[a]	—	—	56
4-D	XXX (n=0, X=p-$SO_3C_6H_4Me$)	—	294–295	—	—	56
4-D	XXXI (Y=Z=O, R=R′=R^3=Me, X=ClO_4)	—	199–200	—	—	56
4-E	XXIX (n=1, Y=Z=S, R=R′=R^1=Et, R^3=Me, X=ClO_4)	—	205–206[a]	—	—	56
4-F	XXXIII (n=0, Y=Z=S, Q=CH:CH, R=R′=R″=Et, X=I)	reddish brown	279[a]	5900, 6200	6400	59
4-G	XXXIII (n=1, Y=Z=Q=S, R=R′=Me, R″=Et, X=I)	dark green	178[a]	6800	—	59
4-H	XXXIV (X=p-$SO_3C_6H_4Me$)	bright yellow	172[a]	—	—	53

[a] Decomp. not recorded.

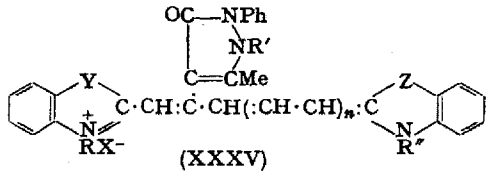
sulphonate, and then heating the resultant salts with pyridine, the compound, XXXIV (X=*p*-$SO_3C_6H_4Me$), was produced.[58]



(XXXIV)

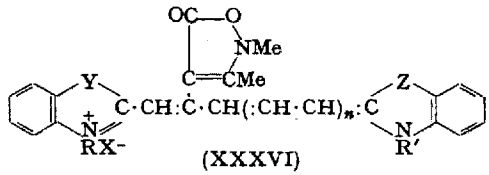
I. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain ·CH:Ċ·CH: with One Tri- and Two Di-methin Segments: A Tetranuclear Derivative

β-Methyldimethinmerocyanines having a pyrazolone residue[60] (XIV-8-A.4) were heated with alkyl toluene-*p*-sulphonate and a base having a 2-methylthio-group, whereby, by interaction of the two salts, there were produced trinuclear dyes of type XXXV (*n*=0). Most of



(XXXV)

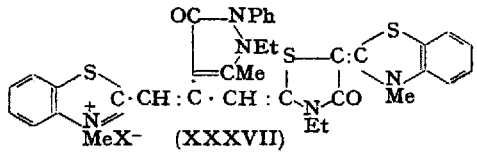
the original dimethinmerocyanines had a benzothiazole residue but there were also examples with a benzoxazole residue, whilst the second quaternary salt belonged to various series. There was one example with an *α*-methyl group on the original dimethin chain and another



(XXXVI)

(prepared from a *β*-ethyldimethinmerocyanine) had a methyl substituent on the new segment of chain. Quaternary salts of *β*-methyldimethinmerocyanines, having a 5-oxoisoxazoline residue could be used similarly, to give trinuclear dyes of type XXXVI (*n*=0).[61] An alternative method of synthesising dyes, such as XXXV (*n*=0, Y=Z=S),

consisted in the condensation of a 2-(di-β-methylthio)vinylbenzothiazolium salt with 3-methyl-1-phenyl-5-pyrazolone to give a β-methylthiodimethinmerocyanine, the quaternary salt of which was then condensed with a 2-methylbenzothiazolium salt. From a comparison of absorption spectra, it was concluded that the pyrazolone nucleus was in a different plane from the two benzothiazole nuclei. The trinuclear dye was a less good sensitiser than the unsubstituted trimethincyanine. An ingenious extension of the method of section 5 led to the tetranuclear XXXVII, which is XXXV (n=0, Y=Z=S),



(XXXVII)

with an additional nucleus inserted; it consisted in the condensation of a β-methyldimethinmerocyanine, having a benzothiazole and a 5-pyrazolone residue, with the quaternary salt of a simple merocyanine, having a benzothiazole and a 3-ethylrhodanine residue.[62] Hexanuclear dyes were also described (see section 7).

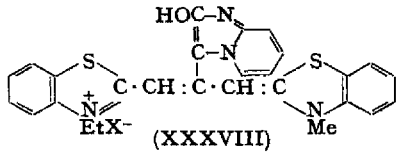
J. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain ·CH:Ċ·CH:CH·CH: with One Di-, One Tetra- and One Penta-methin Segment

Not only could the quaternary salts of β-methyldimethinmerocyanines, having a pyrazolone, or isoxazolone, residue, be condensed with salts having an alkylthio-group (see section 4-I), but they could also be condensed with salts having a β-acetanilidovinyl group, whereby trinuclear dyes of the types XXXV and XXXVI (n=1, Y=S) were prepared. The third nucleus belonged to the benzothiazole, indolenine, or 4-linked quinoline series. A trinuclear dye, XXXVI (n=1, Y=S, Z=CMe_2), was prepared by reaction of the salt of a δ-methyltetramethinmerocyanine with a 2-methylthiobenzothiazolium salt.[61]

K. Non-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene (or Thioketomethylene) Residue, and the Chain :C(·CH:)$_2$ with One Tri- and Two Di-methin Segments: Some Tetranuclear Derivatives

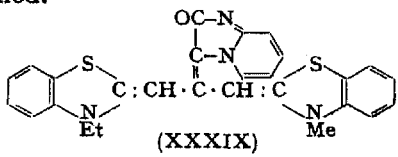
Amongst polymethin dyes containing the 3,7a-diazaindan-2-one nucleus (see XIII-4 and XIV-8-A.2 and 8), was a trinuclear dye having

one such nucleus, which was formulated as XXXVIII. It was prepared either by reaction of a β-methyldimethinmerocyanine, having the above nucleus, with a 2-methylthiobenzothiazolium salt, or by heating the β-methylthiodimethinmerocyanine, having this nucleus, with 2-methylbenzothiazole and an ester. A scale-drawing showed interference



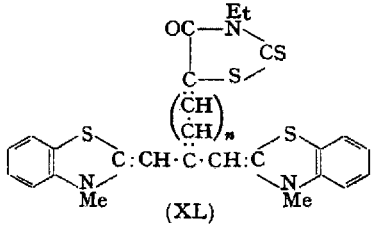
(XXXVIII)

between the sulphur atoms of the benzothiazole nuclei and the third nucleus and it was concluded that the third nucleus must lie in a different plane.[63] Elimination of HX from the di-ionic compound, XXXVIII, could give the mono-ionic XXXIX, whence inclusion in the present section seems justified.



(XXXIX)

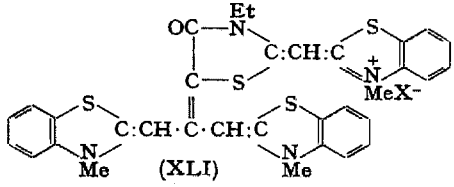
By condensation of a *meso*-(methylthio)thiacarbocyanine with 3-ethylrhodanine in pyridine, there resulted the non-ionic trinuclear dye, XL ($n=0$), and the corresponding derivative of an oxathiacarbocyanine was also made. The absorption maxima of the trinuclear dyes were compared with those of the related dinuclear ones. Since one



(XL)

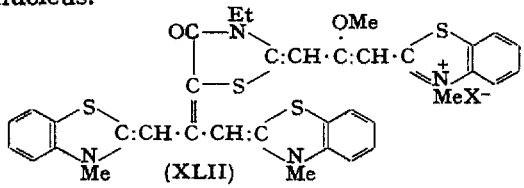
nucleus of the trinuclear compounds contained a thio-group, salt formation and subsequent condensations could take place (cf. section 5), giving rise to tetranuclear derivatives. Thus a quaternary salt of XL ($n=0$) was condensed with a 2-methylbenzothiazolium salt to give

XLI, with a benzothiazolium salt having the group ·CH:CMe(OMe) to give XLII, and with 3-ethylrhodanine to give XLIII. The optical



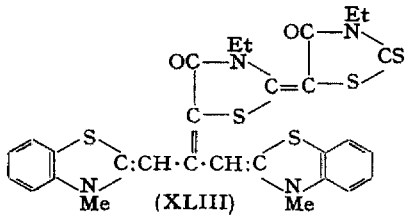
(XLI)

properties of the tetranuclear dyes were compared with those of the related simpler ones. Sensitising power was diminished by introduction of the fourth nucleus.[64]



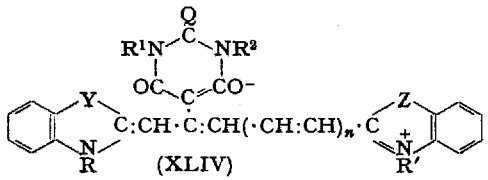
(XLII)

Reaction of various β-methyldimethinmerocyanines with quaternary salts having an alkylthio-group, by heating them with triethylamine in pyridine, gave non-ionised dyes, possessing two methin



(XLIII)

linkages. Instead of formulating them with the chain :CH·C̈·CH:, an alternative :CH·Ċ:CH· was preferred, giving products such as XLIV (n=0). Of the numerous examples, the majority were derived from



(XLIV)

β-methyldimethinmerocyanines of the benzothiazole series, but benzoxazole, benzoselenazole, and indolenine were represented. The quater-

nary salt also usually belonged to the benzothiazole series, but there were examples of the use of salts of the 2- and 4-linked quinoline, benzoxazole, benzoselenazole, benzimidazole, thiazole, and 4-linked pyridine series. The ketomethylene residue was frequently a barbituric or thiobarbituric acid, but nuclei such as 5-isoxazolone, 3-methyl-1-phenyl-5-pyrazolone, indan-1,3-dione, etc. were also used. Moreover thioketomethylene residues were represented by 1-ethyl-2-thio-indoline and 3-ethyl-4-thiorhodanine.[65]

L. Non-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain :CH·C<CH·CH:
CH: with One Tri- and Two Tetra-methin Segments

Condensation of a *meso*-methylthiacarbocyanine with 5-acetanilidomethylene-3-ethylrhodanine, by heating with triethylamine in pyridine, gave the *NN'*-diethyl analogue of XL ($n=1$), and the oxazolidine analogue was made similarly.[48] An alternative route for preparing XL ($n=1$) consisted in the condensation of a *meso*-(methylthio)thiacarbocyanine with 5-ethylidenerhodanine. Its absorption was compared with those of the related simpler dyes. For XL ($n=0$ or 1), it was suggested that one benzothiazole and one rhodanine nucleus were in the same plane, and the second benzothiazole nucleus in a different plane.[64]

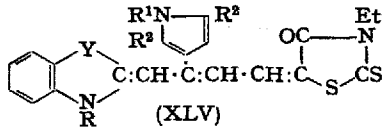
M. Non-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain :CH·Ċ·CH:CH·CH: with One Di-, One Tetra-, and One Penta-methin Segment

β-Methyldimethinmerocyanines were condensed with quaternary salts having a β-acetanilidovinyl group to give non-ionic trinuclear sensitisers, some of which were represented by formula XLIV ($n=1$). In the five examples, the original β-methyldimethinmerocyanines and quaternary salts all belonged to the benzothiazole series, whilst the ketomethylene residue included a barbituric and a thiobarbituric acid, an isoxazolone, and indan-1,3-dione. The condensations were effected by heating with triethylamine in pyridine or in nitrobenzene.[65]

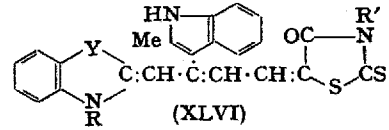
N. Non-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chain :CH·Ċ:CH·CH: with One Di-, One Tri-, and One Tetra-methin Segment

Two dimethinmerocyanines having a pyrrole nucleus, and a methyl group in the α-position to it, were condensed with 5-acetanilido-

methylene-3-ethylrhodanine to give dyes of type XLV (Y=S). Similar dimethinmerocyanines having an indole nucleus gave dyes of type XLVI (Y=S) and there was also a representative of the benzoxazole



(XLV)

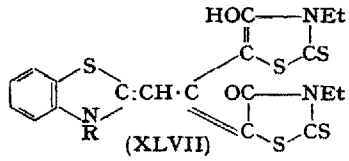


(XLVI)

series; in addition to acetanilidomethylene derivatives of rhodanines, similar derivatives of the thiohydantoin, thiobarbituric acid, and 3-methyl-1-phenyl-5-pyrazolone series were described.[67]

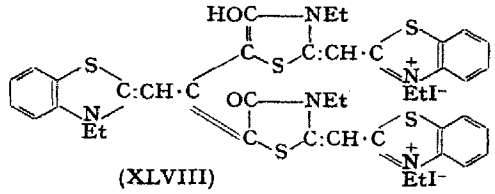
O. Mono-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues, and the Chain :CH·Ċ: with One Methin and Two Dimethin Segments; Some Tetra- and Penta-nuclear Derivatives

By heating a benzothiazolium salt, having a 2-(di-β-methylthio)-vinyl group, with 3-ethylrhodanine and triethylamine in ethanol, followed by pyridine, there resulted XLVII (R=Me or Et), which is mono-ionic because it comprises the structure of a methinoxonol. In formulating a trinuclear dye with two *N*-methyl-2-oxoindoline residues,



(XLVII)

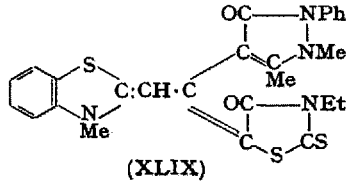
addition of a molecule of acid was assumed, so that the compound was a mono-ionic quaternary salt with the chain ·CH:Ċ· and also had an OH group in each of the carbocyclic nuclei. Since two nuclei of the trinuclear compound, XLVII (R=Et), contained a thio-group, they could undergo salt formation and condensation (cf. section 5): thus by heating the trinuclear dye with ethyl toluene-*p*-sulphonate and 2-



(XLVIII)

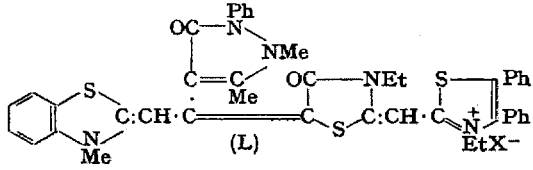
methylbenzothiazole, and then with pyridine, and converting into iodide, the pentanuclear dye, XLVIII, was produced.[53]

The quaternary salt of a β-methylthiodimethinmerocyanine having one benzothiazole and one pyrazolone residue was not only condensed with a quaternary salt having a reactive methyl group (see section 4-I), but also with ketomethylene compounds, such as 3-methyl-1-phenyl-5-pyrazolone, or 3-ethylrhodanine, the latter giving XLIX. As this



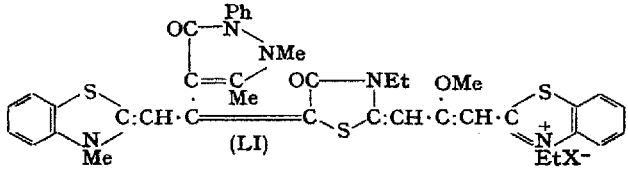
(XLIX)

had a rhodanine nucleus, it could be converted into a quaternary salt having an alkylthio-group (see section 5). This was condensed with a 2-methylthiazolium salt to give the tetranuclear derivative, L, and with



(L)

a benzothiazolium salt having the group ·CH:CMe(OMe) (cf. VI-15) to give the tetranuclear derivative, LI. Absorption and sensitising maxima were recorded.[66]

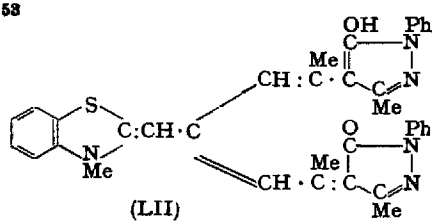


(LI)

P. Mono-Ionic Trinuclear Dye Having One Quaternary Salt Residue, Two Ketomethylene Residues, and the Chain :CH·C<CH:CH·/CH·CH: with One Penta- and Two Tetra-methin Segments

A dye of this kind, LII, comprising the structure of a penta-methinoxonol, in which the chain carried two methyl groups, was

prepared by heating a 2-(di-β-methylthio)vinylbenzothiazolium salt and 4-isopropylidene-3-methyl-1-phenyl-5-pyrazolone with triethylamine in ethanol.[58]



(LII)

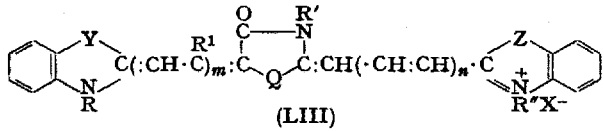
5. Trinuclear Dyes Having a Central Ketomethylene Residue and Two Cyanine Structures, Obtainable by Various Condensations of Quaternary Salts of Merocyanines, and by other Methods

Ref.	Chains	No. of quaternary salt residues	No. of ketomethylene residues	Type
5-A	·CH: direct	2	1	mono-ionic
5-B	·CH: :CH·CH:	2	1[a]	mono-ionic
5-C	·CH: :CH·CH:CH·CH:	2	1	mono-ionic
5-D	·CH: :CH·CH:CH·CH:CH·CH:	2	1	mono-ionic
5-E	·N: direct	2	1	mono-ionic
5-F	·N: :CH·CH:	2	1	mono-ionic
5-G	·CH:CH·CH: direct	2	1	mono-ionic
5-H	·CH:CH·CH: :CH·CH:	2	1	mono-ionic
5-I	·CH:CH·CH: :CH·CH:CH·CH:	2	1	mono-ionic
5-J	·CH:CH·CH:CH·CH: direct	2	1	mono-ionic
5-K	direct direct	1	2	non-ionic
5-L	:CH·CH: direct	1	2[a]	non-ionic
5-M	:CH·CH: :CH·CH:	1	2	non-ionic
5-N	:CH·CH: :CH·CH:CH·CH:	1	2	non-ionic
5-O	·CH: $(:CH\cdot CH)_{0-2}:CH\cdot$	1 1	2 2	di-ionic di-ionic

[a] Including dyes with a thioketomethylene residue.

A. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, One ·CH: Chain, and One Direct Linkage

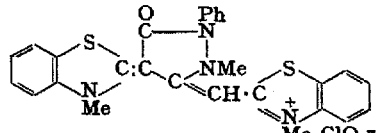
The first patent, in which the quaternary salts of β-methyldimethinmerocyanines were condensed with salts having a reactive methyl group[67] (see section 5-B) was closely followed by another, containing many variants. Thus trinuclear sensitising dyes were obtained by fusion of a simple merocyanine having a rhodanine nucleus, a base containing a reactive methyl group, and alkyl toluene-*p*-sulphonate, followed by heating with pyridine, whereby the two salts condensed to give trinuclear dyes with one methin and one direct linkage. The original merocyanines belonged to various series, leading, for instance, to dyes of the types LIII ($m=n=0$, Q=S, Y=CH:CH, S, or O), when the salts of the merocyanines were condensed with methyl salts of various series.[68]



(LIII)

A simpler method of arriving at trinuclear dyes, of type LIII ($m=n=0$, Q=S), consisted in the condensation of a quaternary salt having an alkylthio-group with a methincyanine in which one quaternary salt residue belonged to the 4-oxothiazoline series.[69] In the five examples, the other quaternary salt residue was of the benzothiazole or benzoselenazole series, and those dyes were condensed with a quaternary salt of the 2-linked quinoline, benzothiazole, or benzoselenazole series.[70] Subsequently the absorption maxima of LIII ($m=n=0$, Y=Z=Q=S, R=R′=R″=Et), and of a similar trinuclear dye having a 4,5-diphenylthiazole instead of a benzothiazole nucleus, were compared with those of analogues having longer chains (see sections 5-B, G, H, and J). Besides the principal band in the visible region, each had a fairly intense band at a shorter wavelength.[71]

A different kind of trinuclear dye, LIV, was prepared from the quaternary salt of a simple merocyanine having a benzothiazole and a



(LIV)

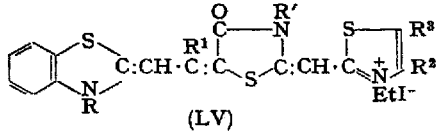
3-methyl-1-phenyl-5-pyrazolone residue; by virtue of its reactive methyl group, this underwent condensation with a 2-alkylthiobenzothiazolium salt.[62]

B. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene (or Thioketomethylene) Residue, and the Chains ·CH: and :CH·CH:

The earliest patent referred to compounds derived from certain β-methyldimethinmerocyanines (see XIV-8-A.1), which were fused with a base, having a reactive methyl group, and excess of alkyl toluene-*p*-sulphonate, followed by heating with pyridine, to give trinuclear dyes of type LIII (m=1, n=0, R=Me). Numerous types of quaternary salt could enter into the composition of the original β-methyldimethinmerocyanine, giving LIII (m=1, n=0, Y=CH:CH, S, O, or CMe_2, R^1=Me), also a lepidinium salt was used; the central nucleus was usually an *N*-methylrhodanine residue, leading to LIII (m=1, n=0, Q=S, R′=R^1=Me), but there were also LIII (m=1, n=0, Q=S or O, R′=Et, R^1=Me); numerous types of quaternary salt were used for the third nucleus.[67] A subsequent patent contained many variants of such dyes, including compounds with an unsubstituted dimethin chain.[68]

Various dimethinmerocyanines, in which a thiohydantoin nucleus was present, were likewise converted into quaternary salts, having a reactive alkylthio-group, which underwent condensation with salts having a reactive methyl group, to give sensitising dyes of type LIII (m=1, n=0, Q=NR^2, R^1=H). The original dimethinmerocyanines belonged to various series, as did the quaternary salts.[72]

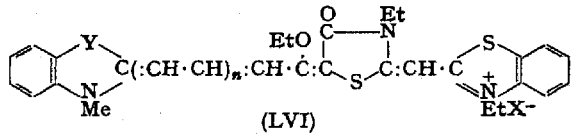
The trinuclear dye, LV (R=R′=Et, R^1=H, R^2=R^3=Ph, X=Br), was prepared by heating together 3-ethyl-2-formylmethylenebenzothiazoline, 3-ethylrhodanine, and methyl sulphate, and condensing the



(LV)

product with 2-methyl-4,5-diphenylthiazole ethobromide in the presence of alkali.[73] In a patent on sensitising or supersensitising by cyanines, in which a benzoxazole nucleus had a substituted 5-phenyl group, there

was included a trinuclear dye with one methin and one dimethin chain; it was prepared from the salt of a dimethinmerocyanine.[74] In another patent in which a benzothiazole nucleus carried a substituted phenyl in the 5- or 6-position, a trinuclear dye, which was the 5-*p*-tolyl derivative of LV (R=Me, R′=C_3H_5, R=R¹=R²=R³=Ph), was included.[75] In the formulation of these dyes, a different extreme resonance configuration was written, in which the nitrogen atom of the central nucleus was quaternary.[73–75] In a patent on sensitising by certain merocyanines having ·$(CH_2)_{2-3}$·OPh attached to the nitrogen of the quaternary salt residue (see XIV-10-B), a dimethinmerocyanine of this kind was converted into a quaternary salt by means of methyl sulphate, and this was condensed with a 2-methyl salt by heating with pyridine, giving two trinuclear dyes, LIII (*m*=1, *n*=0, Y=Z=Q=S, R=$(CH_2)_2$OPh, R¹=H, R′=C_3H_5, R″=Et, X=I; and *m*=1, *n*=0, Y=Q=S, Z=O, R=$(CH_2)_2$OPh, R¹=H, R′=C_3H_5, R″=$(CH_2)_3$OPh, X=I).[76] In a patent on sensitising and supersensitising by β-alkoxydimethinmerocyanines (see XIV-8-A.6), there were included trinuclear dyes, such as LVI (*n*=0, Y=O), which was prepared by converting the dimethinmerocyanine into a salt by means of methyl sulphate and condensing it with 2-methylbenzothiazole ethiodide.[77]

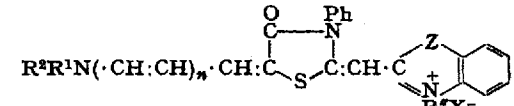


(LVI)

Instead of converting a dimethinmerocyanine, having a rhodanine residue, into a quaternary salt, and condensing that with another salt, an alternative method of arriving at a trinuclear dye, such as LIII (*m*=1, *n*=0, Y=Z=Q=S, R=R″=Et, R¹=H, R′=C_3H_5, X=I), in which the two quaternary salt residues were identical, consisted in heating together 2-methylbenzothiazole ethiodide, 3-allylrhodanine, ethyl orthoformate, and acetanilide.[78]

