THIAZOLE
AND ITS DERIVATIVES

IN THREE PARTS

PART THREE

This is the thirty-fourth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER and EDWARD C. TAYLOR

Editors

THIAZOLE AND ITS DERIVATIVES

PART THREE

Edited by

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UNIVERSITY OF AIX-MARSEILLES
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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.

In order to continue to make heterocyclic chemistry as readily accessible as possible, new editions are planned for those areas where the respective volumes in the first edition have become obsolete by overwhelming progress. If, however, the changes are not too great so that the first editions can be brought up-to-date by supplementary volumes, supplements to the respective volumes will be published in the first edition.

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Preface

Given their theoretical as well as practical interest, five-membered aromatic rings occupy a position of particular significance in the enormous field of heterocyclic chemistry. Thiazole is one of the important members of this family and thus merits a comprehensive study. The purpose of this book is to condense into a volume of reasonable size the chemistry of thiazole, covering the literature of approximately one century, up to December 1976. For technical reasons this work has been limited to the study of monocyclic thiazoles, excluding thiamine and partially reduced thiazoles, but including selenazoles. Though most of the important material has been published in the last twenty years, all the literature concerning thiazoles has been surveyed, and it is of special interest to see with what energy Arthur Hantzsch was obliged to defend his historical discovery of thiazole.

In the first chapter, devoted to thiazole itself, specific emphasis has been given to the structure and mechanistic aspects of the reactivity of the molecule: most of the theoretical methods and physical techniques available to date have been applied in the study of thiazole and its derivatives, and the results are discussed in detail. The chapter devoted to methods of synthesis is especially detailed and traces the way for the preparation of any monocyclic thiazole derivative. Three chapters concern the nontautomeric functional derivatives, and two are devoted to amino-, hydroxy-, and mercaptothiazoles: these chapters constitute the core of the book. All discussion of chemical properties is complemented by tables in which all the known derivatives are inventoried and characterized by their usual physical properties. This information should be of particular value to organic chemists in identifying natural or synthetic thiazoles. Two brief chapters concern mesoionic thiazoles and selenazoles. Finally, an important chapter is devoted to cyanine dyes derived from thiazolium salts, completing some classical reviews on the subject and discussing recent developments in the studies of the reaction mechanisms involved in their synthesis.

The importance of this work, which was begun by Dr. J. M. Swan of Monash University, Melbourne, Australia, was very quickly recognized,

and in 1964 I joined him in his endeavor. Three years later, Dr. Swan was obliged to abandon it, and, for the last decade, 17 distinguished scientists have labored to realize this book. I acknowledge with sincere thanks the cooperation and perseverance of all of them, but I am especially indebted to Michel Chanon and his collaborator René Barone, for the untiring efficiency in management that they have exhibited throughout the preparation of this book. I acknowledge also the help of the numerous heterocyclic chemists of the world who sent so many of their valuable reprints to Marseilles. My thanks are also due to Mrs. J. de Caseneuve and Mrs. G. Formanek who carried out the tedious task of typing the manuscript, and to Thomas Murphy for his help in adjusting the poor original English of most of the manuscript to a hopefully acceptable one. Finally, grateful thanks are due to the University of Aix-Marseilles for financial support and library facilities.

JACQUES V. METZGER

Marseilles, France
December 1978

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THIAZOLE
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This is the thirty-fourth volume in the series

THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

VIII

Mesoionic Thiazoles

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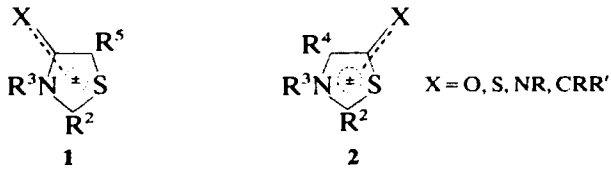
I. INTRODUCTION