Another simplified method for preparing trinuclear dyes of the type LIII (*m*=1, *n*=0, Q=S, R¹=H) consisted in the condensation of a methincyanine, in which one quaternary salt residue belonged to the 4-oxothiazoline series, with a quaternary salt having a β-acetanilidovinyl or a β-alkylthiovinyl group (cf. section 5-A). In the original methincyanines, the second quaternary salt residue usually belonged to the

benzothiazole series, but benzoselenazole, indolenine, and thiazole were also represented. The quaternary salts with which these methincyanines were condensed were again mostly of the benzothiazole series, but other salts used were of the 2- and 4-linked quinoline, benzoxazole, and thiazole series. The substituent on the nitrogen of the central nucleus was usually phenyl, but other substituents were *o*-tolyl, *α*- or *β*-naphthyl, ethyl, or allyl. When the methincyanine was condensed with a quaternary salt having a *β*-alkyl-*β*-alkylthiovinyl group, the trinuclear product had a *β*-alkyl-substituent on the dimethin chain.[69] Methincyanines having a 4-oxothiazoline residue were converted, by heating with diphenylformamidine in acetic anhydride or in ethyleneglycol, into intermediate dinuclear dyes such as LVII (*n*=0, Z=CH:CH, S, Se, or



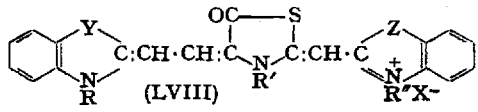
(LVII)

CMe_2, R^1=Ac, R^2=Ph); there was also an example of an anilinomethylene compound (cf. sections 5-C and D).[79] From compounds of this type, by condensation with quaternary salts having a reactive methyl group, there were prepared LIII (*m*=1, *n*=0, Y=CH:CH or S, Z=Q=S, R=R″=Et, R′=Ph, R^1=H, X=I). There were also prepared three dyes with a *β*-ethyl group on the dimethin chain, one of them being LIII (*m*=1, *n*=0, Y=CH:CH, Z=Q=S, R=R″=R^1=Et, R′=Ph, X=I). They were synthesised[80] from methincyanines in which the 5-methylene group of a 4-oxothiazoline residue had been converted into :CEt(SMe).[81]

In 1952 there were described various analogues of LIII (*m*=1, *n*=0, Q=S) in which one or both of the quaternary salt residues belonged to the 4-aryl-5-phenylthiazole series, whilst further series were 4-aryl-5-tolylthiothiazole, 4-aryl-5-aryloxythiazole, and 4,5-diaryloxazole (cf. section 5-L). For comparison, other dyes with a dimethin and a methin chain were synthesised, the total number of compounds compared being twenty-seven.[82]

Trinuclear dyes having a 5-thiazolidone nucleus, instead of the rhodanine or 4-thiazolidone nucleus, were patented.[83] From quaternary salts of dimethinmerocyanines having this 3-alkyl-5-oxo-2-thiothiazolidine residue there were prepared forty-seven trinuclear dyes, mostly of

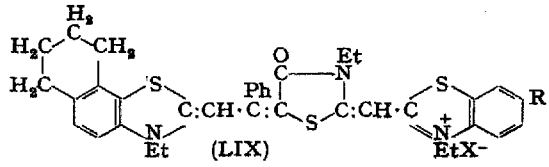
type LVIII, but monocyclic nuclei and the 4-linked quinoline series were also represented. Together with other physical properties, absorption maxima in acetone were recorded. Introduction of the third nucleus always caused a profound bathochromic shift in absorption, which varied according to the nature of the nucleus. The shift, however, did not agree with that expected from the effect of such nuclei in similar dyes. In all instances, the compounds with a 5-oxo-group absorbed at a longer wavelength than the isomers with a 4-oxo-group. The former usually showed double maxima, or an inflection to the



(LVIII)

absorption curve. The resonance systems involved were discussed.[83] Sometimes the yields of trinuclear dyes formed by condensation of dimethinmerocyanine quaternary salts, having a benzothiazole and a 5-oxo-2-thiothiazolidine residue, were low: this was explained as due to the formation of open-chain dyes.[84] A patent of 1956 covered trinuclear dyes having a 4-aryl-5-aryloxy- or 4-aryl-5-arylthio-thiazole nucleus, linked by a dimethin chain to the central nucleus, which was attached by a methin chain to another quaternary salt residue, the central residue being that of a 4- or a 5-thiazolidone. There were also dyes in which a central nucleus of the latter type was linked by a methin chain to the substituted thiazole and by a dimethin chain to the other quaternary salt residue.[85]

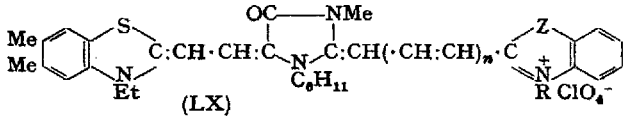
A β-phenyldimethinmerocyanine, having a 3-ethylrhodanine residue, was converted into a quaternary salt, which was condensed with each of three 2-methylbenzothiazolium salts, having an unsaturated



(LIX)

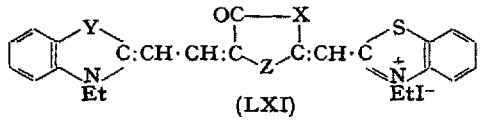
group in the 6-position, to give the dyes, LIX. The bathochromic shifts caused by introduction of the groups styryl, *p*-methoxystyryl, or β-2-thienylvinyl were 150 Å, 190 Å, and 210 Å, respectively.[86]

A dimethinmerocyanine having a 1-cyclohexyl-2-methyl-4-oxo-2-thio-imidazolidine residue (see XIV-1 and 3-C) was converted by methyl sulphate into its quaternary salt, which was condensed with a similar quinaldinium salt by heating them in pyridine, and the trinuclear product was converted into LX (n=0, Z=CH:CH, R=Me).[87]



(LX)

In a study of compounds containing sulphur chromophores, trinuclear dyes of the type LXI (X=Z=S), derived from 1,3-dithiacyclopentan-4-one, were synthesised. Absorption spectra were studied for three series of compounds, in which the quaternary salt residues were



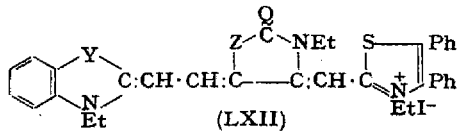
(LXI)

kept constant but the ketomethylene residue was varied. These were LXI (Y=S, X=Z=NMe; Y=Z=S, X=NMe; Y=X=S, Z=NMe; and Y=X=Z=S), the corresponding four of the benzoxazole series, LXI (Y=O), and another four, also of the benzoxazole series, LXI (Y=O), but in which the second quaternary salt residue belonged to the thiazoline instead of to the benzothiazole series. It was concluded that, in the compounds LXI (X=Z=S), the bridge $\cdot\overset{\overset{\cdot\cdot}{O}}{\overset{|}{C}}\cdot S\cdot$ acted as an efficient transmitter of electrons between the auxochromes. An increase in solvent polarity led always to a hypsochromic shift of absorption.[88]

Absorption maxima of LIII (m=1, n=0, Y=Z=O=S, R=R′=R″=Et, R¹=H), and of a similar trinuclear dye having a 4,5-diphenylthiazole in place of a benzothiazole nucleus, were compared with those of analogues having chains of different lengths (cf. sections 5-A, G, H, and J).[71]

Dimethinmerocyanines in which the CO group of the ketomethylene residue had been converted to CS[89] could be converted into quaternary salts; such a salt could be condensed, by heating with triethylamine in pyridine, with another quaternary salt, having a reactive

methyl group, to give trinuclear dyes, such as LXII (Y=Z=S, Q=O or NEt); an analogue of the former, where the original dimethinmerocyanine was of the benzoxazole series and the quaternary salt used at the last stage was 2-methylbenzothiazole ethiodide, was also described; so also was LXII (Y=Se, Z=Q=O).[90]



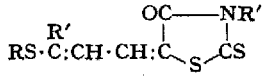
(LXII)

C. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chains ·CH: and :CH·CH:CH·CH:

A tetramethinmerocyanine, having a dimethylthiohydantoin residue, was converted into a quaternary salt by use of methyl sulphate and this was condensed with 2-methylbenzothiazole ethoethylsulphate, by heating in pyridine; the product was converted into iodide, LIII (m=2, n=0, Y=Z=S, Q=NMe, R=R″=Et, R′=Me, R^1=H, X=I).[72]

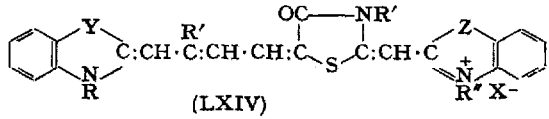
In describing the preparation of tetramethinmerocyanines having a δ-methyl group (see XIV-8-D.1), one of them, having a 3-methylrhodanine residue, was heated with 2-methylbenzothiazole and methyl toluene-p-sulphonate, and the resultant salts then heated with pyridine, and treated with iodide, to give the δ-methyl derivative of LIII (m=2, n=0, Y=CMe_2, Q=Z=S, R=R′=R″=Me, R^1=H, X=I).[91]

Trinuclear dyes having one methin and one β-substituted tetramethin chain were prepared by means of rhodanine derivatives such as LXIII, containing a reactive thio- as well as a reactive alkylthio-group.



(LXIII)

Similar compounds were made having an alkoxy- instead of an alkylthio-group, or having an oxazolidine instead of a thiazolidine nucleus.[92] Trinuclear dyes such as LXIV (Y=Z), in which the two quaternary salt



(LXIV)

residues were the same, were prepared by condensing a quaternary salt, having a reactive methyl group, with a derivative of this kind. Alternatively, a dinuclear dye could first be made from one quaternary salt, and the product condensed with another molecule of salt, which might be different. The substituent on the chain was a methyl or ethyl group.[93]

In a patent on sensitising and supersensitising by δ-alkoxytetramethinmerocyanines (see XIV-8-D.3), there were included trinuclear dyes, such as an analogue of LVI (n=1, Y=S), which was prepared from a δ-ethoxytetramethinmerocyanine by salt formation with methyl toluene-*p*-sulphonate, but here the other quaternary salt was 2-methyl-4,5-diphenylthiazole ethiodide.[77]

A simplified preparation of LIII (m=2, n=0, Y=Z=Q=S, R=R″=Et, R′=Ph, R^1=H, X=I) consisted in the condensation of a methincyanine having a 4-oxothiazoline residue[69] with 4-acetanilidobuta-1,3-dienylbenzothiazole ethiodide.[70] A methincyanine having a 4-oxothiazoline residue was converted into compounds, LVII (n=1, Z=S, R″=Et, R^1=H, R^2=Ph, or R^1R^2=C_5H_{10}, X=I), by reaction with β-anilinoacraldehyde anil hydrochloride and methanol, in the presence of triethylamine or of piperidine, respectively,[79] but the latter preparation was incorrectly reported elsewhere[80,94,95] (cf. section 5-D). This latter compound was condensed with 2-methylbenzothiazole ethiodide to give LIII (m=2, n=0, Y=Z=Q=S, R=R″=Et, R′=Ph, R^1=H, X=I).[80]

A tetramethinmerocyanine of the benzoxazole series, having a 5-thiazolidone as the second residue, was converted into a quaternary salt, which was condensed with 2-methylthiazoline methiodide to give a trinuclear dye.[83]

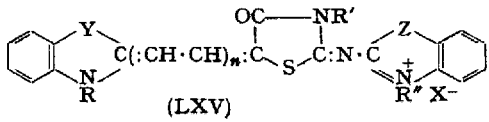
D. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chains ·CH:and :CH·CH:CH·CH:CH·CH:

A simplified method of preparing trinuclear dyes by condensation of a methincyanine, in which one quaternary salt residue belonged to the 4-oxothiazoline series,[69] with a quaternary salt having a 2-(6-anilino-1,3,5-hexatrienyl) group (cf. sections 5-A, B, and C), was applied to the preparation of LIII (m=3, n=0, Y=Q=S, Z=S or Se, R=R″=Et, R′=Ph, R^1=H, X=I).[70] A methincyanine having a 4-oxothiazoline residue was converted into the compound, LVII (n=2, Z=S, R=Et, R^1R^2=C_5H_{10}, X=I), by means of glutaconic aldehyde dianilide hydro-

chloride and piperidine in methanol[79] but the preparation was wrongly reported elsewhere[80,94,95] (cf. section 5-C). The product was condensed with 2-methylbenzothiazole ethiodide to give LIII (m=3, n=0, Y=Z=Q=S, R=R″=Et, R′=Ph, R^1=H, X=I).[80]

E. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, One ·N: and One Direct Linkage

Fusion of a merocyanine having a 3-ethylrhodanine residue with 2-aminobenzothiazole and ethyl toluene-p-sulphonate, and condensation of the resultant salts by heating with pyridine, led to LXV (n=0, Y=Z=S, R=Me, R′=R″=Et, X=p-$SO_3 \cdot C_6H_4Me$).[68]



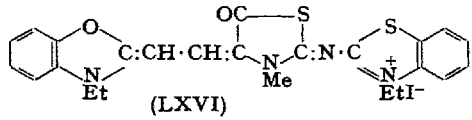
(LXV)

Azamethincyanines having a 4-oxothiazoline residue[96] were condensed with quaternary salts having an alkylthio-group to give trinuclear dyes of the type LXV (n=0), having one azamethin chain and one direct linkage. Out of the five examples, all the original azamethincyanines belonged to the benzothiazole series, giving dyes of the type LXV (n=0, Z=S), and the quaternary salt belonged either to that or to the benzoselenazole series. In four instances, the central residue was 3-phenyl-, and in one 3-allyl-rhodanine. Condensation was effected by heating with triethylamine, usually in methanol, but alternatively in isopropanol.[97]

F. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chains ·N: and :CH·CH:

The quaternary salt of a β-methyldimethinmerocyanine, having a 3-ethylrhodanine residue, was fused with 2-aminobenzothiazole and ethyl toluene-p-sulphonate, the salts were heated with pyridine, and the product was treated with iodide to give the β-methyl derivative of LXV (n=1, Y=Z=S, R=R′=R″=Et, X=I).[67] In a subsequent example, one benzothiazolium salt residue was linked by azamethin and the other by an unsubstituted dimethin chain to the 3-ethylrhodanine residue.[68] In 1952 there was prepared LXV (n=1, Y=O, Z=S, R=R′=R″=Et, X=I) and also, from the salt of a dimethin-

merocyanine having a 3-methyl-5-oxothiazolidine residue, the trinuclear compound, LXVI.[81] In preparing an analogue of the latter, 2-imino-3-methylbenzothiazoline was used instead of a 2-aminobenzothiazolium salt.[83]

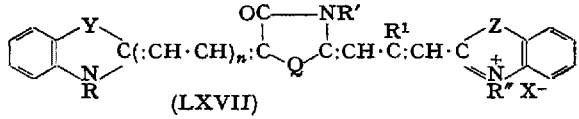


(LXVI)

Azamethincyanines having a 4-oxothiazoline residue were condensed with quaternary salts having a β-acetanilidovinyl group, by heating with triethylamine in methanol, to give trinuclear dyes of type LXV ($n=1$), having one azamethin and one dimethin chain. Of the five examples, the original azamethincyanines belonged to the benzothiazole or thiazole series, and the quaternary salts to the benzothiazole, benzoxazole, or oxazole series. Moreover by condensing a suitable azamethincyanine with 2-(β-ethyl-β-methylthio)vinylbenzothiazole ethiodide, there was prepared the aza-analogue of LV (R=R¹=Et, R′=R²=Ph, R³=Me), in which the dimethin chain carried a β-ethyl substituent.[97]

G. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, One Chain ·CH:CH·CH:, and One Direct Linkage

By converting merocyanines having a substituted rhodanine nucleus into quaternary salts, and condensing these with a quaternary salt having the group ·CH:CMe(OMe), there were obtained trinuclear dyes of type LXVII ($n=0$, Q=S, R¹=OMe), with a β-methoxytrimethin chain and a direct linkage. In the examples and samples, the



(LXVII)

original merocyanines belonged to the 2- and 4-linked quinoline and benzothiazole series and the salts to the benzothiazole series; there was also a trinuclear dye where the central nucleus was a 3-ethyl-4-oxo-oxazolidine residue (cf. section 5-H).[98]

Instead of deriving LXVII ($n=0$, Y=Q=Z=S, R=R″=Me, R′=Et, R¹=OMe), which has been named a rhodacyanine, from a

quaternary salt of the merocyanine and a benzothiazolium salt having the group ·CH:CMe(OMe), it could be prepared from a merocyanine, having the group :CH·COMe in the ketomethylene residue, by heating it with 2-methylthiobenzothiazole and an ester. An analogue of this trinuclear compound, having a *meso*-methyl group on the trimethin chain, was prepared by condensation of the merocyanine quaternary salt, having 2-SR in the rhodanine residue, with a benzothiazolium salt having the group ·CH:CMe_2. The absorption maxima for the dyes formulated, where R^1=H, Me, and OMe, respectively, were 6350 Å, 6130 Å, and 5620 Å, which lie in the same order as for the related thiacarbocyanines.[99]

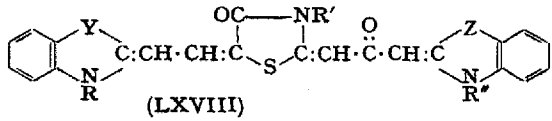
The quaternary salt of a merocyanine, having a benzothiazole and a 2-methyl-4-oxothiazoline residue, was condensed with 2-β-acetanilidovinyl-benzothiazolium, -benzoxazolium, and -pyridinium salts, the first two giving LIII (m=0, n=1, Y=Q=S, Z=S or O, R=R′=R″=Et); it was also condensed with 1,3,3-trimethyl-2-formylmethyleneindoline to give LIII (m=0, n=1, Y=Q=S, Z=CMe_2, R=R′=Et, R″=Me); both it and the quaternary salt of a merocyanine having a 4-linked quinoline and a 2-methyl-4-oxothiazoline residue were condensed with a 2-β-methylthiovinyl-4,5-diphenylthiazolium salt (cf. sections 5-A, B, H, and J). Absorption data were compared. Derivatives of LIII (m=0, n=1, Y=Q=Z=S, R=R′=R″=Et), having a *meso*-methyl or *meso*-ethyl substituent on the trimethin chain, were made by condensing a quaternary salt of the merocyanine with benzothiazolium salts having the group ·CH:CR(SMe).[71]

H. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chains ·CH:CH·CH: and :CH·CH:

Not only were the quaternary salts of merocyanines, having a rhodanine nucleus, condensed with salts having the group ·CH:CMe(OMe) (section 5-G), but one salt of a dimethinmerocyanine was similarly condensed, to give LXVII (n=1, Y=Z=Q=S, R=R′=R″=Et, R^1=OMe, X=SO_3Me). A somewhat analogous dye was prepared from a β-phenyldimethinmerocyanine, the substituent on the trimethin chain being *meso*-ethoxy and the quaternary salt belonging to the benzoselenazole series.[98] From a β-ethoxydimethinmerocyanine there was similarly synthesised a trinuclear dye with β-ethoxy on the dimethin and *meso*-methoxy on the trimethin chain.[77]

Just as trimethincyanines having a *meso*-methoxy- or -ethoxy-

group could, by heating with alkali, be converted into non-ionic sensitising dyes having the chain $OC(\cdot CH:)_2$, so similarly could trinuclear dyes having a *meso*-alkoxytrimethin chain, to give compounds of the type LXVIII. The quaternary salt residue attached to the dimethin



(LXVIII)

chain belonged to the 2-linked quinoline, quinazoline, benzothiazole, benzoxazole, benzoselenazole, or indolenine series; that attached to the trimethin chain was indolenine in one example but belonged to the benzothiazole series in the other fourteen.[100]

A dimethinmerocyanine, having a 1-cyclohexyl-2-methyl-4-oxoimidazoline residue (cf. section 5-B) was converted into its methiodide, which was condensed, by means of triethylamine in pyridine, with 2-β-acetanilidovinyl-5,6-dimethylbenzothiazole ethoethylsulphate, which with perchlorate gave the 5,6-dimethyl derivative of the trinuclear dye, LX (n=1, Z=S, R=Et).[87]

The quaternary salt of a dimethinmerocyanine, having a benzothiazole and a 2-methyl-4-oxothiazoline residue, was condensed with a benzothiazolium salt, having a 2-β-acetanilidovinyl substituent, to give LIII (m=n=1, Y=Q=Z=S, R=R′=R″=Et, R^1=H), and also with a 2-β-methylthiovinyl-4,5-diphenylthiazolium salt (cf. sections 5-A, B, G and J). Absorption maxima were recorded, also for a derivative of the former having a *meso*-methyl group on the trimethin chain, and for LIII (m=n=1, Y=Q=S, Z=CMe_2, R=R′=R″=Et, R^1=H).[71]

I. Mono-Ionic Trinuclear Dyes Having Two Quaternary Salt Residues, One Ketomethylene Residue, and the Chains ·CH:CH·CH: and :CH·CH:CH·CH:

A tetramethinmerocyanine having a 3-ethylrhodanine residue was converted into a quaternary salt, which was condensed with a salt having the group ·CH:CMe(OMe) to give LXVII (n=2, Y=O, Z=Q=S, R=R′=R″=Et, R^1=OMe, X=Br)[98] (cf. sections 5-G and H).

J. Mono-Ionic Trinuclear Dye Having Two Quaternary Salt Residues, One Ketomethylene Residue, One Pentamethin Chain, and One Direct Linkage

The quaternary salt of a merocyanine having a benzothiazole and a 2-methyl-4-oxothiazoline residue, was condensed with a benzothiazo-

TABLE IV. Some Properties of Mono-Ionic Trinuclear Dyes with a Central Ketomethylene and Two External Quaternary Salt Residues

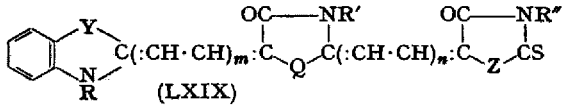
Group	Particulars	Appearance of crystals	M.p. (°C) (decomp.)	Absorption maximum (Å)	Sensitising (Å) Maximum	Extent	Ref.
	1. Effects of Chain-Lengths in LIII (Y=Z=Q=S, R=R′=R″=Et, R^1=H, X=I)						
5-A	$m=n=0$[a]	orange needles	239–241	5020[b]	—	—	71
5-B	$m=1$, $n=0$	green	260	6000[b] 5860[c]	6500[d]	7100[d]	71, 80, 82
5-C	$m=2$, $n=0$[d]	—	223	6850	7400	—	70, 80
5-D	$m=3$, $n=0$[d]	—	204–205	8220	8400	—	70, 80
5-G	$m=0$, $n=1$	green needles	262–263	6330[b]	—	—	71
5-H	$m=n=1$	dark brown needles	243–244	6960[b]	—	—	71
5-J	$m=0$, $n=2$	green needles	214–216	7200[b]	7570	—	71
	2. Effects of *meso*-Substituents on Trimethin Chain of LIII ($n=1$, Y=Z=Q=S, R=R′=R″=Et, R^1=H, X=I)						
5-G	$m=0$, *meso*-H	green needles	262–263	6330[b]	—	—	71
5-G	$m=0$, *meso*-Me	dark green needles	236–237	6120	—	—	71
5-G	$m=0$, *meso*-Et	dark blue needles	231–233	6170	—	—	71
5-G	$m=0$, *meso*-OMe[b,e]	red	180–182	—	—	6150	98
5-H	$m=1$, *meso*-H	dark brown needles	243–244	6960[b]	—	—	71
5-H	$m=1$, *meso*-Me	dark green needles	237	6860	—	—	71
5-I	$m=1$, *meso*-OMe[e]	blue	204–206	6310[f]	6600	7200	66, 98

[a] X=Br. [b] Another absorption maximum at shorter wavelength. [c] Absorption maximum in acetone.
[d] R′=Ph. [e] X=SO_4Me. [f] Absorption for R=Me.

lium salt, having a 4-acetanilido-1,3-butadienyl substituent, to give LIII (m=0, n=2, Y=Q=Z=S, R=R′=R″=Et, R^1=H)[71] (cf. sections 5-A, B, G, and H).

K. Non-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues, and Two Direct Linkages

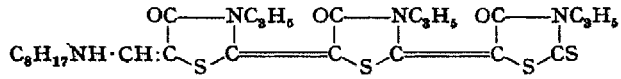
In an extension of the original method[67] (see section 5-B) trinuclear dyes such as LXIX (m=n=0, Y=CH:CH, S, or O, Q=Z=S) were prepared by fusion of simple merocyanines, containing a 3-alkylrhodanine residue, with alkyl toluene-p-sulphonate and 3-alkylrhodanine, followed by heating with pyridine; in one example, thiohydantoin took the place of alkylrhodanine.[68] A simple merocyanine of the



(LXIX)

benzothiazole series, having a 5-thiazolidone residue, was converted into its methotoluene-p-sulphonate, which was condensed with 5-oxo-2-phenyloxazoline to give a trinuclear dye with two direct linkages.[68]

Merocyanines were synthesised in which the quaternary salt residue was that of a 4-oxothiazoline having a substituted 5-aminomethylene group[101,102] (see XIV-1,3-F, and 10-C.1e), so that the



(LXX)

dyes had in fact two ketomethylene residues. One such, in which the second nucleus was a 3-allylrhodanine, was converted into a quaternary salt, whence the trinuclear dye, LXX, was obtained.[102] Like the parent merocyanine, it is peculiar in that the quaternary salt residue is also a ketomethylene residue (cf. section 6-J).

L. Non-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues (or One Ketomethylene and One Thioketomethylene Residue), One Chain :CH·CH:, and One Direct Linkage

According to the first patent, β-methyldimethinmerocyanines (see XIV-8-A.1) were fused with alkyl toluene-p-sulphonate, then heated with a ketomethylene compound in pyridine to give trinuclear dyes,

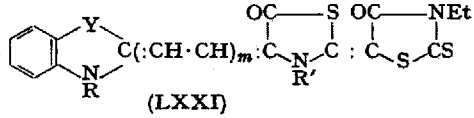
which were the β-methyl derivatives of type LXIX ($m=1$, $n=0$). The quaternary salts entering into the original dimethinmerocyanine were of various types, the other residue being alkylrhodanine, giving the β-methyl derivatives of LXIX ($m=1$, $n=0$, Y=CH:CH, S, or O, Q=S, R′=Me or Et), but the other ketomethylene compound might be 3-alkylrhodanine, thiohydantoin, or 3-methyl-1-phenyl-5-pyrazolone.[67] In an extension of the method there were described dyes, of various series, in which the chain of the original dimethinmerocyanine was unsubstituted.[68]

In a patent on merocyanines in which the ketomethylene residue carried a 3-carboxyaryl substituent (see XIV-1; 10-A.2a, b, and c), there was an example of such a trinuclear dye, which was prepared by heating the quaternary salt of a dimethinmerocyanine with 3-*p*-carboxyphenylrhodanine in pyridine.[103] In another patent where the ketomethylene residue carried a 3-sulphoaryl substituent (see XIV-1; 10-A.2a, b, and c), there were examples of two trinuclear dyes, each of which was made by heating the quaternary salt of a dimethinmerocyanine with 3-methyl-1-*p*-sulphophenyl-5-pyrazolone in pyridine.[104] In a patent on certain merocyanines having an $:N(CH_2)_{2-3}OPh$ group (see section 5-B and XIV-10-B), a dimethinmerocyanine of this kind was converted into a quaternary salt, which was condensed with 3-phenylrhodanine to give LXIX ($m=1$, $n=0$, Y=Q=Z=S, R=$(CH_2)_2OPh$, R′=C_3H_5, R″=Ph).[76]

In 1952 there were described various trinuclear dyes having a central 3-substituted rhodanine nucleus, linked in the 5-position by a dimethin chain to a 4-aryl-5-phenylthiazole residue and in the 2-position directly attached to another ketomethylene residue. Moreover from dimethinmerocyanines, in which the quaternary salt nucleus belonged to the 4-aryl-5-tolylthiothiazole, 4-aryl-5-aryloxythiazole, or 4,5-diaryloxazole series, further trinuclear dyes were synthesised. Other dyes with a dimethin chain and a direct linkage were made for comparison, the total being twenty-four, for which physical constants, including absorption maxima in acetone, were recorded (cf. section 5-B).[82] Two of these dyes were converted into tetranuclear derivatives (section 6-G). A patent of 1956 on trinuclear dyes having 4-aryl-5-aryloxy- or 4-aryl-5-arylthio-thiazole nuclei contained examples of compounds with a dimethin chain and a direct linkage, some of them having a 4- and some a 5-thiazolidone residue as central nucleus.[85]

Trinuclear dyes in which the central nucleus was a 5- instead of a

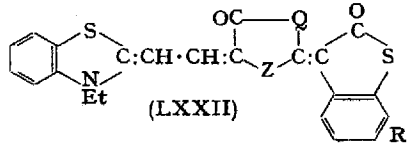
4-thiazolidone were patented.[83] Dimethinmerocyanines having a 5-oxo-2-thiothiazolidine residue were converted into quaternary salts by means of alkyl sulphate or toluene-*p*-sulphonate; the condensation of these with 3-ethylrhodanine gave trinuclear dyes, thirty-six in all, some of which could be represented by the general formula, LXXI (m=1),



(LXXI)

but in others the quaternary salt residue was monocyclic. With the exception of the dyes of the quinoline series, in both the 4-oxo- and the 5-oxo-series, the introduction of the third nucleus, 3-ethylrhodanine, produced a fairly constant bathochromic shift of 500 Å. The absorption for the dyes with a central 5-oxothiazolidine nucleus lay at a longer wavelength than for their 4-oxo-isomers.[82]

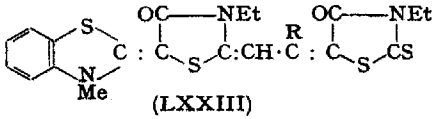
Dimethinmerocyanines having a 3-alkylrhodanine residue, or a 5-oxo-2-thiothiazolidine residue, were converted into quaternary salts, which were condensed with 2-oxodihydrothianaphthene to give trinuclear dyes, such as LXXII (Q=NEt, Z=S, R=H or OEt; and Q=S,



(LXXII)

Z=NMe, R=H or OEt). For comparison with the trinuclear dyes having an unsubstituted 2-oxodihydrothianaphthene residue, their 3-oxo-isomers were synthesised.[105]

Three trinuclear dyes of a different type, LXXIII (R=H, Me, or OEt), were synthesised, in which a central 3-ethylrhodanine residue was

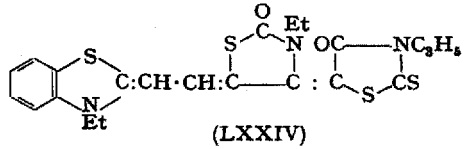


(LXXIII)

directly linked to a benzothiazolium salt residue and by a dimethin chain to a second 3-ethylrhodanine residue. This was achieved by condensing the quaternary salt of a simple merocyanine with 3-ethyl-

rhodanines having the group 5-:CR·Me. The absorption maxima of the three trinuclear dyes were compared with those of three dimethinmerocyanines having the same chains :CH·CR:.[99]

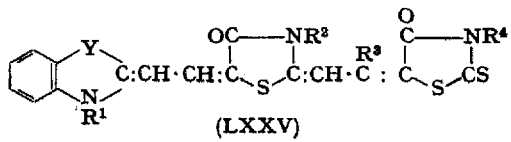
A dimethinmerocyanine in which the CO of the ketomethylene residue had been converted into CS[89] was made into a quaternary salt, which was condensed with 3-allylrhodanine to give LXXIV.[90]



(LXXIV)

M. Non-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues, and Two Chains :CH·CH:

The quaternary salt of a dimethinmerocyanine having a rhodanine residue could be condensed with a rhodanine having a 5-ethylidene group (cf. XIV-3-F) to give a trinuclear dye of type LXIX ($m=n=1$, Q=Z=S) with two dimethin chains, whilst use of a rhodanine having in the 5-position one of the groups :CMe(OMe), :CMe(OEt), :CMe(SEt), or :CMeAc gave dyes of types LXXV (Y=O, R^3=OMe, OEt, SEt, or



(LXXV)

Ac, respectively). Physical properties were given for many others, including LXXV (Y=CH:CH, CMe_2, O, S, Se, or NEt, R^3=OEt), besides a 4-linked quinoline analogue and dyes derived from various monocyclic quaternary salts. Through a rhodanine having the 5-:CMe_2 group, there were prepared trinuclear dyes, LXXV (Y=S or O, R^3=Me). Two dimethinmerocyanines having a 5-oxo-2-thiothiazolidine residue were converted into quaternary salts and condensed with a 2-ethylthio-5-oxothiazoline having a reactive 4-:CMe(SEt) group. These last two thiazolines were also condensed with the quaternary salts of various dimethinmerocyanines having a rhodanine residue. Numerous dimethinmerocyanines with a 5-oxo-2-thiothiazolidine residue were converted into quaternary salts, which were condensed with a 3-carbethoxymethylrhodanine having, in the 5-position, one of the

TABLE V. Some Properties of Non-Ionic Trinuclear Dyes with One Quaternary Salt Residue and a Sequence of Two Ketomethylene Residues

Group	Particulars	Appearance of crystals	M.p. (°C)	Absorption maximum in MeOH (Å)	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
5-K	LXIX ($m=n=0$, Y=CH:CH, Z=Q=S, R=Me, R′=R″=Et)	crimson needles	> 305	—	5900	6200	68
5-K	LXIX ($m=n=0$, Y=O, Z=Q=S, R=Me, R′=R″=Et)	orange	> 305	—	5200	5800	68
5-K	LXX	red needles	199–201	5080	—	—	102
5-L	LXIX ($m=1$, $n=0$, Y=CH:CH, Q=Z=S, R=R′=R″=Et)	green threads	310[a]	6000[b,c]	—	—	82
5-L	LXIX ($m=1$, $n=0$, Y=CMe_2, Q=Z=S, R=Me, R′=R″=Et)	brown; green reflex	290[a]	5440[b]	—	—	82
5-L	LXIX ($m=1$, $n=0$, Y=Q=Z=S, R=R′=R″=Et)	chocolate leaflets	318[a]	5660[b]	6500[d]	7000[d]	68, 82
5-L	LXIX ($m=1$, $n=0$, Y=O, Q=Z=S, R=R′=R″=Et)	red-bronze leaflets	320[a]	5370[b,c]	6200[d]	6600[d]	68, 82
5-L	LXXI ($m=1$, Y=CMe_2, R=R′=Me)	steel-blue	283	5710[b,c]	—	—	82
5-L	LXXI ($m=1$, Y=S, R=R′=Et)	gold-green	292	5990[b,c]	—	—	82
5-L	LXXI ($m=1$, Y=O, R=R′=Et)	steel-blue needles	278	5660[b,c]	—	—	82
5-L	LXXI (Z=S, Q=NEt, R=H)	dark purple rods	221–222	5770	6200	6950	105
5-L	3-oxo-analogue of preceding compound	green prisms	301–303	—	—	—	105
5-M	LXIX ($m=n=1$, Y=Q=Z=S, R=Et, R′=R″=allyl)	green needles	237	6220[e]	—	—	106
5-M	LXIX ($m=n=1$, Y=O, Q=Z=S, R=R′=Et, R″=CH_2CO_2Et)	green needles	275	6100[e]	—	—	106
5-N	LXIX ($m=1$, $n=2$, Y=Z=Q=S, R=Et, R′=R″=allyl)	bronze needles	239	6580[e]	—	—	106
5-N	LXIX ($m=1$, $n=2$, Y=O, Z=Q=S, R=R′=Et, R″=allyl)	gold-green needles	282	6430[e]	—	—	106

[a] Decomp. [b] Absorption in acetone. [c] Inflection also. [d] Sensitising where R=Me.
[e] Absorption in pyridine.

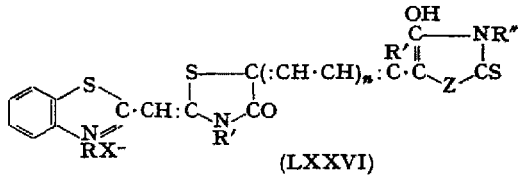
groups :CHMe, :CMe(OR), or :CMe(SR). Dyes of type LXXV (R^3=OR or SR) were of especial practical interest, because these groups on the chain increased the solubility. Introduction of SR on the chain, as with dimethinmerocyanines, led to a bathochromic shift of absorption.[106–108] Some tetranuclear derivatives were synthesised (sections 6-L and M).

N. Non-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues, and the Chains :CH·CH: and :CH·CH:CH·CH:

Condensation of a dimethinmerocyanine having a 3-methyl-5-oxothiazolidine residue with a 3-carbethoxymethylrhodanine having the reactive substituent :CH·CH:CHMe in the 5-position, gave a trinuclear dye with one dimethin and one tetramethin chain. The absorption maxima of four such, belonging to the benzothiazole, benzoxazole, 4,5-diphenyloxazole, and 4,5-diphenylthiazole series were compared. Three dimethinmerocyanines having a 4-oxothiazolidine residue were also converted into trinuclear dyes.[106]

O. Di-Ionic Trinuclear Dyes Having One Quaternary Salt Residue, Two Ketomethylene Residues and the Chains ·CH: and (:CH·CH)$_{0-2}$:CH·

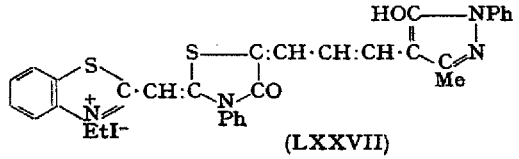
A trinuclear dye, LXXVI (n=0, Z=S, R=Et, R′=*o*-C_6H_4Me, R″=C_3H_5, R^1=H, X=Br), with two methin chains, was prepared from a methincyanine having a 5-acetanilidomethylene-4-oxothiazoline



(LXXVI)

residue,[79] by heating with 3-allylrhodanine and triethylamine in methanol.[94] Alternatively it could be reached from a methincyanine, having a 4-oxothiazoline residue,[89] by condensation with 5-acetanilidomethylene-3-allylrhodanine.[109] A methincyanine in which the 4-oxothiazoline residue had the group :CEt(SMe) in the 5-position[81] was used to give LXXVI (n=0, Z=S, R=R^1=Et, R′=Ph, R″=C_3H_5, X=Br); an analogue of this with a substituted thiazole, instead of a benzothiazole, residue was described: both these dyes comprised the structure of a *meso*-ethylmethinoxonol.[94]

The trinuclear dye, LXXVII, with a methin and a trimethin chain, was prepared by condensation of a methincyanine, having a 4-oxothiazoline residue carrying the group $:CH\cdot CH:CH\cdot C_5H_{10}N$ in the 5-position,[79] with 3-methyl-1-phenyl-5-pyrazolone.[94] Alternatively



(LXXVII)

it was prepared from a methincyanine, having a 4-oxothiazoline residue, by condensation with 4-acetanilidoallylidene-3-methyl-1-phenyl-5-pyrazolone.[109]

The trinuclear dye, LXXVI (n=2, Z=NMe, R=Et, R′=Ph, R″=C_3H_5, R^1=H), with a methin and a pentamethin chain, was prepared by condensation of a methincyanine, having a 4-oxothiazoline residue carrying the group $:CH\cdot CH:CH\cdot CH:CH\cdot C_5H_{10}N$ in the 5-position[79] with 3-allyl-1-methyl-2-thiohydantoin.[94] Another such, LXXVI (n=2, Z=NPh, R=Et, R′=Ph, R″=C_3H_5, R^1=H, X=Br), was reached by the alternative route involving a methincyanine of the 4-oxothiazoline series and 5-(5-acetanilido-2,4-pentadienylidene)-3-allyl-1-phenyl-2-thiohydantoin.[109]

The above types of trinuclear dyes were sensitisers.[95]

6. Tetranuclear Dyes, Mostly Obtained by Condensations of Quaternary Salts of Merocyanines

Ref.	Chain	No. of quaternary salt residues	No. of ketomethylene residues	Type
6-A	:CH·CH:C·CH:CH· ·CH:CH·C:C·CH: R	4	0	di-ionic
6-B	central ·CH: two direct	2	2	mono-ionic
6-C	central ·CH: two :CH·CH:	2	2	mono-ionic
6-D	central ·N: two direct	2	2	mono-ionic

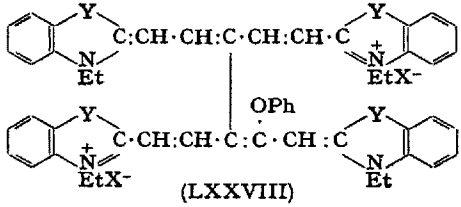
(Table continued)

TABLE *continued*

Ref.	Chain	No. of quaternary salt residues	No. of ketomethylene residues	Type
6-E	central ·CH:CH·CH: two direct	2	2	mono-ionic
6-F	central ·CH:CH·CH: two :CH·CH:	2	2	mono-ionic
6-G	central direct, one ·CH:, one :CH·CH:	2	2	mono-ionic
6-H	central :N·N: two direct	2	2	non-ionic
6-I	central :N·N: two :CH·CH:	2	2	non-ionic
6-J	three direct	1	3	non-ionic
6-K	:CH·CH: two direct	1	3	non-ionic
6-L	two :CH·CH: one direct	1	3	non-ionic
6-M	three :CH·CH:	1	3	non-ionic
6-N	·CH(:CH·CH)$_{0-2}$ two ·CH:	2	2	tri-ionic

A. Di-Ionic Tetranuclear Dyes Having Four Quaternary Salt Residues and Two γ-Linked Pentamethin Chains

When a quaternary salt having a reactive methyl group was heated with OCH·CCl:C(OPh)(CO_2H) (mucophenoxychloric acid) and triethylamine in ethanol, carbon dioxide was evolved and a dye was

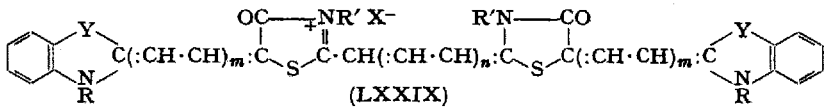


(LXXVIII)

produced. This had the normal pentamethincyanine colour but was formulated as tetranuclear, LXXVIII. The five examples included representatives of the 2-linked quinoline, benzothiazole, and benzoselenazole series.[110]

B. Symmetrical Mono-Ionic Tetranuclear Dyes Having Two Quaternary Salt Residues, Two Ketomethylene Residues, a Central ·CH:, and Two Direct Linkages

Simple merocyanines having a 3-ethylrhodanine residue were converted into quaternary salts by means of methyl toluene-*p*-sulphonate. Salts of this kind were heated with malonic acid in pyridine (cf. II-6-D) and the resultant tetranuclear products were converted into the iodides, LXXIX (n=m=0, Y=O or S, R=Me, R′=Et).[68]



(LXXIX)

The preparation of symmetrical methincyanines, which might be *meso*-substituted, by heating a 2-methylthio-quaternary salt with triethylamine in acetic anhydride (cf. II-6-F; III-A, E, and F), was applied to a similar quaternary salt of a merocyanine to give LXXIX (n=m=0, Y=S, R=Me, R′=Et).[111]

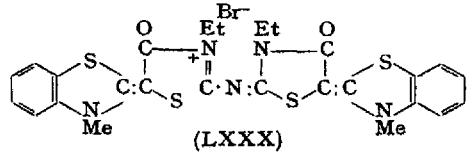
C. Symmetrical Mono-Ionic Tetranuclear Dyes Having Two Quaternary Salt Residues, Two Ketomethylene Residues, a Central ·CH:, and Two Linkages :CH·CH:

In the first patent, β-methyldimethinmerocyanines, having a 3-alkylrhodanine residue (XIV-8-A.1), were converted into toluene-*p*-sulphonates, and the resultant salts were heated with malonic acid in pyridine (cf. II-6-D) to give tetranuclear dyes, which were of type LXXIX (m=1, n=0) except that each dimethin chain carried a β-methyl substituent. Various types of quaternary salt, belonging to the 2-linked quinoline, benzothiazole, or benzoxazole series, entered into the original dimethinmerocyanines.[67] The quaternary salts of similar dimethinmerocyanines, but having unsubstituted chains, were likewise condensed with malonic acid in pyridine to give LXXIX (m=1, n=0, Y=S, R=Me or Et, R′=Et, X=Br); a dye with substituted benzothiazole was also described.[68]

D. Symmetrical Mono-Ionic Tetranuclear Dyes Having Two Quaternary Salt Residues, Two Ketomethylene Residues, a Central ·N:, and Two Direct Linkages

By converting a simple merocyanine having a 3-ethylrhodanine residue into an alkylthio-quaternary salt, by means of alkyl toluene-*p*-

sulphonate, and heating this with ammonium nitrate and pyridine (cf. XII-1, and 2-C), and treating the product with potassium bromide, there resulted the azamethin compound, LXXX.[68]



(LXXX)

E. Symmetrical Mono-Ionic Tetranuclear Dyes Having Two Quaternary Salt Residues, Two Ketomethylene Residues, a Central Chain ·CH:CH·CH:, and Two Direct Linkages

A merocyanine having a 3-ethylrhodanine residue was fused with ethyl toluene-*p*-sulphonate, and the resultant alkylthio-salt was heated in pyridine with glutaconic acid or crotonic anhydride (cf. IV-14) to give LXXIX ($m=n=1$, Y=S, R=Me, R′=Et, X=*p*-$SO_3 \cdot C_6H_4Me$). When the quaternary salt of the merocyanine was heated with indene in pyridine (cf. IX-1 and 2) it gave an analogue, in which the $\alpha\gamma$-carbon atoms of the trimethin chain entered into the indene residue.[68]

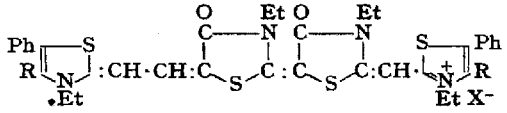
F. Symmetrical Mono-Ionic Tetranuclear Dyes Having Two Quaternary Salt Residues, Two Ketomethylene Residues, a Central Chain ·CH:CH·CH:, and Two :CH·CH: Chains

The quaternary salts of β-methyldimethinmerocyanines having a 3-ethylrhodanine residue were condensed with glutaconic acid to give dyes of the types LXXIX ($m=n=1$, Y=CH:CH, S, or O), but in which each dimethin chain had a β-methyl substituent. By use, at the final stage, of cyclopentadiene or indene in pyridine (cf. IX-1 and 2), there resulted analogues in which the $\alpha\gamma$-atoms of the trimethin chain entered into these carbocyclic rings.[67]

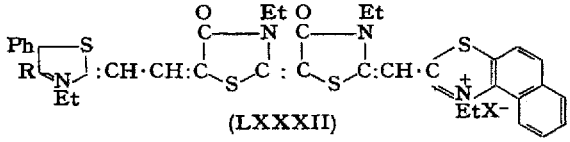
G. Mono-Ionic Tetranuclear Dyes Having Two Central Ketomethylene Residues, Directly Linked, and Attached by One Methin and One Dimethin Chain to Two Quaternary Salt Residues

In 1952 a non-ionic trinuclear dye, having a substituted thiazole, a sequence of two 3-ethylrhodanine residues, a dimethin chain, and a direct linkage (see section 5-L) was converted into an alkylthio-quaternary salt, which was condensed with a 4-*m*,*p*-dimethoxyphenyl-2-

methyl-5-phenylthiazolium salt, by heating with triethylamine in ethanol, to give the symmetrical LXXXI (R=*m*,*p*-$C_6H_3(OMe)_2$). The unsymmetrical compound, LXXXII (R=*p*-C_6H_4OMe), was made similarly.[82]



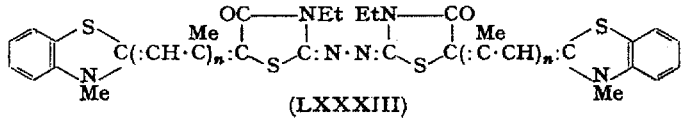
(LXXXI)



(LXXXII)

H. Symmetrical Non-Ionic Tetranuclear Dye Having Two Central Ketomethylene Residues, Linked by :N·N:, and Two External Quaternary Salt Residues, Directly Attached

Following on the first patent,[67] a simple merocyanine, having a 3-ethylrhodanine residue, was converted into its methylthio-salt by methyl toluene-*p*-sulphonate, and this was condensed with hydrazine hydrochloride, by heating them in pyridine, to give LXXXIII (*n*=0).[68]



(LXXXIII)

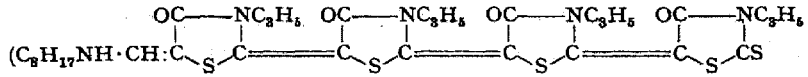
I. Symmetrical Non-Ionic Tetranuclear Dyes Having Two Central Ketomethylene Residues, Linked by :N·N:, and Two External Quaternary Salt Residues, Linked by Chains :CH·CH:

In the first patent, a *β*-methyldimethinmerocyanine, having a 3-ethylrhodanine residue (XIV-8-A.1), was converted into a quaternary salt, which was condensed with hydrazine hydrochloride, by heating them in pyridine, to give LXXXIII (*n*=1).[67] The method was later applied to the preparation of a similar tetranuclear compound having two unsubstituted dimethin chains.[68]

J. Non-Ionic Tetranuclear Dye Having One Quaternary Salt Residue, a Sequence of Three Ketomethylene Residues, and Three Direct Linkages

From a quaternary salt of the abnormal trinuclear dye, LXX (see section 5-K), the tetranuclear dye, LXXXIV, was synthesised.[102] It had

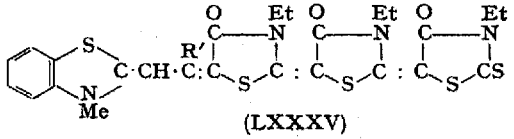
the same peculiarity, that the quaternary salt residue was also a keto-methylene residue.