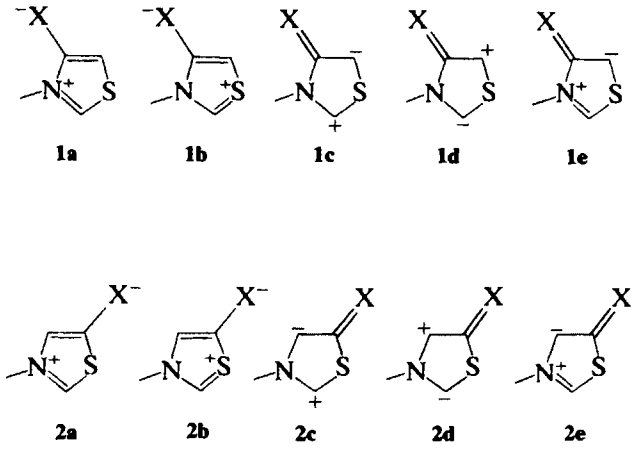
Mesoionic compounds are heterocyclic compounds that cannot be represented by any uncharged formula but only as a hybrid of dipolar structures (1, 2).

Only noncondensed thiazoles in which mesoionic charge delocalization involves atoms directly bonded to the thiazole ring are considered here. Two such systems, **1** and **2**, exist (Scheme 1). Structure **1** (X = O) is

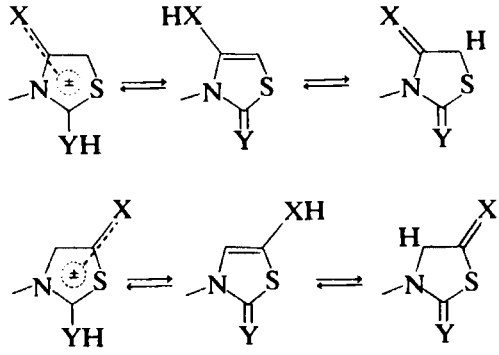


Scheme 1

denoted as a 4-hydroxythiazolium hydroxide inner salt (*Chem. Abstr.*, Index Guide, 1139G, 1977) but the terms *anhydro*-4-hydroxythiazolium hydroxide (3) or mesoionic thiazol-4-one (4) are also in current use. Structure **1** is a hybrid of the dipolar structures **1a** to **e** and **2** a hybrid of **2a** to **e** (Scheme 2). Prototopy may abolish the mesoionic structure if R^2 in **1** or **2** possesses an α hydrogen atom (Scheme 3). Observations indicate that the nondipolar tautomers prevail when Y = O, S, or NR, (5–7), whereas both tautomers may be present when Y = CRR′ (8).



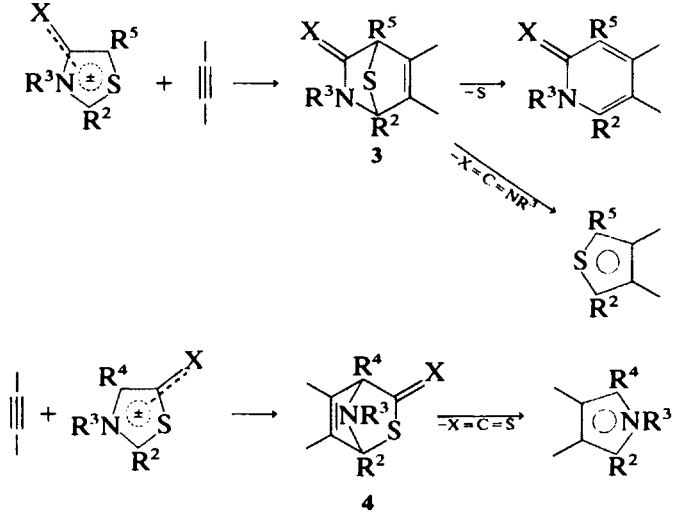
Scheme 2



X, Y = O, S, NR, CRR'

Scheme 3

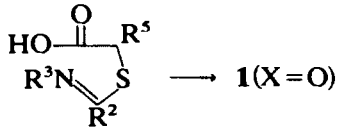
As apparent from the contributing resonance structures, both mesoionic systems contain an azomethinylide contribution, accounting for the reaction with representative dipolarenophiles to give cycloadducts such as **3** or **4** (Scheme 4). The cycloadditions and extrusion reactions of the adducts have been the main object of investigation since previous reviews on mesoionic thiazoles (2, 9). Results appearing since 1969 and before June 1976 are reported for each type of compound in this chapter. Tables VIII-1–5 contain all mesoionic thiazoles described before June 1976.