(LXXXIV)

K. Non-Ionic Tetranuclear Dyes Having One Quaternary Salt Residue, Linked by the Chain :CH·CH: to a Sequence of Three Ketomethylene Residues, with Two Direct Linkages

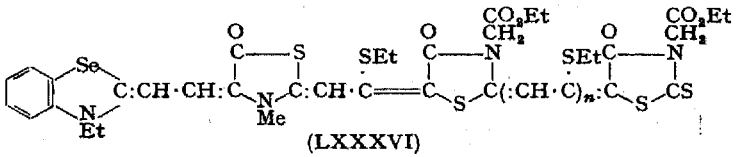
Certain non-ionic trinuclear dyes having a quaternary salt residue, attached by a dimethin chain to a sequence of two ketomethylene residues, the end one being 3-ethylrhodanine, were converted into quaternary salts, which, on boiling with 3-ethylrhodanine in pyridine, gave the tetranuclear derivatives, LXXXV (R^1=H or Me).[68]



(LXXXV)

L. Non-Ionic Tetranuclear Dyes Having One Quaternary Salt Residue, a Sequence of Three Ketomethylene Residues, Two :CH·CH: Linkages, and One Direct Linkage

Certain non-ionic trinuclear dyes, having two dimethin chains, of type LXXV (see section 5-M), were converted into quaternary salts, whence were derived tetranuclear derivatives, such as LXXXVI (n=0).[106]



(LXXXVI)

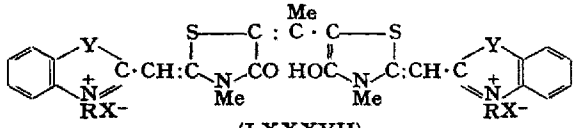
M. Non-Ionic Tetranuclear Dyes Having One Quaternary Salt Residue, a Sequence of Three Ketomethylene Residues, and Three :CH·CH: Linkages

By a repetition of the procedure applied in synthesising non-ionic trinuclear dyes having a substituted dimethin chain (section 5-M), these

were converted into tetranuclear derivatives, such as LXXXVI (n=1). Two of its analogues were made, in one of which the first nucleus again belonged to the benzoselenazole series, in the other to the 4,5-diphenylthiazole series, and in both the fourth nucleus was a 2-ethylthio-5-oxothiazoline residue; an analogue of the last tetranuclear dye but with two ethoxy-groups on the chain, instead of two ethylthio-groups, was also synthesised; the absorption maxima of these three dyes in pyridine lay at 8220 Å, 8650 Å, and 7720 Å, respectively.[106]

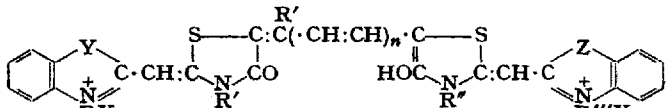
N. Tri-Ionic Tetranuclear Dyes Having Two Central Ketomethylene Residues, Linked by ·CH(:CH·CH)$_{0-2}$:, and Two External Quaternary Salt Residues, Each Linked by ·CH:

Meso-methylmethinoxonols, having two 3-alkylrhodanine residues[112] (XIII-4-A and B), were heated with a heterocyclic base and an alkyl toluene-*p*-sulphonate, and the resultant mixture of salts was heated with pyridine. This gave symmetrical tetranuclear compounds, of type LXXXVII (Y=CH:CH, S, or O), which comprised useful dyes for fabrics.[113] Compounds similar to LXXXVII in having the structure



(LXXXVII)

of *meso*-alkylmethinoxonols, but different in being unsymmetrical, were reached by a different route. This consisted in the condensation of a methincyanine having a 4-oxothiazoline residue[69] with another in which the 5-methylene group of such a residue had been converted into :CR(SMe).[81] This led to a tetranuclear dye, LXXXVIII (n=0, Y=S,



(LXXXVIII)

Z=CMe_2, R=R‴=Et, R′=R″=Ph, R^1=Et, X=Br), in which the indolenine residue had a 6-methyl substituent. Instead of this residue, a 5-methyl-4-phenylthiazole residue was present in an analogous diiodide; a *meso*-propyl compound also had a substituted thiazole residue.

TABLE VI. Properties of Some Tetranuclear Dyes

Group	Particulars	Appearance of crystals	M.p. (°C)	Absorption maximum in MeOH (Å)	Sensitising (Å) Maximum	Sensitising (Å) Extent	Ref.
4-O	L (X=I)	—	286–287	6130	6450	—	66
4-O	LI (X=SO_4Me)	—	260–262	6570	7000	—	66
6-A	LXXVIII (Y=S, X=Cl)	blue	—	—	6950	—	110
6-B	LXXIX ($m=n=0$, Y=S, R=Me, R'=Et, X=I)	golden	310	5640[a] 5690[a]	6000	6300	68,111
6-C	LXXIX ($m=1$, $n=0$, Y=S, R=Me, R'=Et, X=Br)	golden	285	—	—	—	68
6-D	LXXX	scarlet; gold reflex	217	—	—	—	68
6-E	LXXIX ($m=0$, $n=1$, Y=S, R=Me, R'=Et, X=p-$SO_3C_6H_4Me$)	dark gold	303	—	—	—	68
6-G	LXXXI (R=$C_6H_3(OMe)_2$, X=p-$SO_3C_6H_4Me$)	bronze	192	6500	—	—	82
6-H	LXXXIII ($n=0$)	lemon-yellow	> 292	—	—	—	68
6-I	LXXXIII ($n=1$)	golden brown	292	—	—	6200	68
6-J	LXXXIV	red	263	5480[b]	—	—	102
6-K	LXXXV (R^1=H)	blackish purple	> 300	—	6500	7200	68
6-L	LXXXVI ($n=0$)	golden	288	7650[b]	—	—	106
6-M	LXXXVI ($n=1$)	bronze	260	8320[b]	—	—	106

[a] Sensitising data for X=p-$SO_3C_6H_4Me$. [b] Absorption in pyridine.

The sensitising maxima of these three dyes were at 7250 Å, 6950 Å, and 7000 Å respectively.[114]

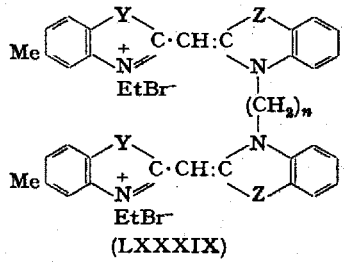
Tetranuclear dyes, comprising the structure of a trimethinoxonol, were prepared by condensation of a methincyanine, having a 4-oxothiazoline residue,[69] with a derivative of such a dye, in which the 5-methylene group had been converted into $:CH\cdot CH:CH\cdot NC_5H_{10}$.[79] This led to the symmetrical LXXXVIII ($n=1$, Y=Z=S, R=R‴=Et, R′=R″=Ph, R^1=H, X=I); another example differed only in having one 3-allylrhodanine in place of one of the 5-phenylrhodanine residues, and this compound had its sensitising maximum at 7600 Å.[114]

Tetranuclear dyes, which included the structure of a pentamethinoxonol, were synthesised from a methincyanine having a 4-oxothiazoline residue[69] and another in which the 5-methylene group of such a residue had been converted into $:CH\cdot CH:CH\cdot CH:CH\cdot NC_5H_{10}$.[79] This led to the symmetrical compound, LXXXVIII ($n=2$, Y=Z=S, R=R‴=Et, R′=R″=Ph, R^1=H, X=I), and to an analogue having one 4-methylthiazole residue: the latter dye had absorption maxima at 4470 Å and 8110 Å, and its sensitising maximum at 8500 Å.[114]

7. Polymeric Cyanines in which Dye Units are Linked through their Nitrogen Atoms by a Chain $(CH_2)_n$

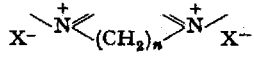
In 1947 quaternary salts comprising two 2-methylbenzothiazole nuclei, in which the nitrogen atoms were linked by $(CH_2)_2$, $(CH_2)_3$, or $(CH_2)_6$ were described. They were made by heating the base with 1,2-dibromoethane, 1,3-dibromopropane, or 1,6-dibromohexane. A similar salt of 2-methylbenzoselenazole was also made.[115] The preparation of five polymeric thiacarbocyanines, some of them *meso*-substituted, by heating a salt, which had been prepared from 2-methylbenzothiazole and 1,3-dibromopropane, with an ortho-ester in the presence of pyridine, was described, and their sensitising action was patented. In the sixth example, 1,6-dibromohexane had been used for salt formation.[116,117] The preparation of polymeric 2′-cyanines, of type LXXXIX, was also described: these were of less complexity, in that only one of the quaternary salts was a bis-salt. The dye, LXXXIX ($n=2$, Y=Se, Z=CH:CH), was prepared from *NN′*-ethylenebis-(2-methylthioquinoline) dibromide by its condensation with 2,5-dimethylbenzoselenazole ethobromide; it had its sensitising maximum at 5570 Å.

Analogues where n=3, 4, 5, and 6, had their sensitising maxima at 5350 Å, 5570 Å, 5600 Å, and 5570 Å, respectively,[118] whereas the

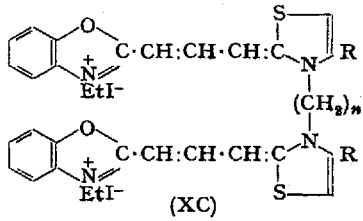


(LXXXIX)

sensitising maximum of 3,1′-diethylselena-2′-cyanine iodide has been recorded as 5340 Å.[119] As with the thiacarbocyanines,[116,117] the possibility of carrying out a 2′-cyanine condensation where both quaternary salt molecules comprised a structure



was visualised.[118] Although reaction of a bis-quaternary salt, having a methyl group in the α- or γ-position to each nitrogen atom, with a similar salt, having chlorine (which, incidentally, is not a very reactive substituent), or alkylthio- in the α- or γ-position to each nitrogen, was patented, only one such dye was formulated. It was a polymeric thia-2′-cyanine, with its sensitising maximum at 4800 Å,[120] whereas 3,1′-diethylthia-2′-cyanine iodide had its maximum at 5300 Å.[121] The constitution of the polymers, even as to whether they were cyclic or possessed a chain structure, was unknown.[120] Emulsions sensitised with bis-oxathiazolocarbocyanines were patented. The examples were of the type XC (n=2 or 3, R=Me or Ph), and sometimes the benzoxazole

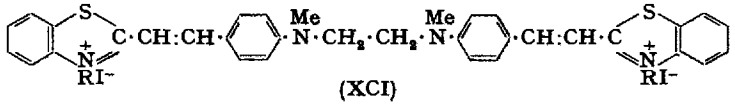


(XC)

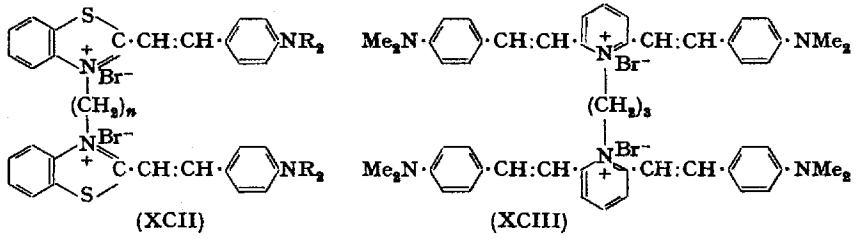
nucleus was substituted. For XC (n=2, R=Ph) the sensitising maximum was at 5600 Å,[122] whilst for 3,3′-diethyl-5,6,4′-trimethyloxa-

thiazolocarbocyanine iodide the maximum of 4150 Å had been recorded.[123]

Polymers analogous with *p*-dimethylaminostyryl salts (cf. XIII-1) were prepared by condensing a quaternary salt having at least one reactive methyl group with a *p*-NR^1R^2 aromatic aldehyde, having at least one CHO group, with the proviso that at least one of the reactants must have two such groups. Use of a dialdehyde gave tetranuclear di-ionic salts of type XCI; use of an *NN*-alkylene bis-quaternary salt gave another of type XCII; use of a bis-quaternary salt having two reactive methyl groups led to the hexanuclear product, XCIII; moreover a bis-quaternary salt having reactive methyl groups might be



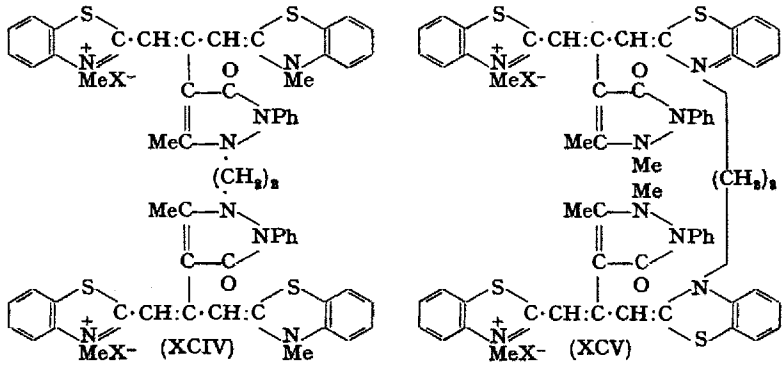
(XCI)



(XCII) (XCIII)

condensed with a tertiary aromatic amine having two CHO groups.[124]

A di-ionic hexanuclear dye, XCIV, resulted when ethylene dibromide was used for converting a *β*-methyldimethinmerocyanine having a pyrazolone nucleus into a diquaternary salt (cf. section 4-I), which was subsequently condensed with a 2-methylthiobenzothiazolium



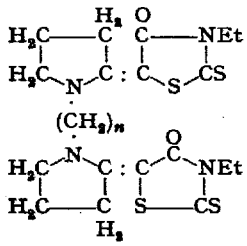
(XCIV) (XCV)

salt. On the other hand, by using an *NN*-ethylenic salt at the last stage, the isomeric product, XCV, was obtained.[62]

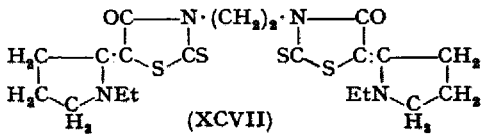
A patent of 1955 on merocyanines having the nucleus



(XIV-10-C.1a) included non-ionic tetranuclear compounds, of the type XCVI (n=2 or 6), with their sensitising maxima at 4420 Å and 4390 Å, respectively, whereas a simple dinuclear merocyanine with an *N*-butylpyrrolidine ring had its maximum at 4360 Å. The tetranuclear compound, XCVII, differed in that the *NN*-linkage was through the ketomethylene instead of the quaternary salt residues; its sensitising

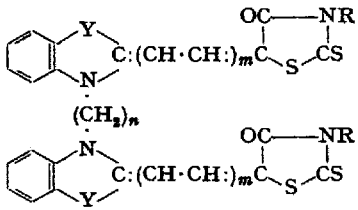


(XCVI)



(XCVII)

maximum was at 4400 Å.[125] Other non-ionic tetranuclear dyes had the units linked through the nitrogen atoms of their quaternary salt residues, and comprised the types XCVIII (n=2–5), whilst another had



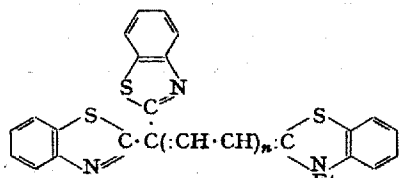
(XCVIII)

two 3-methyl-1-phenyl-5-pyrazolone residues. The tetranuclear compounds, XCVIII (m=0, 1, or 2), were of the simple merocyanine, or di- or tetra-methinmerocyanine types, whilst the quaternary salt residues

belonged to the 4-linked quinoline, benzothiazole, benzoxazole, 1,3,4-thiadiazole, and thiazoline series. Absorption maxima were quoted.[126]

8. Some Trinuclear Bases from Methylenebisazoles

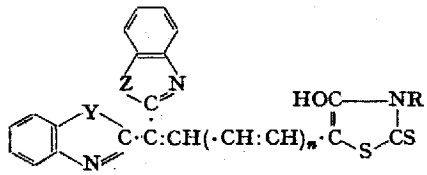
Methylenebis-2-benzothiazole[127] was condensed with 2-β-acetanilidovinylbenzothiazole ethiodide, or with 2-(4-acetanilido-1,3-butadienyl)benzothiazole ethiodide, respectively, to give XCIX (n=1 or 2). By condensing the bisazole with 2-(β-ethyl-β-methylthio)vinylbenzothiazole ethiodide, or with its 6-methyl derivative, there resulted derivatives of XCIX (n=1), in which besides the α-heterocyclyl substituent,



(XCIX)

there was a β-ethyl substituent on the trimethin chain. Both the bases and their quaternary salts were patented as sensitisers,[128] but as only one salt was described, and that inaccurately, it has not been included as a di-ionic dye in an additional class in section 3.

By condensation of a 3-substituted rhodanine, which had, in the 5-position, one of the groups :CH·NAcPh, :CH·CH:CH·NAcPh, or :CH·CH:CH·CH:CH·NAcPh, with methylenebis-2-benzothiazole, there resulted α-heterocyclyl-di-, -tetra-, and -hexa-methin dyes, such as C (n=0, 1, or 2, Y=Z=S).[129] Methylenebis-2-benzoxazole and unsymmetrical methylenebisazoles[130] were also used, and instead of



(C)

rhodanines there were used barbituric acid, thiobarbituric acid, and 2-diphenylamino-4-oxothiazoline. The sensitising action of such dyes was patented,[129] as were filter layers comprising their heavy metal salts.[131]

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CHAPTER XVI

The Relationship Between Colour and Constitution in the Cyanine Series

1. Introduction

Compounds of the cyanine series include dyes, many of them valuable sensitisers, and are mostly characterised by a single narrow absorption band, although some are double-banded. Their range is so great that not only is the whole of the visible spectrum covered, but there are also cyanines which absorb in the ultraviolet or near infrared. As the sensitising and absorption bands are closely related (see XVII-2), a study of the connection between colour and constitution is of prime importance to the photographic industry. Besides this, the series is of unique scientific interest, because it presents a wealth of variable factors, which may influence the colours of the products. Such are the nature of the nuclei, the length of chain joining them, the positions of linking, the effect of substitution in the nuclei or on the chain, and the inclusion of part of the chain in a ring. Other subjects are the colour of *p*-dimethylaminostyryl salts, of anhydronium bases, and of dyes in which one or more :CH groups of the chain are replaced by :N·. They will be dealt with in that order. Additional colour changes due to polymerisation are included elsewhere (XVII-2).

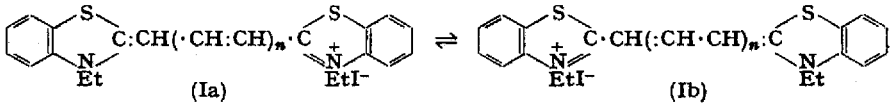
Physical conditions affect absorption. In 1928 absorption curves of alcoholic solutions, of aqueous solutions, and of solutions in 6% aqueous gelatin were given for some methin-, trimethin-, and apocyanines.[1] Soon afterwards it was recorded that absorption is affected not only by the nature of the solvent but also by the temperature.[2] With the cyanines no displacement of absorption was observed on change of the polar moment of the solvent but changes did occur in non-polar solvents of increasing refraction and dielectric strength.[3,4]

It was pointed out in 1935 that the tautomeric formulae which had been proposed for cyanines (see I-3-A and E) were identical in principle with resonance formulae and it was suggested that the quantum-mechanical resonance conception could be applied to explain the colours of cyanines, the function of the auxochrome being to make resonance possible.[5] Resonance within conjugated systems results in a tendency towards planarity of the molecule.[6] Since resonance can only take place between co-planar parts of the molecule, applications of the theory have led to inferences as to the steric structure of certain cyanine molecules. In 1940 steric inhibition of planarity of the molecule was suggested as the cause of modified spectral absorption and of inefficient optical sensitising.[7] Two years later, replacement of two *N*H by two *N*Me groups to give symmetrical 2,2′-pyrrolocyanines (see X-5-A) necessitated a departure of the molecule from planarity and this required energy: the observed shift of the absorption maximum to a longer wavelength was thus explained.[8] In 1947, in a review on steric hindrance to planarity in dye molecules, various instances were given of a shift of absorption, which was attributed either to non-coplanarity of the nuclei, or to increased distortion in a molecule which was already non-planar. The non-planar cyanines always absorbed less intensely than the planar ones. It was argued that where a scale-drawing of a dye molecule, with the accepted interatomic distances, van der Waals radii, and bond angles, showed planarity to be possible, the molecule would be planar. Where *cis–trans* isomers could be drawn, the choice was restricted to the planar forms.[9]

A mathematical study of the colours of cyanines by the valence bond method, considering a system with two auxochromes at the ends of a polymethin chain[10] is outside the scope of this chapter. It was claimed that the bathochromic shifts on increasing the length of the chain and the strength of the auxochromes was thus explained.[10] Other mathematicians applied both this method and one based on the linear combination of atomic orbitals to the problem.[11–13] Subsequently a one-dimensional free-electron gas model was used as an approximation for the quantitative study of cyanines, a given electron being considered as a particle in the potential field of the molecular frame. It was considered that this treatment was simpler and more satisfactory than the other two.[14] An application of the metallic model, taking account of branching of the chain, was used to calculate the spectra of 2,2′- and 4,4′-pyrido- and pyridocarbo-cyanines, with moderate success.[15]

2. Effect of the Nature of the Nuclei

There were published in 1936 absorption curves of methanolic solutions of thirty-nine symmetrical *NN'*-diethylcyanine iodides belonging to eleven different heterocyclic series, and representing the methin-, trimethin-, pentamethin-, and heptamethin-cyanine types. Only twelve of the salts had a secondary absorption band, which lay at a shorter wavelength than the principal band; it appeared that the presence of quinoline nuclei tended to produce a secondary band.[16] In the following year, absorption data were given for one hundred and five unsymmetrical cyanines belonging to the first three types. The absorption maximum of each unsymmetrical dye was compared with the arithmetic mean of those of the related pair of symmetrical dyes and the agreement was often exact, or nearly so, but the presence of a quinoline nucleus was liable to introduce anomalies.[17] It was noted in 1939, when absorption data were given for thirty unsymmetrical dyes, of the tri- and penta-methincyanine groups, that, from the conception of quantum resonance as a cause of colour, it was to be expected that when the nuclei differed greatly in character, the absorption maxima would show a hypsochromic shift.[18] Agreement would only be expected when the two nuclei were approximately equal in basicity.[19] According to the resonance theory, symmetrical cyanines are resonance hybrids between two identical low energy structures, e.g., Ia and Ib, in which the quantum mechanical degeneracy is complete. An unsymmetrical cyanine, on the other hand, is a resonance hybrid between two structures of unequal energy. A strongly basic



nitrogen takes up an additional positive charge to become quaternary more readily than does a weakly basic one. Hence deviation occurs between the observed absorption maximum and the mean of the maxima of the pair of related symmetrical dyes. For a constant chain-length, the deviation is greater the greater the imbalance of basicity of the nuclei.[20,21] Each of a series of unsymmetrical dimethincyanines characterised by having a 2,5-dimethyl-1-phenylpyrrole nucleus, which is very weakly basic, absorbed at a shorter wavelength than the mean

of the related symmetrical dyes. The greater the basicity of the second nucleus, the greater the deviation, whence it was possible to give as the order of basicity indolenine < benzoxazole < benzothiazole.[22] The same method was applied to the arrangement of other heterocyclic nuclei,[20,21] twenty-five of which were thus covered.[23] Absorption data were also given for thirty-six unsymmetrical *NN'*-diethylcarbocyanines, comprising nine different heterocyclic nuclei. Ten of them, which were obtained by combining nuclei of the benzothiazole, 4,5-benzobenzothiazole, benzoxazole, and 2- or 4-linked quinoline series, showed negligible deviations, of 30 Å or less. If these five nuclei were combined with the 3,3'-dimethylindolenine nucleus, deviations of 65–220 Å resulted, and the deviations increased as progressively less basic nuclei were used, the greatest being 725 Å.[24]

In 1950 eleven heterocyclic nuclei, which were introduced into dimethinmerocyanines (see XIV-12), were also introduced into symmetrical trimethincyanines, for which absorption maxima of solutions in ethanol and in chloroform were given.[25]

The high basicity of a 3-linked isoquinoline nucleus was confirmed in 1951 by the observation of the high deviation (1005 Å in nitromethane) of an unsymmetrical dimethincyanine,[26] which had been prepared from 3-methylisoquinoline ethiodide and 3-formyl-2,5-dimethyl-1-phenylpyrrole.[27] Because of the high basicity of this nucleus, the carbocyanine derived from 3-methylisoquinoline ethiodide absorbed at a much shorter wavelength, and much less strongly, than pinacyanol. An unexplained observation is that the carbocyanine derived from 3-methylisoquinoline methiodide had its absorption maximum at a shorter wavelength by 340 Å than that derived from the ethiodide.[26] In view of this anomaly, it is a pity that the absorption maxima of the methiodide and ethiodide of 3-*p*-dimethylaminostyrylisoquinoline[26,27] were not compared.

3. Effect of the Length of Chain Joining the Nuclei

In 1932 the colours of alcoholic solutions of symmetrical cyanines —a tri-, a penta-, and a hepta-methincyanine of each of the series indolenine and 2- and 4-linked quinoline—were compared, as well as the sensitising maxima of the dyes (see XVII-2-C). In the first series, the three compounds gave red, blue, and blue-green solutions.[28] When heptamethincyanines were described in 1933, the absorption maxima

of alcoholic solutions of ten of them were recorded as lying at a longer wavelength, by 1900 to 2050 Å, than those of the corresponding trimethincyanines, and it was noted that they showed no sign of a secondary band.[29] With the thirty-nine symmetrical *NN'*-diethylcyanine iodides which have been mentioned (section 2), the bathochromic shifts of absorption for successive vinylene increments on ascending the series varied from 820–1410 Å, 900–1060 Å, and 1000–1220 Å.[16] With the one hundred and five unsymmetrical cyanines (section 2), the bathochromic shifts on passing from methin- to trimethin-cyanines (18 values) varied from 1060–1400 Å, whilst those on passing from tri- to penta-methincyanines (6 values) varied from 940–990 Å, in those series where quinoline was absent, but anomalies were apt to accompany the introduction of a quinoline nucleus.[17] Besides a bathochromic shift on lengthening the chain, there was an increase in intensity of absorption.[21] Where the nuclei differed in basicity, the deviation, $\lambda_{calc.}$—$\lambda_{obs.}$, increased with increasing chain-length.[20,22] Many unsymmetrical cyanines, in which the nuclei did not differ too greatly in basicity, formed non-convergent series, a vinylene increment causing a bathochromic shift of roughly 1000 Å whatever the length of chain, and this was attributed to the degeneracy of the extreme structures.[19–21] Three other similar non-convergent series were benzothiazole ethiodides each having a 2-substituent $\cdot(CH:CH\cdot)_nNR^1R^2$, and each group consisting of three members, where $n=1$, 2, and 3. In the first group $R^1=H$, $R^2=Ph$; in the second $R^1=Me$, $R^2=Ph$; in the third $R^1R^2=C_5H_{10}N$; in all three, both nitrogen atoms were strongly basic. In a fourth series where $R^1=Ac$, $R^2=Ph$, the basicity of the nitrogen atom carrying the acetyl group was greatly reduced and the vinylene shifts on ascending the series were 620 Å and 350 Å; hence the series was convergent and this was related with the non-degeneracy of the extreme structures.[20,30] From the different degrees of convergence presented by various unsymmetrical series, it appeared that there may be gradation between typically non-convergent and typically convergent series.[19]

In a series of symmetrical cyanines of varying length of chain, not only the two identical extreme structures, but also intermediate, carbonium structures must be considered. For the dye of shortest chain-length, the number of such intermediate structures is least, the resonance splitting of the energy levels of the extreme structures is greatest, the frequency is highest, and the wavelength of absorption is

shortest. This theory was supported by the observation that the acidity required to decolorise a series of symmetrical cyanines was greatest for the dye of shortest chain-length; presumably the action involved addition of a proton to the chain and destruction of resonance stabilisation.[21]

The ultraviolet absorption of symmetrical cyanines of the benzothiazole series, in the region 2850–3850 Å, was considered to depend on the shifting of electrons in the heterocyclic nuclei. The maximum moved progressively to longer wavelengths on ascending the series methin-, trimethin-, pentamethin-, and heptamethin-cyanine.[31]

4. Effect of Positions of Linking of the Nuclei

With the quinoline and the pyridine nucleus, linking may occur either in the 2- or in the 4-position. For each linking of the latter type, the chain joining the nitrogen atoms in the cyanine molecule is longer by two methin groups than it is for the former. Comparison of three 2,2'- with three 4,4'-symmetrical cyanines showed that the four extra cyclic carbon atoms of the latter group gave only about half the bathochromic shift of absorption expected for four non-cyclic carbon atoms.[16] With the isoquinoline nucleus on the other hand, where linking may be through the 1- or through the 3-position, the relationship is an entirely different one (see X-5-A), and it is unfortunate that absorption maxima have not been recorded for any comparative pair of dyes.

5. Influence of Substituents

A. In the Nuclei

(*I*) *Dyes of the Quinoline Series*

The early work on the influence of substituents was concerned with cyanines having quinoline nuclei, because those were the first known. Later studies have dealt chiefly with substitution in cyanines of the benzothiazole series, partly perhaps because such dyes are readily prepared but also, presumably, because they are especially likely to be of practical value in photography. Substitution in the quinoline series will be considered first.

In 1920 a preliminary survey was made, when there were published

preparative details, with absorption and sensitising curves, for a series of nineteen 2,4′-cyanines, having substituents in one or other nucleus, or with various *NN′*-dialkyl groups.[32] It was followed by a comparison of fifteen 2,4′-cyanines, having an amino-, acetylamino-, or cinnamoylamino-group in one of five different positions in the molecule, with the unsubstituted 2,4′-cyanine.[33] Hence it appeared that the influence of the substituent, on absorption and sensitising, depended not only on its nature but also on its position (II-1-C).[32,33] A preliminary survey of symmetrical 2,2′-carbocyanines, dealing with eighteen salts of this type, was likewise made (IV-2-B).[34] In 1922 three 2,2′-carbocyanines, having ethoxy-groups in the 5,5′-, 6,6′-, and 7,7′-positions, showed double-banded absorption, the principal maxima lying at 6030 Å, 6220 Å, and 6170 Å, respectively.[35]

According to a rule first laid down in 1879, an increase in the molecular weight of organic dyes leads to a deepening in colour, the sequence being yellow, red, violet, and blue.[36] An examination of methincyanines, styryl compounds, and anils, of various heterocyclic series, published in 1930, showed that in eleven instances out of thirteen, increase in molecular weight did indeed lead to a bathochromic shift.[37] One way of increasing the weight of cyanine molecules is by introduction of fused-on nuclei: it was noted that 2,2′-cyanines with 5,6,5′,6′-dibenzo-substituents absorbed at a somewhat longer wavelength than the corresponding unsubstituted dyes.[38] The same effect was observed with a 2,2′-carbocyanine and a 2,2′-dicarbocyanine having these substituents[16] and also with unsymmetrical dyes where one 5,6-benzo-substituent was introduced.[17] The hypsochromic shift, of 270–500 Å, on passing from three 2,2′-cyanines to the corresponding compounds with one pyridine in place of one quinoline nucleus, was considerable.[38] There are many exceptions to the rule: thus despite the extra benzo-group, 2,4′-cyanines prepared from 5-methylacridine methiodide and 2-iodoquinoline alkiodide (see X-5-A) had a broad absorption band in the same position as that of the simple 2,4′-cyanine.[39] Moreover in three methincyanines and a symmetrical carbocyanine, in which 3,4-benzo-quinoline, i.e., phenanthridine, nuclei were involved, the absorption maxima lay at a shorter wavelength than those of the isomers having 5,6-benzoquinoline nuclei.[40]

Scale-drawings were made, in order to study the crowding effects caused by the introduction of 3,3′-substituents into the molecules of 2,2′- and 2,4′-cyanines and of 2,2′-carbocyanines.[9]

The introduction of electropositive substituents into the molecule of a symmetrical 2,2′-carbocyanine gave bathochromic shifts, which increased with the basicity of the substituents and were greater in the 6,6′- than in the 5,5′-positions; but introduction of AcNH or NH_2 into the quinoline nucleus of a thia-2′- or an indo-2′-carbocyanine gave hypsochromic shifts, and these were greater with the more basic heterocyclic nucleus.[41]

(2) *Dyes of the Benzoxazole Series*

In the benzoxazole series, the introduction of dibenzo-groups into the 4,5,4′,5′- or 6,7,6′,7′-positions of symmetrical oxacyanines shifted the absorption maximum 250–400 Å towards the red.[42] The effect of the introduction of dibenzo-groups was also recorded for the corresponding tri- and penta-methincyanines,[16] and the effect of the 4,5- or 6,7-benzobenzoxazole nucleus was compared with that of the benzoxazole nucleus in various unsymmetrical cyanines.[17]

On the introduction of 5,5′- or 7,7′-diphenyl groups into the molecule of an oxacarbocyanine and of a *meso*-bromo-oxadicarbocyanine, a weak bathochromic shift was noted for 5,5′- and a weaker one for 7,7′-disubstitution.[43]

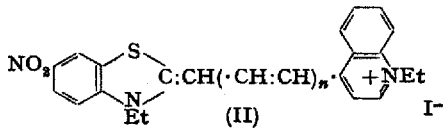
(3) *Dyes of the Benzothiazole Series*

In the benzothiazole series the first substituent to be considered will be the benzo-group. Eight thia-2′-cyanines having one 4,5- or 6,7-benzobenzothiazole nucleus absorbed at a longer wavelength than those without the substituent. Six symmetrical thiacarbocyanines, including two with a *meso*-methyl group, all having 4,5,4′,5′- or 6,7,6′,7′-dibenzo-substituents, absorbed at a longer wavelength by 350–400 Å than the unsubstituted compounds.[44] Two thiacyanines with 6,7,6′,7′-dibenzo-groups had their absorption maxima at a longer wavelength by 150–200 Å than the unsubstituted dyes, whilst it seemed surprising that two 4,4′-dimethylthiazolocarbocyanines should absorb at a wavelength shorter by only 100 Å than that of a thiacarbocyanine, where each methyl had been replaced by a benzo-group.[45] In the series of symmetrical and unsymmetrical dyes which have been already referred to, the introduction of a 4,5- or 6,7-benzo-group into the benzothiazole nucleus was included.[16,17] In general, symmetrical thiacarbocyanines with 4,5-

benzobenzothiazole nuclei absorbed at a longer wavelength than their isomers with 6,7-benzobenzothiazole nuclei;[46] there was a similar relationship in dyes of the thia-2'- and thia-4'-cyanine series, whilst three cyanines, in which one or two 4,5,6,7-dibenzobenzothiazole nuclei occurred, absorbed, as expected, at a longer wavelength than the corresponding cyanines, having one or two 4,5- or 6,7-benzobenzothiazole nuclei.[47] Symmetrical thiacarbocyanines with two 4,5- or 6,7-benzobenzothiazole nuclei absorbed at a longer wavelength, by 530 Å and 570 Å, than the isomeric compound having two perinaphtho-1,3-thiazine nuclei, and similarly with the thiadicarbocyanines.[48]

The presence of hydrogenated benzo-groups in symmetrical dibenzothiacarbocyanines led, as compared with the dibenzothiacarbocyanines, to a hypsochromic shift of absorption.[49] Thus a thiacarbocyanine with 4,5,4',5'-bis(tetramethylene) groups absorbed at a shorter wavelength by 210 Å than one with 4,5,4',5'-dibenzo-groups.[50]

In seven types of symmetrical cyanines having 6-halogenobenzothiazole nuclei, the two halogen atoms led to a bathochromic shift of 50–100 Å, and the shift was about the same for chlorine as for bromine atoms, whilst two bromine atoms had much less effect than two benzo-groups. Hence it was evident that the influence of weight is unimportant as compared with other factors.[51] Introduction of a 6-nitro-group into the benzothiazole nucleus to give a series of cyanines, II



(II)

(n=0, 1, or 2), led to marked deviations and the series was convergent, effects which were ascribed to the non-degeneracy of the extreme resonance configurations.[19, 21]

The introduction of electropositive substituents into the 6,6'-positions of 3,3'-diethylthiacarbocyanine iodide caused a bathochromic shift of absorption, which increased on ascending the series H, Cl, Br, CO_2Me, Me, I, OMe, OEt, OH, SH, $NHSO_2C_6H_4Me$, NHCOMe, SMe, NHCOPh, NH_2, S-, NHMe, NHEt, $NHPr_2^n$, NMe_2, $NEtCH_2Ph$, O-, NEt_2, NPr_2^n. It was attributed to the appearance of resonant structures with a negative charge on the carbon atoms of the polymethin chain.[52] These dyes were discoloured by caustic alkali more slowly than was the unsubstituted parent dye. Introduction of electronegative

substituents into the 6,6′-positions likewise had a bathochromic effect, which increased on ascending the series H, $\overset{+}{N}H_3$, $\overset{+}{N}HEt_2$, $SO_2\bar{O}$, SO_2OMe, SO_2OEt, SO_2NH_2, SO_2NEt_2, SO_2OPh, SO_2NHPh, $SO_2\bar{N}Ph$, $SO_2NH(\alpha\text{-}C_{10}H_7)_2$, CN, $CONH_2$, CO_2H, $C\bar{O}\bar{O}$, CO_2Et, NO_2. This shift was explained by the appearance of resonant structures with a positive charge on the carbon atoms of the polymethin chain. The compounds of this series were more rapidly discoloured by caustic alkali than was the unsubstituted dye.[53] According to the resonance theory, destruction of the symmetry of a dye molecule leads to a hypsochromic shift of absorption. On introducing two 6,6′-substituents of opposite character into the thiacarbocyanine molecule, the hypsochromic shift increased with increase in this difference of character. The values found and calculated for the absorption maxima of derivatives with the following pairs of substituents were given: 6-OH/6′-MeO, 6-NO_2/6′-NMe_2, 6-NO_2/6′-OH, 6-NO_2/6′-OAc, 6-NO_2/6′-$NHSO_2C_6H_4Me(p)$, 6-NO_2/6′-NH_2, 6-NO_2/6′-NMe_2.[54] Into the molecule of *NN′*-diethylthiacarbocyanine iodide, and into those of its *meso*-methyl and *meso*-ethyl derivatives, two methoxy groups were introduced in various positions. In the 4,4′- and 7,7′-positions they exerted only a slight bathochromic effect but in the 5,5′- and 6,6′-positions there were larger, and approximately equal, shifts, whence, similarity of resonance structures for the pairs 4,4′- and 7,7′-, on the one hand, and 5,5′- and 6,6′- on the other, was deduced.[55] Similarly introduction of dimethylamino-groups into the 7,7′-positions of the thiacarbocyanine molecule produced a smaller bathochromic shift than in the 5,5′- or 6,6′-positions.[56] Further bathochromic shifts occurred in passing from di- to various tetra-methylthiacarbocyanines, some of which had also a *meso*-methyl or -ethyl substituent. In each series, the 5,6,5′,6′-tetramethyl dyes absorbed at the longest wavelengths.[57] With two hydroxy-groups, on the contrary, introduction into the 4,4′-, 7,7′-, 5,5′-, and 6,6′-positions gave bathochromic shifts of 290 Å, 50 Å, 370 Å, and 420 Å, respectively. Introduction of acetoxy-groups into the 4,4′-, 5,5′-, and 6,6′-positions caused a hypsochromic shift.[58] It was noted that when tertiary butyl groups were introduced into the 5,5′- or 6,6′-positions of a symmetrical thiacarbocyanine, and of its *meso*-methyl and -ethyl derivatives, their effect was about the same as that of methyl groups.[59]

Symmetrical thiacarbocyanines, having two groups ·NH·CS(NHR) or ·NH·CNR(SEt) in the 6,6′-positions, had their absorption maxima

at a shorter wavelength than that of the 6,6′-diamino-derivative.[60] Whereas an *NN′*-dimethylthiacarbocyanine with 5,5′-diamino-6,6′-dimethyl substituents had its absorption maximum at 5945 Å, replacement of the two amino- by two dimethylamino-groups caused a hypsochromic shift of 195 Å: this was imputed to disturbance of the coplanarity of the chromophore by the two bulky substituents.[61] Absorption maxima were tabulated showing the effect of introducing 5,5′-dimethoxy-groups into symmetrical *NN′*-diethylthiacarbocyanines, having in the 6,6′-positions H, NH_2, NHMe, NMe_2, NHCOMe, NMeCOMe, $NHSO_2 \cdot C_6H_4 \cdot Me(p)$, or $NMeSO_2 \cdot C_6H_4 \cdot Me(p)$. The bathochromic effects of the two pairs of substituents were additive, but introduction of 5,5′-dimethoxy-groups into a thiacarbocyanine having 6,6′-bis-diNMe_2 groups gave a hypsochromic shift, which was attributed to steric interaction between NMe_2 and the *o*-OMe group.[62] The absorption maxima of twelve symmetrical thiacarbocyanines, having in the 5,5′-positions H, NH_2, NHCOMe or NMe_2, and in the 6,6′-positions H, Me, or CMe_3, the *NN′*-dialkyl groups being Me or Et, were recorded. Only the NMe_2 group caused lowering of the intensity of absorption. Its effect was lessened by introduction of 6,6′-dialkyl groups. These results also were explained by the supposition that introduction of a large group, *o*- to NMe_2, caused the latter to move out of the plane of the ring, so that its influence on absorption was eliminated. It was assumed that, with these particular alkyl groups, the electronic effect could be neglected.[63] A hypsochromic shift of 150–220 Å, which occurred on acylation of 6,6′-diaminothiacarbocyanine, increased with the nature of the acyl groups in the order $CO_2Me < COMe < COH$. It was considered to be related to increases in the diversion of electrons from N to CO, resulting in a diminution of electron shifts from N to the chain.[64]

On an unsubstituted thiacarbocyanine ($\lambda_{max.}$ 5580 Å), introduction of 6,6′-dinitro-groups conferred auxochromic activity ($\lambda_{max.}$ 5840 Å), so that these groups must lie in the same plane as the nucleus. Their effect was suppressed by introduction into the 5,5′-positions of Me, Et, or CMe_3 groups, especially by the last large groups: the absorption maxima lay at 5820 Å, 5800 Å, and 5650 Å, respectively.[65]

(*4*) *Dyes of Other Series*

An especially interesting effect of saturation of the nuclei is the hypsochromic shift on passing from thiazole to thiazoline, which was

described in 1936 as yielding cyanines which absorbed at a shorter wavelength than those derived from any other heterocyclic base.[66] At about the same date it was noted that certain 4-substituted-oxazolo-2′- and -thiazolo-2′-cyanines had the same absorption whether the substituent was methyl or phenyl. Introduction of a 5,6-benzo-group into the molecule of a thiazolo-2′-cyanine caused a bathochromic shift of 180 Å, the absorption maximum approximating to that of the isomeric thia-2′-cyanine.[67] Many years later it was found that a bathochromic shift occurring on introduction of either electropositive or electronegative substituents into the the molecule of a symmetrical thiazolocarbocyanine, or of its *meso*-methyl or -ethyl-derivatives.[68] Cyanines containing 4,5-disubstituted thiazole nuclei proved to be more soluble in organic solvents than were analogous compounds containing 4-arylthiazole, benzothiazole, or naphthothiazole nuclei, a fact which was attributed to the non-planarity of the molecules of dyes of the first type. Whereas the introduction of substituents into the 4-aryl group had little effect on absorption, substitution in a 5-phenyl group did have an effect.[69] A comparison of the absorption maxima of cyanine dyes having a 4-aryl- or a 4,5-disubstituted-oxazole nucleus threw some light on the spatial configuration of the 4- and 5-aryl substituents. Both 5-aryl and 4,5-diaryl substitution had a strong bathochromic effect, but 4-aryl substitution had less, whence it was concluded that the 5-aryl group was co-planar with the oxazole nucleus and thus able to contribute to the resonance hybrid.[70] Complex cyanines and merocyanines, having 4,5-disubstituted thiazole or oxazole nuclei and, as central nucleus, a 3-ethyl-4-oxothiazolidine (XV-5-B and L), were regarded as having two separate resonance systems, both of them capable of causing absorption.[71]

B. On the Chain

(*I*) *Trimethincyanines*

An examination of five pairs of symmetrical thia- or selena-carbocyanines showed that the introduction of a *meso*-methyl substituent caused a hypsochromic shift, which could be as much as 200 Å, but with an oxacarbocyanine a *meso*-methyl substituent resulted in a bathochromic shift of 60 Å.[72] With a symmetrical thiacarbocyanine, replacement of *meso*-methyl by *meso*-ethyl gave a bathochromic shift of 50 Å but no further shift occurred on the introduction of higher alkyl groups

up to n- and iso-amyl. Replacement of the central hydrogen atom by benzyl and by phenyl gave a hypsochromic shift of 75 Å, and a bathochromic shift of 25 Å, respectively. Similar results were obtained with 4,5,4′,5′- and 6,7,6′,7′-dibenzo-compounds, and in the selenacarbocyanine series, but again the oxacarbocyanines were exceptional.[46] Many years later, the hypsochromic action of a *meso*-methyl substituent in thia- and selena-carbocyanines was attributed to its hyperconjugative effect. It was considered that in the oxacarbocyanines the effect might be annulled by hydrogen-bonding.[73,74]

By a comparison of the absorption spectra of certain *meso*-substituted thiacarbocyanines with those of the simpler related compounds, conclusions were drawn as to which was the planar principal resonance structure in each.[75] Absorption data for several α-substituted and αα′-disubstituted thiacarbocyanines were compared with those of the appropriate unsubstituted dye. They showed the decrease in intensity of absorption,[61,76] which had been recognised as typical of steric effects.

(*2*) *Penta- and Hepta-methincyanines*

Absorption maxima for an αα′-dimethylthiadicarbocyanine, and for eight β-methyl- and nine γ-methyl-dicarbocyanines, of the 2,2′-, 4,4′-, indo-, oxa-, selena- or thia-dicarbocyanine groups, were compared with those of the appropriate unsubstituted compounds. The β-methyl derivatives absorbed at a longer wavelength, by 30—190 Å, than the parent dye, and in six instances at a longer wavelength than the γ-methyl isomer.[77]

Absorption maxima for a β-, a γ-, a δ-methyl-, four ββ′-dimethyl-, and two βδ-dimethyl-tricarbocyanines, of the thia-, selena-, or thiazolino-tricarbocyanine classes, were likewise compared with the unsubstituted substances. Here the methyl group caused a greater bathochromic shift in the δ-position than elsewhere.[78]

(*3*) *Methincyanines*

The colour of chain-substituted methincyanines in relationship to the planarity of their molecules was considered in 1947. Two scale-drawings from this review are given in chapter III, Figure 1, where data as to absorption are included in Table I.