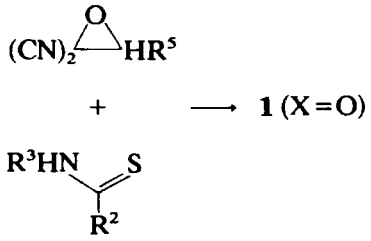
Scheme 4

II. 4-HYDROXYTHIAZOLIUM HYDROXIDE INNER SALTS

The preparation of these [4-hydroxy-THISs, (**1**), X = O] by cyclization of α-carboxy-*N*-arylthiobenzimides (5) by treatment with acetic anhydride and triethylamine has been investigated in detail, and the structure has been revised for the compound previously described as 2,3-diphenyl-4-hydroxythiazolium hydroxide inner salt (**1**, X = O, $R^2 = R^3 = Ph$, R^5 = H) (Scheme 5) (3, 10). 4-Hydroxy-THISs also arise by condensation of *gem*-dicyanoepoxides with thioamides (Scheme 6) (8).



Scheme 5

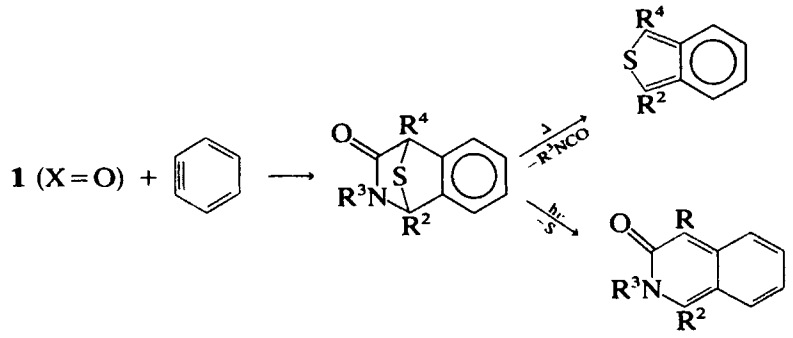


Scheme 6

The 4-Hydroxy-thiazoles are characterized by infrared absorption near 1610 cm^{-1} (KBr) (3) or 1620 to 1650 cm^{-1} (CCl_4) (8), indicating a strongly polarized carbonyl group. H-5 resonates near 5.6 ppm in the ^1H NMR spectrum like similar protons in other mesoionic compounds (3). Two fragmentations of the molecular ion are observed in the mass spectra. The first involves rupture of the 1,2 and 3,4 bonds with loss of $C_2R^5OS^{\cdot}$. In the second, the 1,5 and 3,4 bonds are cleaved with elimination of $C_2R^5O^{\cdot}$.

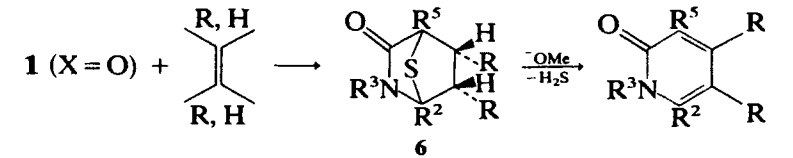
The 4-hydroxy-THISs are extremely hygroscopic; hydrolysis affords the parent thiobenzimide (3). When R^2 = Me and R^5 = *p*-ClPh or Ph, but not *p*-NO_2Ph the nondipolar tautomer **3** (X = O, Y = CH_2) is present according to NMR and infrared spectra, the latter exhibiting carbonyl absorption at 1710 to 1720 cm^{-1}.