Absorption data for eleven *meso*-substituted thiacyanines were

compared with those of the unsubstituted thiacyanines. In this series, there was steric hindrance to planarity, which was manifested by a bathochromic shift of the absorption maximum and by a decrease in the intensity of absorption. Moreover the non-planar dyes had a lower melting point, and a greater solubility in alcohol than had the unsubstituted parent dyes, and they were also more readily decolorised by alkali than were these.[61,76] Subsequently similar large bathochromic shifts were noted on the introduction of methyl, 2-benzothiazolyl, phenyl, or *p*-nitrophenyl groups into the chain of methincyanines of various series, but a carbethoxy-group gave a small bathochromic shift in one instance and a hypsochromic shift in another.[79]

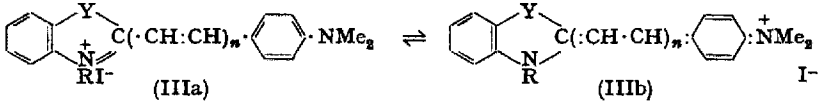
Abnormal colour changes which occurred in *meso*-substituted bis-2(3,5-diphenylpyrrole)methins on salt formation were attributed to loss of nuclear planarity of the molecule.[80]

6. Inclusion of Part of the Chain in a Ring

Chapter IX, Table I, includes absorption maxima, and the sensitising maxima which are related to them (see XVII-2-C) for thiacarbocyanines in which $\alpha\gamma$-substituents make the chain cyclic, and Table II in Chapter IX gives the latter property for thiadicarbocyanines in which part of the chain is cyclic.

7. *p*-Dimethylaminostyryl Salts, Analogues, and Related Bases

In 1930 absorption data were given for ten *p*-dimethylaminostyryl salts and for the higher vinylene analogues of two of them.[37] In 1937 the absorption maxima of nine *p*-dimethylaminostyryl salts were compared with those of their higher vinylene analogues, which lay at a longer wavelength by 500 Å.[81] In 1941 the resonance theory was used to explain why the red *p*-dimethylaminostyrylquinoline methiodide absorbs at 5220 Å but the yellow *p*-dimethylaminostyrylquinoline at



3960 Å. The salt could be represented by two alternative formulae, IIIa and IIIb (n=1, Y=CH:CH, R=Me), but it was not possible to give a plausible second formula for the base. The salt showed consider-

able deviation between λ_{max} observed and calculated. The shift of λ_{max} for a vinylene increment was 360 Å for the salt but only 150 Å for the base. The deviation for the absorption maximum of the salt was reduced on replacing the quinoline nucleus by a less basic one. The presence of the benzene ring favoured the state represented by IIIa but reduction of the basicity of the nucleus favoured IIIb. It was possible to arrange *p*-dimethylaminostyryl salts having certain heterocyclic nuclei in order of basicity by putting them in order of decreasing deviation of λ_{max}.[82] In the salt, III (n=1, Y=S, R=Et), progressively smaller deviations occurred as the ethyl group was replaced by phenyl and by *o*-nitrophenyl, and the smallest of all for the 6-nitro-derivative of III (n=1, Y=S, R=Et). With the *p*-dimethylaminostyryl salts, the deviations increased on lengthening the chain.[19] There was good agreement with the order of basicity of the nuclei as deduced from *p*-dimethylaminostyryl salts and from unsymmetrical dimethincyanines having a 2,5-dimethyl-1-phenylpyrrole nucleus, increasing deviation in both series indicating increased basicity of the variable nucleus. The basicity was expressed in terms of the relative stabilisations of the charged and uncharged forms of the nuclei.[23] Introduction of a 3-methyl substituent into a 2- or 4-*p*-dimethylaminostyrylquinolinium salt led, as with cyanines (see section 5-A.1), to crowding of the molecule and a consequent decrease in intensity of absorption. There was, however, a marked difference with the present 3-substituted salts, in that the shift of absorption maximum was hypsochromic.[9] The exceptionally high basicity of a particular 3-linked isoquinoline nucleus has already been mentioned (section 2); it was further manifested by the high deviation (1455 Å for a nitromethane solution) of 3-*p*-dimethylaminostyrylisoquinoline ethiodide.[26]

The correlation of non-planarity of the molecule with a bathochromic shift of absorption, and a decrease in intensity, applies only to dyes in which the extreme resonance structures differ only slightly in energy. Introduction of a substituent, in the α-position to the heterocyclic nucleus, into a *p*-dimethylaminostyrylbenzothiazolium salt might disturb planarity. Where the substituent was alkyl, a hypsochromic shift, with decrease in intensity, was noted for numerous such salts, and similarly for an α-phenyl group, though the shift was less. For a β-alkyl group, the shift was again hypsochromic but less than for α-alkyl. It was considered that the steric effects were reinforced by electronic influences.[61,83] Introduction of methyl, phenyl, *p*-nitrophenyl, carbe-

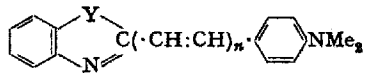
thoxy, or 2-benzothiazolyl into the α-position of *p*-dimethylaminostyryl compounds (cf. section 5-B.3) all gave hypsochromic shifts.[79]

TABLE I. Absorption Maxima for Some *p*-Dialkylaminostyryl Compounds and their Lower Vinylene Analogues[84]

Nature of base	Base	Absorption maxima (Å) in ethanol Sulphate	Ethiodide
IV ($n=1$, Y=O)	3940	4830	4950[a]
IV ($n=1$, Y=S)	4000	5100	5300
6,7-benzo-derivative of IV ($n=1$, Y=S)	3700[b]	5170	5370[a]
IV ($n=1$, Y=Se)	4030	5160	5370
IV ($n=0$, Y=O)	2950	3970	4000[c]
IV ($n=0$, Y=S)	3620	4320	4230
6-Me derivative of IV ($n=0$, Y=S)	3640	4350	4270[d]
6,7-benzo-derivative of IV ($n=0$, Y=S)	3700	4450	4300
IV ($n=0$, Y=Se)	3640	4390	4300

[a] Methiodide.
[b] Possibly an error, as the wavelength is shorter than for IV ($n=1$, Y=S)
[c] Ethoperchlorate.
[d] NEt_2 compounds.

Table I contains absorption maxima for some *p*-dimethylaminostyryl salts, the corresponding anhydronium bases, and their sulphates, and for the lower vinylene analogues of these three types of compound. In both series the absorption maximum of the base lay at a shorter wavelength than that of its sulphate or quaternary salt. The two series differed in that, in the former, the alkiodides of IV ($n=1$) absorbed at



(IV)

a longer wavelength than the corresponding sulphates; in the latter, the quaternary salts of IV ($n=0$) absorbed at a shorter wavelength than the sulphates, in four out of five instances. This was attributed to destruction of co-planarity of the molecule in quaternary salts of the latter series. The fifth instance, where the quaternary salt absorbed at a longer wavelength than the sulphate, was explained as due to the

lack of steric hindrance owing to the smaller radius of the oxygen atom as compared with sulphur and selenium.[84]

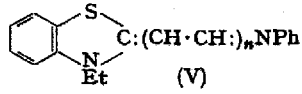
8. Anhydronium Bases

It was noted in 1940 that on passing from a base to the thia- or selenathia-cyanine which is its alkiodide, the bathochromic shift was about the same as on passing to an acid salt. The shifts were greater on passing from a trimethin base to a thiacarbocyanine or to an acid salt (1020 Å and 950 Å, respectively). Corresponding with the thia-2'-cyanine series, there were two types of base, with different absorptions.[85] In the same year, three symmetrical dyes of the benzothiazole series, a methin-, a trimethin-, and a pentamethin-cyanine, were compared with the three anhydronium bases[86] and the curves have been reproduced in an earlier chapter (see XI-1. Fig. 1). The information about the salts and bases[86] was summarised[87] and is given in Table II.

TABLE II. Absorption of Symmetrical Cyanines and the Corresponding Anhydronium Bases[87]

n	Cyanines of formula I Abs. max. (Å)	$\varepsilon_{max} \times 10^{-4}$	Corresponding bases Abs. max. (Å)	$\varepsilon_{max} \times 10^{-4}$
0	4230	8.45	3960	5.85
1	5575	14.8	4580	5.65
2	6500	22.9	4900	6.4
3	7680	24.6	5100	6.8

Each cyanine absorbed at a longer wavelength than the corresponding base. The bathochromic shifts which occurred on lengthening the polymethin chain were less in the bases than in the cyanines. Resonance was more restricted in the bases.[86] Whereas the symmetrical cyanines form a non-convergent, the bases form a convergent, series; ε_{max} is approximately constant for the bases.[20] The anhydronium base of an unsymmetrical dimethincyanine having a 2-methylindole nucleus absorbed at a longer wavelength than its methiodide.[86] Such reversed halochromism[88] was explicable on the basis of the resonance theory, according to which the internal energies of the two extreme structures were widely different (see XI-1). The dipole moments of the bases were higher than those calculated from the classical formulae.[86]



(V)

A series of amidine bases, V (n=0, 1, 2, or 3), mostly absorbed at a much shorter wavelength than their ethiodides or hydriodides and the vinylene shifts decreased on ascending the series. This was attributed to inhibition of degeneracy.[30]

9. Dyes in which One or More :CH· Groups of the Chain are Replaced by :N·

In 1924 a hypsochromic shift of 990 Å was recorded on replacement of the :CH· group of a 2,2′-cyanine by nitrogen,[89] whilst later instances, in 1937, were 1020 Å and 700 Å. With each of three $\alpha\beta$-diazatrimethincyanines (see XII-5), the principal absorption maximum lay at a shorter wavelength than the secondary maximum, whereas the reverse is usual with other cyanines. The principal absorption maxima of the $\alpha\beta$-diazatrimethincyanines lay at a shorter wavelength by 800 Å, 770 Å, and 820 Å than those of the corresponding trimethincyanines. $\alpha\gamma$-Diaza-groups had a more powerful hypsochromic effect: 2620 Å.[90]

The absorption maxima of ten *p*-dimethylaminoanils (see XIII-2-B) lay at a longer wavelength than those of the corresponding *p*-dimethylaminostyryl salts. Each anil had a single broad absorption band.[37]

According to an application of the resonance theory in 1951, the hypsochromic shift which occurs on replacing :CH· by :N· in the chain of cyanines is due primarily to the increased significance of the excited structure.[91] It was possible, with certain exceptions, to arrange various heterocyclic nuclei in order of basicity, through the shifts of absorption which resulted on replacement of :CH· by :N· in the chain of various cyanine dyes and quaternary salts.[92]

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CHAPTER XVII

Photographic Sensitisation and Some Other Properties and Uses of Cyanine Dyes

1. General

When the beautiful blue of cyanine was first observed, the compound was naturally thought of as a dye for textiles, but proved of no use because of its instability to light. Then in 1875 its power of making photographic material sensitive to light other than blue was discovered, in 1903 the practical utility of the isocyanines for this purpose was observed (see I-1), and it is because of their value as photographic sensitisers that compounds of the cyanine class have been so extensively exploited. For many years erythrosin was the only sensitiser, *not* belonging to the cyanine or related groups, that was in commercial use, and in Russia even that has been superseded by 3,3'-diethyl-4,5,4',5'-dibenzoxacarbocyanine toluene-*p*-sulphonate, which sensitised 2–4 times as strongly in the green.[1] Although it has been stated that some dyes which sensitise strongly are quite stable,[2] useful dyeing properties have been claimed for extremely few cyanines (see section 4). A few cyanines of certain groups have been found suitable for combating halation. This defect is especially troublesome with photographic plates, owing to the thickness of the glass, which reflects unwanted light, but it can occur also with film, and anti-halation layers (see section 5) are also used in multi-layer processes. From time to time, compounds of the cyanine group have been examined for possible use in chemotherapy but very few applications have been found (see section 6). One photographic firm, over a period of twenty-five years, was puzzled by small orders for the infrared sensitiser, dicyanine, and the demand was finally correlated with a publication[3] describing how, by looking through a screen of dicyanine, the eye is sensitised so as to perceive the human aura, which phenomenon may be used in medical diagnosis. All the foregoing uses are of minor importance compared

with that of photographic sensitation, which, with its ramifications, is considered first (see section 2). The chapter concludes with some additional properties of cyanines (see section 7).

2. Sensitisation

A. Methods of Applying the Sensitiser, and Factors Influencing Sensitisation

The optimum quantity of sensitiser varies from 5 to 100 parts per million of photographic emulsion. The longer the wavelength of sensitisation, the less is the amount of sensitiser required. If the optimum amount is exceeded, chemical fogging and desensitisation may result. In the past, scientific workers tested their dyes by bathing plates for about 3 minutes in an aqueous alcoholic solution, containing, e.g., 1 part of dye in 75,000 of solution, draining them, and exposing in a spectrograph.[4] In practically all patents on sensitising, the method of adding the dye to the emulsion before coating is preferred to subsequent bathing. As typical instances, the dye is dissolved in methanol or acetone, or in a mixture of acetone and pyridine, and the solution may be diluted with water; a volume containing 5–100 mg. of dye is slowly added, with stirring, to 1000 c.c. of gelatino silver halide emulsion, containing about 40 g. of silver halide, and stirring is continued until the dye has been completely dispersed, whereupon the emulsion is ready for coating. Fine grained emulsions may require a greater concentration of sensitiser solution than more coarsely grained emulsions.[5,6] In a study of the methods of adding the sensitiser, it was found that the maximum increase of sensitivity was given by addition just before coating.[7]

Whilst addition of potassium iodide to a dye-bath containing 3,3'-diethyl-9-methylthiacarbocyanine lessened the sensitivity which it conferred on a bathed plate, such a decrease did not take place on bathing a sensitised emulsion in potassium iodide solution; on the other hand, the latter treatment produced a greater decrease of the blue sensitivity.[8] The degree of optical sensitisation was not greatly affected by chemical sensitisers.[9]

Temperature has an effect on the distribution of spectral sensitivity. With various brands of photographic plates, the sensitivity between 6500 Å and 7500 Å was more than tripled on passing from room temperature to 70°. At the same time the tendency to fog was

increased. The increase of sensitivity at shorter wavelengths was less. Some plates seemed to show a maximum sensitivity at 60°.[10] The sensitivity of panchromatic and process emulsions was determined at 20°, —70°, and —180°. There was a relatively small drop in both the original and the conferred sensitivity from 20° to —70° and a large drop from —70° to —180°, but some sensitivity persisted even at —180°.[11] With eosin and Pinachrome Violet the red sensitivity was reduced more than the original sensitivity, whereas with pinacyanol they were equally reduced.[12] Subsequently spectral sensitivity was determined at 25°, —75°, and —185° for several commercial emulsions. For six that were optically sensitised, the efficiency of sensitisation decreased as the temperature was lowered, but with three of them the decrease did not begin till below —75°.[13]

The tendency to give chemical fog depends on the emulsion as well as on the nature of the sensitiser,[14] but both are important. Thia- and selena-carbocyanines sensitise more powerfully, and with less fog, than do carbocyanines having quinoline nuclei.[15] In fact thiacarbocyanines not only sensitise but also act as stabilisers; they are more independent of the nature of the emulsion than are the carbocyanines with quinoline nuclei.[16] It was observed that certain cyanines form complexes with silver nitrate, and that these gradually decompose with precipitation of silver. The capacity to form complexes was related to the fog-forming tendency, both increasing with increasing length of chain. Potentiometric titration of the dyes with silver nitrate could be used to determine their tendency towards fog-formation.[17] Subsequently the power of thirty-two symmetrical cyanines, with chains of various length, to form complexes with silver ions was studied: that and the fog-forming tendency increased with basicity of the dye as well as with length of chain.[18]

B. Adsorption of the Sensitiser

Some sensitisers have been examined chromatographically (see section 7).

For optical sensitisation, adsorption of the dye to the silver halide grains is of the first importance, and adsorption is essential if sensitisation is to take place.[19, 20] With certain dyes, there are some correlations between adsorption and strength of sensitising but in general these are not parallel properties.[20, 21] It was recorded in 1937 that the amount of dye which produces the maximum sensitisation is directly

proportional to the silver halide surface, whence it was concluded that, at the optimum concentration, the dye was adsorbed in a unimolecular layer.[22] The first layer of dye was supposedly adsorbed through the polar nitrogen atoms, with the molecules projecting upwards; a second layer might be oriented in the opposite direction. There were at least two states of aggregation, with different absorption and sensitising (see section 2-F).[23] Examination of seven cyanine dyes showed that each of them was adsorbed in two forms, which were revealed by two stages in the adsorption curve. It was suggested that the dyes were adsorbed as single molecules attached by the nitrogen atoms to the surface, and possibly lying flat, and partly as molecules oriented as units packed parallel, adsorbed edge-on, and again attached by the nitrogen atoms.[24] The physicochemical and photographic properties of five thiacyanines with 1–9 membered chains was studied. Adsorption on silver bromide increased with lengthening of the chain. At first adsorption was monomolecular. The aggregative state (see section 2-F) was manifested by another band in the region of longer wavelength.[25] Subsequently the heat of adsorption of sensitising dyes was computed and the area occupied per dye molecule was calculated. If only a unimolecular layer is present at saturation, the molecules must adhere to the surface edge-on. They appear to be stacked on the surface with their long axes parallel to it and with the planes of the heterocyclic nuclei projecting from it. Probably the edge nearest the surface is that containing the positive charge. With the cyanines, the dyes are held by van der Waals forces in addition to inter-ionic forces, whilst the merocyanines are held by van der Waals forces and ion-dipole interactions. Probably the van der Waals forces tend to make isolated sensitiser molecules lie flat on the silver halide but, as the concentration increases, they become arranged edge-on. The optimum amount of dye for sensitisation is usually one half to one third of the available surface.[20] In the saturated mono-layer, the molecules are oriented with their planes parallel and projecting away from the surface at an average intermolecular distance of about 4.6 Å.[21] On the other hand, a crystal analysis of one trimethincyanine (see section 7) suggested that the possibility of a double layer of head-to-tail cations should also be considered.[26]

According to an early calculation, only 7 % of the total grain area is covered by pinacyanol molecules.[27] One molecule of pinacyanol is adsorbed to approximately ten bromine atoms.[28] A recent estimate is that at normal sensitising concentrations half the grain is covered by

dye. Probably sensitisers of the cyanine classes are attached to the surface in islands of closely packed oriented molecules, with relatively bare intervening spaces.[29] The adsorption of twelve symmetrical cyanines by silver bromide grains of standard size, from a standard gelatin solution of definite p_H and p_{Ag} at 40°, increased with lengthening of the methin chain and with increasing basicity of the nuclei. The partial covering of the grain surface by dyes of low basicity indicated that it is heterogeneous, and that such dyes occupy only sites of high activity.[30] The suggestion was made that those *NN'*-dimethylcarbocyanines which had a much lower sensitising power than the *NN'*-diethyl analogues (see section 2-C) were adsorbed on the emulsion microcrystals in the *H*-state[31] (see section 2-F).

C. Maxima of Sensitisation of the First Type, and their Relationship with Absorption Maxima

It was recorded in 1874 that the sensitising maximum for visible light conferred by each dye approximates to the absorption maximum of a solution of the dye, but lies at a slightly longer wavelength (see I-1) and this applies also to sensitisers for the infrared. Optical sensitisers act very inefficiently, or not at all, for high energy quanta, such as X-rays and γ-rays, or for corpuscular rays, such as α-rays, protons, and electrons.[32] The relationships between absorption maximum, sensitising maximum, and chemical constitution have been extensively studied.

Examination of the sensitising maxima of four isocyanines in 1908 revealed that they lay at a longer wavelength by 100–150 Å, than the maxima of aqueous solutions of the compounds.[33] In 1920 the preparations of twenty isocyanines were described and spectrograms of their sensitising and absorption were published. An interesting fact that emerged was that sensitisation was depressed by the presence, in the 4-linked quinoline nucleus, of a 2-cyano-, 2-methyl, or 2-phenyl group.[4] A series of eighteen 2,2'-carbocyanines was similarly studied; the *NN'*-diethyl dye sensitised more strongly than the *NN'*-dipropyl, and that more strongly than the *NN'*-dibutyl dye, but the *NN'*-dimethyl compound was the weakest of all.[34] In the following year, the absorption and sensitising spectra of isocyanines having an amino-, acetylamino-, or cinnamoylamino-group in various positions in one or other of the nuclei were studied.[35,36] It was recorded in 1923 that whilst ten *p*-dimethylaminostyryl derivatives of heterocyclic salts were sensitisers, the *p*-dimethylaminoanils related to three of them were de-

sensitisers.[37] Absorption curves in three different solvents, and sensitisation curves were given for fifteen typical cyanines comprising representatives of the apocyanine, methincyanine, and trimethincyanine classes: the relative speeds of the sensitised material were compared with the speeds to blue light.[38] Sensitising and desensitising properties of thirty-two salts of the cyanine and related types were recorded: they included methincyanines, *p*-dimethylaminostyryl and *p*-dimethylaminocinnamylidene salts, also ten *p*-dimethylaminoanils, which last were all desensitisers.[14]

The introduction of substituents may influence the position of both absorption (see chapter XVI) and sensitising bands. The normal effect of weighting the nuclei is to cause a bathochromic shift. Thus eight thia-2′-cyanines with a benzo-substituent in the benzothiazole nucleus had their sensitising maximum at a longer wavelength by 100–200 Å than those without this substituent. Whilst two *NN′*-diethylthiacarbocyanines were powerful sensitisers, the corresponding *NN′*-dimethyl compounds were weak. An *NN′*-diethyl-*meso*-methylthiacarbocyanine sensitised powerfully and the corresponding *NN′*-dimethyl dye weakly.[39] A 4,5,4′,5′-dibenzothiacarbocyanine was a stronger sensitiser than the 6,7,6′,7′-dibenzo-analogue, and its *meso*-methyl derivative was used commercially.[16] Although symmetrical 2,2′-, oxa-, and thia-carbocyanines with *NN′*-dimethyl groups were weaker sensitisers than those with *NN′*-diethyl groups, the two types were about qeual with symmetrical benzimidazolo-, indo-, 1,3,4-thiadiazolo-, and thiazolino-carbocyanines.[31] It was noted that thiacarbocyanines with ·NH·CS(NHR) groups in the 6- and 6′-positions were weak sensitisers, whilst the corresponding compounds with ·NH·C(SEt)(NR) groups were good: this was attributed to reactivity of the latter groups with silver ions.[40] In the thiacarbocyanines series, most 6,6′-diacylamino-derivatives sensitised as well as the 6,6′-diamino-compounds, and did not fog or depress the blue sensitivity.[41] 7,7′-Bis(dimethylamino)thiacarbocyanines, including *meso*-methyl or -ethyl derivatives, were rather weak sensitisers.[42]

Just as the nature of the heterocyclic nuclei has a profound influence on the positions of the absorption maxima (see chapter XVI), so it has a parallel influence on the sensitising maxima. Another factor which influences both absorption and sensitising is the length of the chain linking the nuclei. The positions of both sets of maxima were recorded for tri-, penta-, and hepta-methincyanines of the 2- and

4-linked quinoline, the substituted indolenine,[43,44] the benzothiazole, thiazole, 4-methylthiazole,[45,46] and thiazoline series.[47] Subsequently the physicochemical and photographic properties of five symmetrical cyanines of the benzothiazole series, with one, three, five, seven, and nine methin groups, respectively, were compared.[25] Figure 1[48] illustrates the sensitising action of the first four members of this series. On passing from the *p*-dimethylaminostyryl quaternary salts of nine heterocyclic bases to their higher vinylene analogues, the sensitising maxima shifted 400–1000 Å towards the region of longer wavelength.[49,50]

An abnormality was noted with certain dicyanomethylene compounds (see XIV-13-B.1), where the sensitising maximum lay at a shorter wavelength than the absorption maximum.[51]

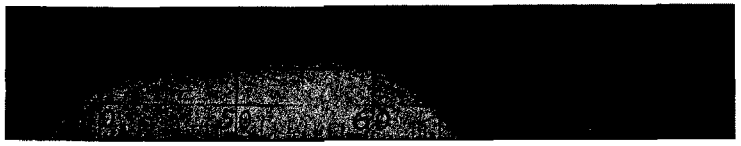
Although the sensitising maximum is usually at a longer wavelength than the absorption maximum of a solution of a dye, quantitative measurements of absorption and sensitising for orthochromatic and panchromatic film from 4000–7000 Å showed that the absorption of dyed silver bromide corresponds with its sensitisation.[52] Four emulsions sensitised with four different thiacarbocyanines likewise showed correspondence of their absorption and sensitising curves.[53] It was observed independently that the sensitising maxima of plates sensitised with erythrosin, phloxin, or rhodamine B lie at the same wavelengths as the absorption maxima of the dyes when adsorbed on to a layer of sublimed silver bromide, a method which avoided the difficulty of measuring absorption in turbid media.[54] Many years later, when absorption and sensitising curves were given for *meso*-ethyl-5,5′-dihalogenothiacarbocyanines, the dyes were adsorbed on silver bromide from alcoholic solutions: the halogens were fluorine, chlorine, bromine, and iodine.[55]

D. Sensitisation to the Infrared

As early as 1910, there were presented infrared landscape photographs, which were taken on plates sensitised with pinacyanol, with a filter to cut out light of wavelength shorter than 7100 Å. They showed the dark sky and light foliage which are characteristic of infrared photographs.[56] Although this light appearance of green leaves has been attributed to the reflecting power of chlorophyll for infrared light, it is in fact caused by infrared fluorescence at 7380 Å.[57] The use of dicyanines (see I-1; I-3-G) gave sensitising to 9000 Å or beyond,[58] the practical limit being 9800 Å.[59] Kryptocyanine (see I-3-F) with its



A.



B.



C.



D.

Fig. 1. Wedge spectrograms of sensitising by cyanines having two benzothiazole nuclei. (A) Chloride emulsion dyed with methincyanine; (B) bromide emulsion dyed with trimethincyanine; (C) bromide emulsion dyed with pentamethincyanine; (D) bromide emulsion dyed with heptamethincyanine. [From Hamer[48] Plate 2. By courtesy of the Chemical Society.]

sensitising maximum at 7430 Å, was stable and easy to use. To obtain the maximum sensitising, only one part of dye in 500,000 parts of emulsion was needed.[60] Neocyanine (see XV-3-A) was applied in 1928 to the photography of lines between 10,000 Å and 10,750 Å.[61] It led to no appreciable advance in the study of infrared spectra,[59] partly because of the discovery of the heptamethincyanines (see chapter VIII), which sensitised much more powerfully. One of these, xenocyanine (see VIII-2-A), with its maximum at 9600 Å, was useful for the range 8000–11,000 Å. Through these dyes infrared arc spectra of numerous elements were photographed and new lines were discovered.[59] Not only did the heptamethincyanines sensitise powerfully but they were relatively stable and did not cause chemical fog.[15] By use of cyanines with nine- and eleven-membered chains (see VIII-1, 7, and 8), plates sensitive to 13,600 Å were made.[62] The keeping qualities of such plates was poor and decreased with increasing wavelength.[63] They should be stored at a low temperature and hypersensitised with ammonia just before use.[59] Such hypersensitisation increased the speed 4–6 times.[64]

Owing to the penetrating power of infrared light, photography by use of it, with a filter to cut out the light of shorter wavelength, has had applications in medicine, plant pathology, and microscopy,[65] in the photography of old documents,[66] and of fossils which are opaque to visible light,[67] as well as for distance photography. Whilst infrared light penetrated haze, it was somewhat scattered by fog particles.[68–70] Specialised emulsions have been described for various spectral regions, including the ultraviolet and infrared.[71–74] A silver halide emulsion, which contained one sensitiser for the yellow-green and another for infrared light, with a sensitising gap of 5000–6200 Å, was recommended as a dual purpose emulsion.[75]

It appeared that infrared sensitisers, such as pinacyanol, kryptocyanine, or neocyanine, reduced silver nitrate in neutral solution, one mol. of dye giving 1 Ag.[76] In alkaline solution, one mol. of sensitiser produced 4 Ag by immediate reduction, and more silver slowly.[77] The mechanism of the action of red and infrared sensitisers was regarded as a true photochemical reaction of dyes unstable to light. The dyes, which were adsorbed on silver chloride, could be removed by treatment with ammonia. By exposure to infrared light, however, silver was formed, and the colour was then no longer restored by ammonia.[78] An emulsion sensitised with neocyanine became less sensitive on treatment with ammonium salts, owing to reduction of alkalinity; the same effect

was produced by salts having the same anion as the silver salt, owing to reduction in silver ions.[79] The number of silver atoms formed during exposure of infrared sensitised emulsions was determined and was related to the number of sensitiser molecules present. The figures indicated that for sensitising maxima of 7000 Å, 8500 Å, 9500 Å, and 10,500 Å, the respective dye acted at least 15, 90, 160, and 8 times, in causing decomposition of one silver bromide molecule.[80]

E. Fluorescence of Cyanines

In 1935 it was noted that an oxadicarbocyanine was a beautiful violet-red dye with magnificent fluorescence.[81] In the following year, alcoholic solutions of dyes of this type and their dibenzo-derivatives, five in all, were described as fluorescent. Of thirty-nine symmetrical cyanines, which were examined for visible fluorescence excited by ultraviolet radiation, only nine gave negative results: there was no fluorescence with cyanines of the 2'- and 4'-cyanine series.[82] In 1950 such monomeric fluorescence was studied for solutions of various symmetrical cyanines, as well as for hemicyanines and merocyanines, with chains of various lengths. For the twenty-seven compounds examined, the wavelength of fluorescence was longer, by 100–910 Å, than that of absorption. The instances of non-fluorescence were usually amongst the first members of series and some steric factor was regarded as responsible.[83] Carbocyanines derived from the 7-methiodide of 2,3,3-trimethyl-3*H*-1,7-diazaindene differed from those derived from its 1-methiodide in showing brilliant fluorescence in solution.[84]

On the other hand, fluorescence of a different kind has been described. When an aqueous solution of a 2,2'-cyanine became sufficiently concentrated, a new narrow absorption band appeared at 5725 Å, with fluorescence at a wavelength very slightly longer, and the relatively broad molecular absorption bands became weaker. At the same time, increase of viscosity occurred, and the solution became a gel, owing to polymerisation.[85–87] Such fluorescence at almost the same frequency as the exciting radiation was called resonance fluorescence. Its occurrence with a solution had been unknown before[88] and cyanines are unique in showing it.[89] The sharp absorption band of 2,2'-cyanine has been called the *J*-band.[90]

A comparison was made between the fluorescence of 1,1'-diethyl-2,2'-cyanine chloride and that of Quinoline Red chloride. With a

monomer, such as the latter, the fluorescence in solution was only slightly sensitive to foreign substances, but with reversible polymers like the former (see section 2-F), it was very sensitive, owing to propagation of excitation energy in the polymeric molecule. Formulae for determining the degree of polymerisation were proposed, and this was estimated at 10–10^5, according to the dye concentration.[91] The occurrence and behaviour of the narrow absorption and fluorescence band of 1,1′-diethyl-2,2′-cyanine chloride was studied with thin films deposited on glass. It was dependent on the presence of water, and an attempt was made to determine the number of water molecules required per dye molecule for polymerisation.[92] The fluorescence and absorption of 1,1′-diethyl-2,2′-cyanine chloride were examined in various solid solutions and at various concentrations. The fluorescence occurred not only in the polymerised state, but also when the dye was embedded in a medium such as an aqueous gelatin solution, and it was concluded that it is not necessarily connected with polymer formation.[93] The resonance fluorescence of cyanines is quenched by non-planar dyes (see section 2-G). These capture the energy of excitation and it undergoes thermal degradation.[29]

F. Polymerisation and Sensitisation of the Second Type

The absorption spectra of some trimethincyanines were observed in 1936 to be strongly modified by the solvent, and water played an exceptional part. That the solvent can change the degree of polymerisation of the dissolved dye was concluded from measurements of the partition coefficient between two solvents[94] In the following year it was recorded that dyes of the 2,2′-cyanine and 2,2′-carbocyanine classes show in aqueous solution absorption bands which vary considerably in position and intensity with varying concentration: this was ascribed to ionic dissociation, followed by polymerisation. In dilute solution polymerisation was induced by addition of salts. The increase in viscosity supported the theory. Changes of temperature, as well as of concentration, had an effect,[96] polymerisation being favoured by lower temperatures and higher concentrations.[95] Dispersions of 1,1′-diethyl-2,2′-cyanine chloride in sodium chloride solutions were independently studied, and it was suggested that the dissolved state was succeeded by a short molecular phase, and that by the formation of very thin threads of dye.[96] The observers in both countries noted the development of a

new band of absorption and fluorescence (see section 2-E). At varying concentrations the 2,2′-carbocyanine chloride showed different absorption bands, which were attributed to monomolecular, dimolecular, and polymolecular forms. As the viscosity was not markedly raised at the higher concentrations, the presence of spherical particles was inferred. Certain cyanines showed a new absorption band, in which a great number of dye molecules was believed to be involved; water was concerned in the production of this, whilst sodium chloride induced instability and crystallisation.[97] It was suggested that at least one water molecule was present between each pair of dye molecules.[98] It was estimated that the polymers were composed of at least 150 individual dye molecules, which were about 4 Å apart.[99] Figure 2 is a diagram of

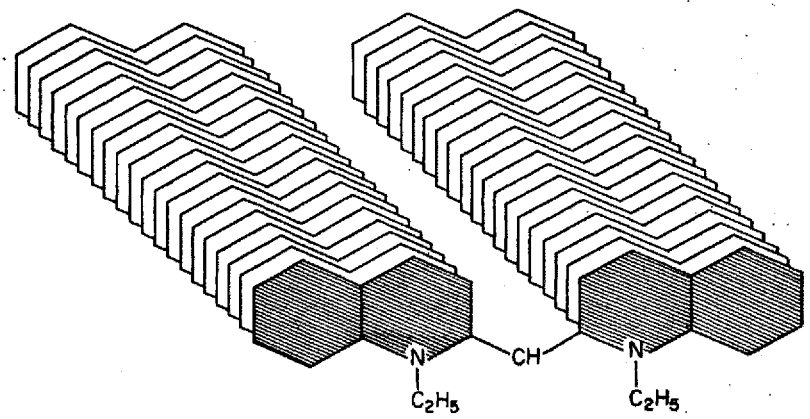


Fig. 2. Type of giant molecule postulated by Scheibe[88] [From Dickinson.[102] By courtesy of the author and the Royal Photographic Society].

the type of giant molecule of 2,2′-cyanine that was postulated. These giant ions, which were present at great concentrations, were regarded as dissociating on warming or dilution, but this reversible polymerisation took place only in aqueous solution. Absorption curves were given for 3,3′-diethyl-*meso*-methylthiacarbocyanine chloride at different temperatures. The polymerisation point was shifted to a lower concentration by adsorption of the dye to surfaces.[88] Reversible dye polymerides were considered to be important in sensitisation. When a photographic plate was immersed in an aqueous solution of 2,2′-cyanine chloride, it was supposed that the unimolecular form was adsorbed initially and the polymerised form after about 30 minutes. Not only

was water important, but also the nature of the *N*-alkyl groups: the polymeric form of 1,1'-diethyl-2,2'-cyanine iodide was more stable than that of the dimethyl analogue. On immersing dyed plates in water, there resulted a polymeric dye, which sensitised at a long wavelength, corresponding with absorption at a long wavelength, but sufficient time must be allowed for the dye to assume polymeric addition to silver bromide.[100] The degree of aggregation can be measured by the osmotic pressure, conductivity, and diffusion. Hence it was concluded that many dyes exist as dimeric ions in dilute solutions.[99,101] It was recorded that erythrosin sensitised immediately, but a merocyanine, which was believed to polymerise, produced no sensitisation until a certain quantity had been reached.[102] In 1950 the changes of absorption which occur with 2,2'-cyanine were summarised as follows. A new band develops at high concentrations and possibly association of two molecules takes place. Further concentration causes development of the *H*-band, due to *H*-aggregate, which is hypsochromic to the dimeric band. At high concentrations a very sharp, intense band, the *J*-band, appears at a longer wavelength than the monomeric band, and this is associated with the colloidal nematic state. The changes monomer → dimer → *H*-aggregate occur with ease in all planar cyanines but the occurrence of *J*-aggregation is more restricted. It takes place more readily on the grain surface than in solution.[20]

In 1937, again, the same problem was approached from the view point of the photographic results. By means of a special spectrophotometer, where bleaching of the complex was avoided, absorption measurements were made on emulsions sensitised with a thiacarbocyanine. It was concluded that there were two types of adsorption of cyanines to silver bromide, molecular and aggregated. Emulsions sensitised under suitable conditions could show sensitivity in different spectral regions, corresponding with the characteristics of these two states, as was illustrated by spectrograms.[53] In 1939 it was recorded that *meso*-alkylcarbocyanines, besides showing sensitisation of the first type, in which the maximum is at a longer wavelength by 250–500 Å than the absorption maximum, also showed sensitisation of a second type. In this, for the twelve dyes examined, the sensitising maximum was at a longer wavelength by 700–1150 Å than the absorption maximum, the sensitisation curve falling off sharply beyond the maximum. It was noted that instances of such sensitisation at an unusually long wavelength were to be found in the patent literature. The six sensitisa-

tion curves in Figure 3 are those given for 3,3'-diethyl-*meso*-methylthiacarbocyanine iodide, the first five showing sensitisation of the first type for the five experimental emulsions of Table I, and the sixth curve

TABLE I.[103]

Emulsion (%)	A	B	C	D	E	R
Chloride	98	80	10	—	—	—
Bromide	2	20	90	98	96	
Iodide	—	—	—	2	4	

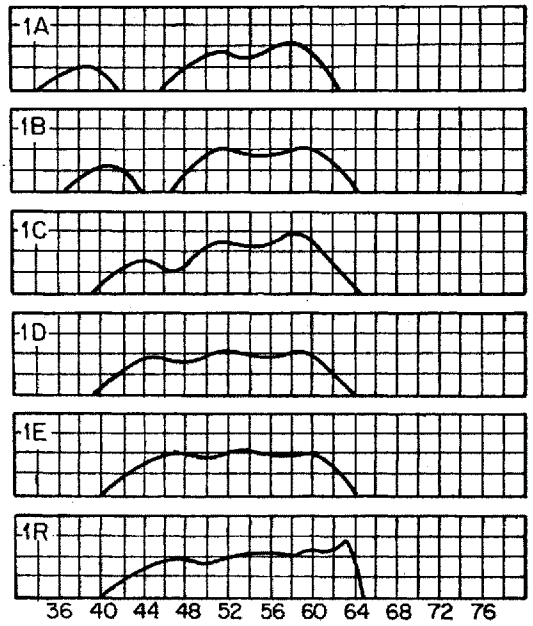


Fig. 3. Sensitisation curves for 3,3'-diethyl-*meso*-methylthiacarbocyanine iodide. [From Schwarz.[103] By courtesy of the author and the Journal.]

showing sensitisation of the second type. This second type of sensitisation was favoured by circumstances which favour adsorption, such as increase of concentration, excess of bromide, and ripening the emulsion by melting in the presence of the dye. It was manifested only in iodo-

bromide emulsions and was attributed to molecular aggregates greater than those which give sensitisation of the first type.[103]

In seven instances it was recorded that the position of maximum absorption of a dried film of dye, deposited from aqueous solution on a support, was the same as the position of maximum sensitising.[104] Another observer found that the absorption of most dye films deposited on glass did vary with the concentration of dye, the rate of drying, and the nature of the solvent. Layers of dye deposited on glass from concentrated solutions were examined for thirteen thiacarbocyanines and sodium erythrosinate. One of them, *meso*-ethyl-3,3′-dimethyl-4,5,4′,5′-dibenzothiacarbocyanine halide, formed two differently coloured layers, and that was the only one that gave sensitisation of the second type. The two absorption bands which characterised these layers were considered to correspond with sensitisation of the first and second types.[105] Absorption maxima for this dye and for pinacyanol chloride in various media and at various concentrations were given. In organic solvents, or in dilute aqueous solutions, the thiacarbocyanine showed one molecular band. In water at higher concentrations, or in the presence of lyophilic colloids, there was a second band at a shorter wavelength, the polymeric band. When the dye was deposited on glass, or in the presence of electrolytes, or of lyophilic colloids at higher concentrations, there was a third band at a longer wavelength. This approximated to the sensitisation spectrum of the dye on silver bromide and represented an aggregated state.[106]

The absorption spectra of certain thia- and selena-carbocyanines, which show sensitisation of the first type, have two maxima, of which the one at shorter wavelength was attributed to a polymeric state of the dye arising in aqueous solutions. The bathochromic shift on passing from the absorption maximum in water to the sensitising maximum at shorter wavelength was of the same order as that on passing from the absorption maximum in an organic solvent to the molecular sensitising maximum. Besides these two absorption maxima, a third band, at a longer wavelength, was only observed with dyes capable of sensitisation of the second type. All states of the dye that arise in solution are effective for sensitisation.[107] According to a subsequent summary, dilute solutions of *meso*-ethyl-3,3′-dimethylthiacarbocyanine bromide showed the molecular-, or *M*-, absorption band. As the concentration increased, the shoulder of the curve developed, becoming the dimer-, or *D*-, band. At a concentration of 10^{-2} molar, the *H*-band (hypsochromic to the

M-band) was observed. In the presence of electrolytes, the *J*-band, indicating a highly aggregated form, appeared. In the molar state the dye is free to wander, but the dye for *H*- and *J*-sensitisation is firmly held.[89]

An investigation of the capacity of over five hundred dyes to produce sensitisation of the second type showed that it is by no means manifested to the same extent by different sensitisers. It is inherent in dyes which in the presence of electrolytes, or on evaporation, assumed a highly aggregated state, with a characteristic absorption spectrum. It was studied for thia-, and for some selena-, carbocyanines, and occurred especially with *meso*-substituted derivatives. 6,6′-Disubstituted, and still more 5,5′-disubstituted, dyes showed it: the substituents in order of decreasing favourable influence were PhCO, MeO, Me, EtO, Cl, AcO, MeS, HO, AcNH, NH_2, NR_2. *meso*-Alkyl-3,3′-dimethylthiacarbocyanines, both unsubstituted and 6,6′-disubstituted, showed it; so did *meso*-alkyl-3,3′-diethylthiacarbocyanines and their 5,5′-disubstituted derivatives, but it was weaker when higher alkyl groups occupied the 3,3′-positions. Selenacarbocyanines had a stronger tendency towards sensitisation of the second type than had thiacarbocyanines.[108] It is interesting that thiacarbocyanines with 4,5,4′,5′-bis-(tetramethylene) groups, unlike those with 4,5,4′,5′-dibenzo-groups, do not give sensitisatoin of the second type.[109] Comparison of 1,1′-dimethyl-2,2′-cyanine chloride and Isoquinoline Red in respect of light absorption, sensitising, osmotic pressure, and electric conductivity, led to the conclusion that the former dye is aggregated and the latter monomeric. This may be due to the non-planar structure of the latter, and planarity may determine power of aggregating.[101] A salting-out technique was applied to obtain the polymeric forms of eight thiacarbocyanines. The polymers, which had narrow absorption bands, were considered to have electronic coupling, with electric polarisation of the band along the polymer axis. As already noted, the nature of the emulsion is important for giving sensitisation of the second type.[110] For three 1,1′-dialkyl-3,3,3′,3′-tetramethylindocarbocyanines, the tendency to give sensitisation of the second type increased on passing from 1,1′-dimethyl to 1,1′-diethyl to 1,1′-dipropyl.[31]

G. Effects of Non-Planarity of the Dye Molecule

An examination of four 2,2′-cyanines in 1937 revealed that although all of them were adsorbed by silver bromide, only two sensitised.

Those which gave a negative result had a 3,4-benzo-substituent in one quinoline nucleus, and the lack of sensitising was attributed to the steric effect of that group.[53] Possible forms of the planar unsubstituted 2,2'-cyanine molecule were considered.[88] In 1940 steric inhibition of planarity of the dye molecule was suggested as a cause both of modified spectral absorption and of inefficient sensitisation.[111] The observation that non-planar dyes are less efficient sensitisers than planar ones applies only to co-planarity of the skeleton. Non-planarity diminishes both intensity of absorption of light and adsorption, but these causes are insufficient to account for low sensitisation (see section 2-I). Anti-sensitisers (see section 2-H) are non-planar.[20] A study of the spatial configuration, absorption, and sensitisation of cyanine dyes led to the conclusion that it is logical to regard the dyes as a continuous series between two extreme types. Whereas marked non-planarity may affect both absorption and sensitising, a lesser degree of non-planarity may have little effect on the absorption whilst depressing sensitisation to a greater extent.[112]

H. Supersensitisation and Anti-Sensitisation

The term hypersensitisation, which has been in use for over thirty years,[113] covers the increased sensitivity which is conferred on colour sensitised photographic material by treatment with water or aqueous ammonia, or certain other agents. It is an unstable condition, which depends on altering the sensitivity by increasing the silver ion concentration or decreasing the hydrogen ion concentration. Whether the colour-sensitivity is increased more than the blue-sensitivity depends on the nature of the emulsion.

The word supersensitisation was originally applied to the same effect[113] but was used in another sense in 1937[114, 115] to describe a remarkable phenomenon, of which the first recorded observation was in 1918,[116] when the improvement of the sensitising power of pinacyanol, effected by addition of auramine, was noted. Supersensitisation consists in the use of a sensitising mixture, which gives a result superior to the sum of the actions of the components taken separately. The first patents referred to the use of two dyes, of which the one used in greater amount was called the sensitiser and the one used in lesser amount the supersensitiser. Subsequently the term supersensitising combination was introduced: the sensitiser and supersensitiser might be indistinguishable, the proportions varying from 10:1 to 1:10.[117] It has been

recorded that the optimum effect may be obtained at a molar ratio of 1 : 100 and a detectable effect at 1 : 1000. Supersensitisation increases the strength of the band, or may give it a bathochromic shift of 100–200 Å and broaden it. The former type of action is liable to occur with methincyanines.[102] Most sensitiser/supersensitiser combinations are highly specific. The aggregated state is particularly responsive to supersensitisation, but this phenomenon is not limited to dyes showing *J*-bands on silver halide grains. When sensitising dyes fluoresce in the *J*-

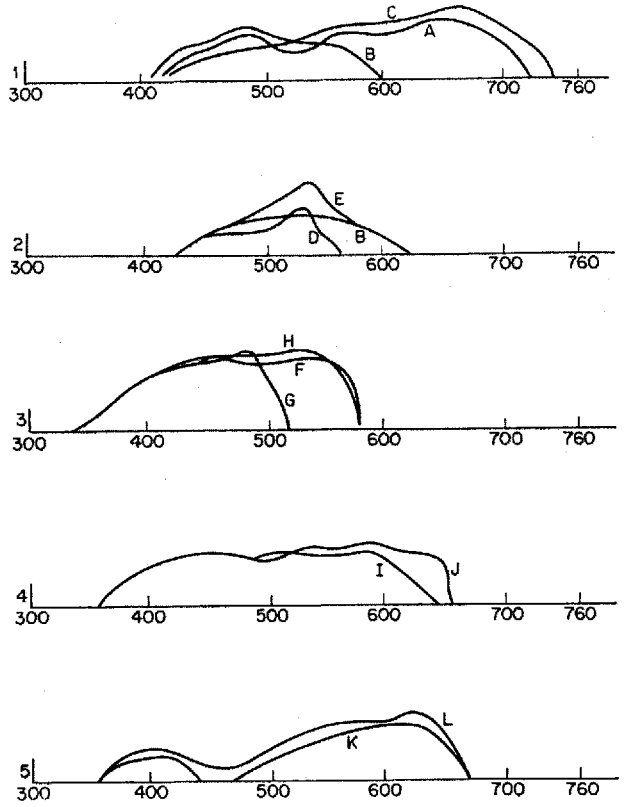


Fig. 4. (1) A. Pinacyanol; B. dialkylaminostyryl derivative of alkyl quaternary salt of simple nitrogen-containing heterocyclic base; C. combination of these two.[114]
(2) D. 2,2′-Cyanine; B. as B above; E. combination of these two.[115]
(3) F. 9-Ethyl-3,3′-dimethyloxacarbocyanine iodide; G. 3,1′-diethyl-4-phenyl-oxazolo-2′-cyanine iodide; H. mixture of these two.[120]
(4) I. 3,3′-Diethyl-9-methylselenacarbocyanine bromide; J. the same with 6-acetoxyquinoline.[121]
(5) K. 3,3′-Diethyl-5,5′,7-triphenylthiazolocarbocyanine iodide; L. the same with cadmium chloride.[122]

state on the grain, this fluorescence is quenched by supersensitisers, to an extent related to their efficiency as supersensitisers. Dyes like thiacarbocyanines, of which the spectrum on silver halide resembles the molecular spectrum, are least susceptible to supersensitisation. There seems to be no close connection between the efficiency of a dye as a sensitiser and as a supersensitiser. Although non-planar dyes are devoid of sensitising properties, these may be induced by a supersensitiser.[20,29]

It was noted in 1939 that the action of a sensitiser might be increased by an organic compound which was not a dye. This effect was more general but was regarded as a kind of supersensitisation; the proportions suitable varied from 10:1 to 1:100.[118] It was recorded in 1957 that even inorganic salts could exert a supersensitising influence.[119] The curves in Figure 4 are copied from patents and illustrate supersensitisation. In a recent review of the methods and mechanisms of supersensitisation, supersensitisers that absorb at a longer wavelength, or at a shorter wavelength, than the sensitisers were considered separately. Evidence for incorporation of a supersensitiser in the dye polymer was adduced. The supersensitising action of bases, and of cationic, zwitterionic, and anionic substances was considered.[123]

The following is a brief summary of examples of supersensitisation that have been described. In the first patents on this subject, the sensitising action of a definite methin- or trimethin-cyanine was enhanced by means of a small amount of a heterocyclic *p*-dimethylaminostyryl salt.[114,115] Subsequently a heterocyclic base with a *p*-dimethylaminostyryl group,[124,125] or the higher vinylene analogue,[126] or α-aza-analogue[127] of such a base was used as supersensitiser. Together with numerous instances of a supersensitising combination consisting of a methin- and a trimethin-cyanine[117,120,128–138] is one comprising a tri- and a penta-methincyanine,[139] whilst a pair of methincyanines,[137] or a pair of trimethincyanines[138,140] were also patented. Methin- or trimethin-cyanines were supersensitised by use of di- or tetra-methinhemicyanines,[141,142] including salts with an anilino- or acetanilidovinyl group,[143] also a tetramethinhemicyanine was supersensitised by a base having a *p*-dimethylaminostyryl group.[124] A methincyanine was supersensitised by an anhydronium base of the trimethincyanine series,[144] and a trimethincyanine by one of the methincyanine[144] or dimethinhemicyanine series.[145]

Numerous dimethinmerocyanines, some of them with a substituent on the chain, could act as supersensitisers to certain methin- or

trimethin-cyanines, but two simple merocyanines could not.[146] On the other hand, a mixture of specific types of mero- and dimethinmerocyanines was recommended for use in emulsions for photographic papers.[147] Certain di- and tetra-methinmerocyanines were supersensitised by specific compounds of the methin- and trimethin-cyanine, *p*-dimethylaminostyryl, and dimethinhemicyanine types;[148] complex merocyanines were used for supersensitising methin- and trimethincyanines.[149–151] So also were other trinuclear non-ionised dyes, comprising a dimethinmerocyanine structure.[152,153]

Certain methin- or *meso*-alkyltrimethin-cyanines were supersensitised by a tri- or penta-methinoxonol, in which part of the chain might be cyclic.[154] Also a methincyanine was supersensitised by a methinoxonol,[155] and, conversely, certain pentamethinoxonols, themselves poor sensitisers, had their sensitising power improved by a dye of the methin- or trimethin-cyanine, *p*-dimethylaminostyryl, or dimethinhemicyanine type.[156]

The enhancement of the sensitising action of certain carbocyanines by specific heterocyclic bases, which were themselves not sensitisers[118] was followed by the supersensitisation of methin-, trimethin-, or pentamethin-cyanines with various other types of heterocyclic basic compounds.[121,157–165] Certain aldehydes, ketones, and their derivatives,[166–169] and certain cyclic ketones[170,171] were used as supersensitisers, also heterocyclic and aromatic esters,[172,173] aromatic nitriles,[174] and complex heterocyclic triazines such as hydromelonic, cyameluric, and melonic acid, or their salts.[175,176] Other supersensitisers, that were applied with specific dyes, were the α-thiol derivatives of fatty acid arylamides,[177] quaternary salts of complex silicanes,[178] and complex stilbenes.[179] Moreover inorganic salts, such as cadmium or zinc chloride, were used to supersensitise methin- and trimethin-cyanines.[119,122,180]

Various dicyano-compounds, having a heterocyclic nucleus and a polymethin chain (see XIV-13-B), were supersensitised by a dicyanopolymethin base[181] or by a pyridine base.[182] Other types, in which part of the polymethin chain was cyclic, were supersensitised by a pyridine base,[183] or by ketones of certain kinds.[184]

Anti-sensitisation occurs with a small proportion of anti-sensitiser to sensitiser and is especially liable to occur with sensitisers in the *J*-state. It differs from desensitisation (see section 3) in that the depressant action is greater on the conferred than on the original sensitivity. Anti-sensitisers are non-planar. Such a compound can anti-sensitise a dye

with its absorption maximum at a shorter wavelength than its own, but not a dye with its maximum at more than 700 Å longer. There is a decrease in the efficiency of an anti-sensitiser towards a series of sensitisers as their maxima lie at longer wavelengths. A non-planar dye, bis-[2-(1,3-dimethylquinoline)]methincyanine iodide, may act as an anti-sensitiser towards one dye and as a weak supersensitiser towards another. As non-planar anti-sensitisers, there are mentioned bis-[2-(1-ethylquinoline)] *meso*-methyl (or phenyl)trimethincyanine iodide and bis-[4-(1,3-dimethylquinoline)]methincyanine iodide. Some anti-sensitisers also cause general desensitisation.[29]

I. Mechanism of Sensitisation, etc.

It was noted in 1933 that a sensitising dye must absorb the light which is effective, must be adsorbed to the silver bromide, must transfer the adsorbed energy to silver bromide, and will probably affect the stability of the union between silver and bromine. Since only a few dyes actually sensitise, chemical structure must play some part in their action.[19] The problem of the mechanism of sensitisation was approached in 1937 by studying the photolysis, by monochromatic light of λ 5460 Å, of a simple silver halide hydrosol, stabilised with Br^- and sensitised with erythrosin. Dye was destroyed progressively on exposure and 1–2 silver atoms were formed per mol. of dye. In the presence of a halogen acceptor, however, the sensitiser facilitated the transfer of an electron from Br^- to Ag^+ without itself undergoing decomposition.[185] For cyanines, as well as for erythrosin, the photolysis of dyed silver halide yielded one atom of silver for each quantum of light absorbed by the dye.[186] The fact that less sensitiser is required the longer the wavelength of sensitisation, was attributed to the greater efficiency of energy transfer from dye to silver halide at the longer wavelengths.[52] The photolysis of silver bromide sensitised with dyes was followed by chemical and photometric determination of the silver produced. The maximum sensitivity was achieved before adsorption saturation. Photovoltaic experiments indicated the release of photoconductance electrons.[187] There was definite optical sensitisation of the photovoltaic effect.[188] It was established later that only dyes which were sensitisers produced photocurrents in the sensitised region. Good sensitisers gave strong photocurrents and vice versa. Supersensitisers increased the photocurrent.[189] As desensitisers did not reduce the

photocurrent, desensitisation must be exerted at a later stage.[190] As an additional cause of the low sensitising power of non-planar dyes (see section 2-G), inefficiency of energy transfer was postulated.[20]

As regards the mode of action of a supersensitiser, there is no evidence that it increases the adsorption of the sensitiser.[21] The effect of the supersensitiser can only be to increase the efficiency of energy transfer to the silver halide, but it is a complex effect. The supersensitiser is a substance which provides a singularity in the co-operative layer, where, on account of a slowing of the rate of propagation at disturbance, transfer of energy to the silver halide occurs. The molecule of the supersensitiser must be sufficiently like that of the sensitiser to allow of incorporation with it, yet sufficiently unlike to constitute a perturbation. It must neither acquire nor lose energy itself.[20,29]

Anti-sensitisation is probably due to an interruption of the propagation of energy within the co-operative layer of sensitiser by a molecule which captures the energy and degrades it internally.[20,29]

3. Desensitisation

The subject of desensitisation by compounds of the cyanine or related groups has two aspects, of which incidental desensitisation will be considered first. A dye may act both as a sensitiser and as a desensitiser. Thus a typical desensitiser may confer weak colour sensitivity[113] and when more than the optimum quantity of a sensitiser is used, desensitisation may occur. In the presence of potassium bromide, both the original sensitivity and that conferred by a sensitiser may be reduced, the greatest effect being obtained at a low bromine-ion concentration.[191] Desensitisation by concentrations of sensitisers higher than the optimum were ascribed to the facility of rebromination by the dye/bromine addition compound.[187] Desensitisation by a sensitising dye began at much lower concentrations for silver-digested than for sulphur-digested emulsions; hence it was concluded that the dyes can bring about rearrangement or complete oxidation of the silver produced by silver-digestion.[9] The effect of certain non-diffusing colour-formers in suppressing sensitisation was attributed mainly to adsorption displacement of the sensitisers at the silver bromide surfaces. The high affinity of the colour-formers for silver bromide was related to their long-chain aliphatic groups.[192] Accepting the oxidation theory of

desensitisation,[113] one reason for the high sensitising efficiency of cyanines may be their high resistance to reduction.[20]

Desensitisation which may arise in thickly coated X-ray film on kinking, is reduced by addition of an oxacyanine to the emulsion.[193]

The second aspect of desensitisation to be considered is the application of cyanines as practical desensitisers to permit of development in a relatively bright light. Such a procedure was first explored by Lüppo-Cramer about 1920. The desensitiser could be applied either in a bath preceding development, or as an addition to the developer. Desensitisation is not a screening effect. A perfect desensitiser should be conveniently soluble in water, stable, colourless, rapid and complete in destroying sensitivity, but without action on the developer or on the latent image, non-fogging, non-staining, and non-poisonous.[113] There are amongst cyanines a few types with outstanding desensitising capacity, but some that were thoroughly examined did not meet the exacting demands made of a practical desensitiser.

According to early patents, styryl salts prepared by condensing a 2-methyl-pyridinium or -quinolinium salt with an aldehyde without basic properties were desensitisers.[194,195] They proved of no value because their action was destroyed by the developer.[196] Whereas *p*-dimethylaminostyryl salts (see XIII-1) were often sensitisers, the desensitising properties of their *β*-aza-analogues (XIII-2-A and B) were first noted in 1923,[37] and numerous instances of other such anils, in general desensitisers, were added.[14,39,196–199] Although their action was sometimes very powerful, compounds of this type proved too unstable to be of practical value.[196] It was suggested that their desensitising power was due to an even-numbered chain linking the nitrogen of the nucleus to that of the chain (see XIII-2-A).[200] Other desensitisers which have been described are *αβ*-diazatrimethincyanines (see XII-1 and 5,A),[199,201] azadimethincyanines having a 3-linked indole nucleus (see XII-1 and 7),[202,203] and diazadimethincyanines having a 3-linked indole nucleus (see XII-1 and 8).[204]

The desensitising properties of certain nitro-derivatives of cyanine and related dyes have been recorded. Thus the dinitro-compound prepared from pinacyanol by the action of dilute nitric acid[205] was a more powerful desensitiser than safranine, but its practical application was precluded because the effect was annulled by the developer.[196] Cyanines and carbocyanines of certain series, carrying a nitro-group as substituent, were recommended as desensitisers, which might, for

instance, be usefully included in X-ray emulsions, with the object of reducing fogging by light.[206] So, similarly, might symmetrical thiazolocarbocyanines with 4,4'-di(nitrophenyl) substituents.[207] Nitrostyryl derivatives of quaternary salts of cinnoline or quinazoline were desensitisers, which could usefully be incorporated in an emulsion for giving direct positives.[208]

3-Substituted rhodanines carrying in the 5-position a group :CMeAc or :CMe(CO_2R) were strong desensitisers[209,210] and this property was enhanced in merocyanines derived from them.[209]

4. Use of Cyanines as Dyes for Textiles

Although patents occasionally refer to cyanines as valuable dyes for textiles, there is so little evidence of their practical application that it does not seem worth listing instances of such references. Symmetrical cyanine chlorides of the substituted indolenine series with one-, three-, five-, and seven-membered methin chains have indeed been referred to by names such as Indolenine Yellow,[211,212] Indolenine Red[211] or Astraphloxin FF[213] or Basic Red 12,[212] Indolenine Violet,[211] and Indolenine Blue,[211] respectively, indicating that they were thus described commercially. In this series substituted trimethincyanines and certain styryl derivatives have also been listed as dyes.[212] In this connection, it is of interest that the oxidative fading rates of cyanines (see section 7) show those of the indolenine series to be the most stable.[214] It was stated in 1933 that Thiazole Purple (see IV-6-E) but not Pinacyanol (see IV-2-B) was useful for dyeing fabrics.[15]

5. Use in Photographic Filter Layers

To be useful in a filter layer, which may be applied in a backing or, in multi-layer processes, in an intermediate layer, a compound must possess intense colour in a desired region of the spectrum and be readily dispersible in the medium; besides this, it should be non-diffusing, photographically inert, and easily removable by one of the processing solutions to be applied after exposure. Certain cyanines that are not useful as photographic sensitisers have, on the other hand, proved valuable as filter dyes. Such were symmetrical methin- and trimethin-cyanines having two 3-linked pyrrole (including indole) or two pyrrocoline nuclei,[215,216] and di- and tetra-methincyanines with

one 3-linked pyrrole or indole nucleus (X-5-A).[217] Pyrrocoline salts with a group $:CH\cdot C_6H_4\cdot NMe_2(p)$ or $:CH\cdot CH:CH\cdot C_6H_4NMe_2(p)$ were also used (XIII-1-A and O).[218] Symmetrical methin-, trimethin-, and pentamethin-cyanines with 2-linked 3,5-diphenylpyrrole nuclei, some of them sulphonated, were also patented (X-5-A).[219] A useful method of preparing symmetrical methincyanines with 3-linked pyrrole nuclei was given. They were photographically inert and were destroyed by an alkaline developer.[220] They were rendered water-soluble by the presence of *NN'*-diCH_2CO_2H groups (X-5-A).[221] Dimethincyanines having a 2,1,3-triazole nucleus, whilst devoid of photographic action, were suitable for anti-halation layers (XII-10).[222] So also were azo dyes, which were prepared by coupling diazotised amines with methin cyanines possessing a 3-aryl-4-oxothiazolidine nucleus (X-4-C).[223]

Various styryl compounds were patented in 1930 for anti-halation layers[224,225] and styryl derivatives of complex triazole and tetrazole salts were used later[226] (see XIII-1). Another suggestion was the use of a salt of glutaconic dialdehyde or of a higher vinylene analogue.[227]

Proposals to use compounds of the oxonol group covered certain symmetrical methin-, trimethin-, and pentamethin-oxonols (XIII-4-A, B, C, and D),[228] unsymmetrical pentamethin- (XIII-4-A and D),[229] trimethin-, and methin-oxonols (XIII-4-A, B, and C),[230] β-hydroxy-pentamethinoxonols (XIII-4-A),[231] and trimethinoxonols in which two extra carbon atoms of the chain were cyclic (XIII-4-A and C).[232] The silver salts of certain double hemioxonols were also recommended (XIII-4-G.4).[233,234] Anti-halation properties were claimed for various unsymmetrical oxonol analogues with an open chain carrying a cyano-group (XIII-5-A and C).[235] Other open-chain filter dyes were *p*-dimethylaminocinnamylidene salts (XIII-5-A and B),[236] and *p*-dialkyl aminobenzylidene compounds (XIII-5-A and D).[237,238] Certain pyrylium, benzopyrylium, and xanthylium salts were described as intensely coloured, non-diffusing, and suitable for filter layers (XIII-6-B).[239]

In the merocyanine group, di- and tetra-methinmerocyanines having one benzoxazole and one pyrazolone residue, the latter carrying a $C_6H_4CO_2H$ or $C_6H_4SO_3H$ substituent to confer solubility, were useful filter dyes (XIV-1 and 10-A.2b).[240] Dyes with a pyrrocoline nucleus linked by a tri- or penta-methin chain to a nucleus such as diethylthiobarbituric acid were also suitable,[241] whilst others had one substituted pyrrole nucleus linked in the 3-position, through a methin group, to a barbituric or thiobarbituric acid residue (XIV-1 and 9-B, 1 and 2).[242]

The silver salts of merocyanine dyes having one 3-linked pyrrole and one thiobarbituric acid residue, linked by a methin group, were also employed in filter layers, being subsequently discharged by an acid fixing bath.[243] Previously it had been claimed that certain trinuclear dyes were not only excellent sensitisers but formed stable silver salts, which were non-diffusing and thus suitable for filter layers, to be applied as a backing or else intermediately (XV-8).[244]

6. Uses of Cyanines in Chemotherapy

As early as 1922, the possible applications of certain commercial sensitisers to chemotherapy were considered and Sensitol Green (see II-1-C) was described as a good antiseptic for *Bacillus coli*.[245] The action of cyanine itself on tubercle bacilli was only temporary.[246] The possible antiseptic action of apocyanines (see I-5), isocyanines, and carbocyanines was explored in 1924,[247] and the antiseptic and trypanocidal powers of numerous styryl compounds (see XIII-1-B, E, and I) and of anils (see XIII-2-B.1), mostly of the quinoline series, were tested.[248–252] In 1944 attempts to find new anti-malarials included tests on a symmetrical trimethincyanine with complex nuclei (see X-5-B).[253] In 1947 an account was given of the examination of extensive series of styrylquinolines, dimethincyanines with a 3-linked pyrrole nucleus, 2,2′-methin- and 2,2′-trimethin-cyanines, as well as of numerous cyanines of other types, all of which were prepared in a soluble form. It was found that they possessed anti-filarial and anthelmintic properties; their anti-malarial activity was not equal to that of other known drugs.[254] Pyrimido-2′-cyanines (see X-5-B) were patented as useful therapeutics for worm infestations.[255] The effect of such a compound on adult worms was studied. It appeared that the dye was metabolically altered. Any modification which destroyed resonance reduced the activity.[256] The anti-filarial activities of a series of cyanines were compared.[257] Amongst dimethincyanines with a 3-linked pyrrole nucleus, the compound [2-(6-dimethylamino-1-methylquinoline)] [3-(2,5-dimethyl-1-phenylpyrrole)]dimethincyanine chloride dihydrate (see X-5-A)[258] was used, under the trade name of Poquil, for treating worm infections in humans.[259–262] An improved form of the drug, its bis-salt with the dibasic pamoic acid, was also tested,[262] and was marketed under the name Povan in the United States, and as Vanquin elsewhere.

A symmetrical indotricarbocyanine, having 4,5-benzo-3,3-dimethylindolenine nuclei, absorbed infrared light and hence proved useful in diagnosing congenital heart defects.[263]

7. Some Other Properties of Cyanines

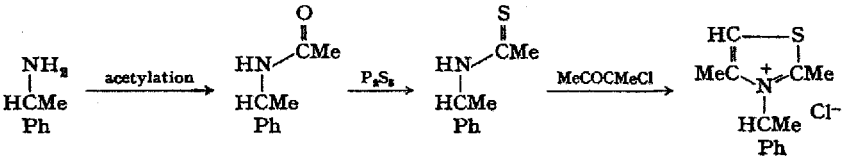
The reduction of three 2,2′-carbocyanines was effected by heating with excess of hydriodic acid, which gave a methylenediquinaldine dialkiodide (for the converse process see chapter IV-5).[264] When 2-*p*-dimethylaminostyrylquinoline ethiodide was heated with hydriodic acid, the product was 2-*p*-aminobenzylquinaldine ethiodide.[264] Certain cyanines could readily be reduced at the ordinary temperature by the action of zinc on their pyridine solutions, containing a little moist acetic acid. Of symmetrical cyanines having substituted indolenine nuclei, the heptamethin dye was extremely readily, and irreversibly, reduced, the pentamethin dye was very easily reduced, and the trimethin dye easily, but reduction was very difficult with the methin dye. The resultant leuco-base from the pentamethin dye partially regenerated the dye by the action of oxygen or air, but to restore the colour to the leuco-base from the trimethin dye, quinone or potassium ferricyanide was required.[265]

The oxidative fading of cyanines and related dyes has been investigated. The colour of pinacyanol chloride was caused to fade by paraffin chain salts, such as $NaO_3S(CH_2)_9 \cdot Me$. This was due to oxidation, because it was decreased by removing oxygen and increased by hydrogen peroxide. It was also increased by exposure to light but was unaffected by addition of sodium chloride.[266] The fading rates, to tungsten light, of methanolic solutions of twenty-one symmetrical trimethincyanines and of fourteen dimethinmerocyanines, having a 3-carbethoxymethylrhodanine nucleus, were measured. The half-lives varied from 2 hours to about 5·5 years. The sequence of fading values was roughly the same in both series, stability increasing with decreasing basicity of the nuclei. Two series of symmetrical methin-, trimethin-, pentamethin-, and heptamethin-cyanines became less stable with increasing length of chain. The results were explained by an oxidative fading mechanism.[214]

A chromatographic analysis of aqueous pyridine solutions of a series of indocyanine chlorides was made in 1935. The heptamethin compound was strongly adsorbed by alumina, the pentamethin less

strongly, the trimethin still less, and the methin dye was only weakly adsorbed. Further, in the indolenine series, a *p*-dimethylaminostyryl salt was more weakly adsorbed than its higher vinylene analogue.[211] At a much later date, a theoretical consideration of the spectral bands of symmetrical cyanines suggested the presence of *cis–trans* isomers[267] and evidence for this was sought by chromatographic analysis of 3,3′-diethylthiatricarbocyanine chloride, by use of ethylene chloride, acetone, and calcium carbonate. Three zones were isolated and each, on re-treatment, again gave three zones, whence it was concluded that the dye consisted of a stereoisomeric equilibrium mixture.[268] Other cationic dyes behaved similarly. Paper-chromatography was used to investigate the spatial configuration of sensitisers. R_f values (= distance travelled by zone ÷ distance travelled by liquid) were determined for forty-seven cyanines, mostly trimethincyanines. They were almost unaffected by the anion. Those with compact molecules had lower R_f values than those with non-planar molecules. The results indicated that the molecule of 1,1′-diethyl-2,2′-cyanine iodide is non-planar in the mono-molecular state, but progressive replacement of the quinoline by benzothiazole nuclei gave dyes with a more compact structure.[269]

In 1938 an optically active thiazolo-2′-cyanine and an optically active thiazolo-4′-cyanine were prepared. This was achieved by the synthesis of 2,4-dimethylthiazole α-phenylethoperchlorate from optically active α-phenylethylamine (equation 1). The salt was condensed with 2-iodoquinoline ethiodide and with *p*-toluquinoline ethiodide,



(1)

both dyes being isolated as optically active perchlorates. The thiazolo-2′-cyanine, prepared from a quaternary salt of rotation $[\alpha]_D$—68°, showed $[\alpha]_D$ + 1500°. The thiazolo-4′-cyanine, prepared from a quaternary salt of $[\alpha]_D$ + 62°, showed $[\alpha]_D$ — 1800°. Such extraordinarily high rotation values were attributed to the proximity of the asymmetric carbon atom and main conjugated system.[270]

Although it was difficult to obtain crystals suitable for X-ray crystallographic examination, two projections of unsolvated 3,3′-diethylthiacarbocyanine bromide were made. Hence it was concluded

that the cation is planar, except for the methyl groups of the 3,3'-diethyl substituents, and that the conjugated chain is in the extended form with the sulphur atoms in the *cis*-position with respect to it. Such unsolvated crystals undergo spontaneous disintegration[26] but those of the 1:1 solvate of ethanol and the dye do not. Two projections of such solvated crystals, by X-ray single-crystal methods, showed their structure to be similar. The methyl groups of the ethyl substituents lay on opposite sides of the cationic plane; the cation was not quite planar.[271]

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