The 4-hydroxy-THISs react with electron-deficient alkynes to give cycloadducts (**3**) that spontaneously eliminate sulfur, producing 2-pyridones (3). Bulky 5-substituents lead to a decrease in the addition rate, and elimination of isocyanate with formation of thiophenes becomes favored (3, 12, 13). Benzyne yields an isolable adduct that exclusively extrudes isocyanate on thermolysis, but sulfur on irradiation (Scheme 7)



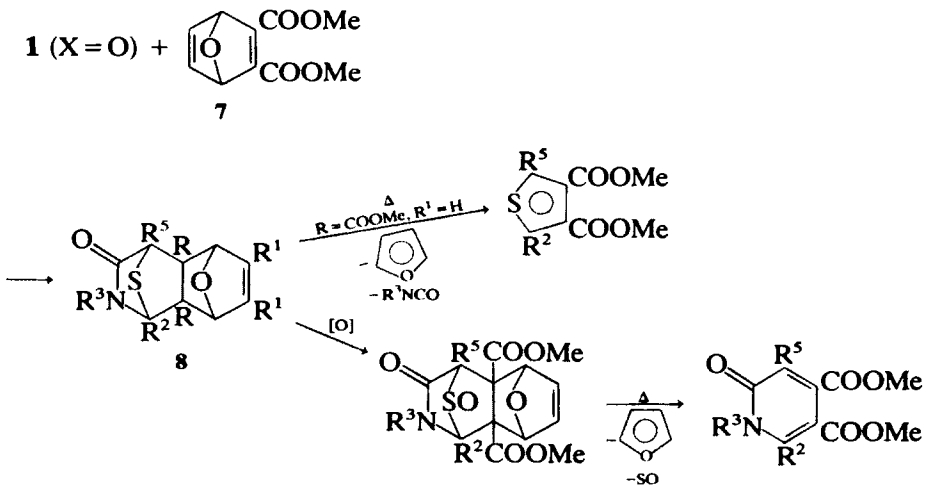
Scheme 7

(14, 15). Electron-deficient alkenes add stereospecifically to 4-hydroxy-THISs with formation of *endo*-cycloadducts. Only with methylvinylketone considerable amounts of the *exo* isomer are produced (Scheme 8) (16). The adducts (**6**) may extrude hydrogen sulfide on heating with methoxide producing 2-pyridones. The base is unnecessary with fumaronitrile adducts. The alternative elimination of isocyanate or sulfur may be controlled using **7** as the dipolarenophile. The cycloaddition produces two products, **8a** (R = H, R^1 = COOMe) and **8b** (R = COOMe, R^1 = H) (Scheme 9) (17). Pyrolysis of **8b** leads to extrusion of furan and isocyanate to give a thiophene. The alternative S-elimination can be effected by oxidation of the adduct and subsequent pyrolysis.



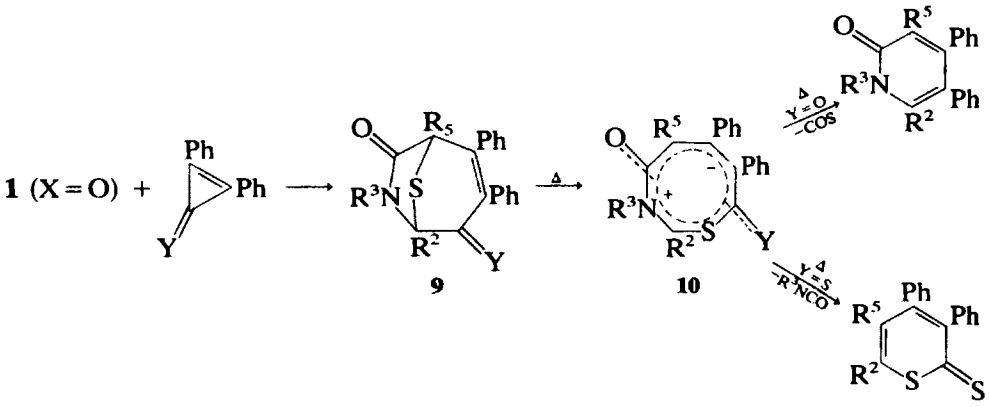
6

Scheme 8



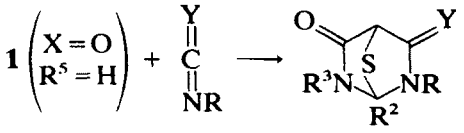
Scheme 9

4-Hydroxy-THISs add to the C–C bond of diphenylcyclopropenethione (18). Inner salts without substituents in 5-position react similarly with diphenylcyclopropenone (Scheme 10) (4, 18). Pyrolysis of the stable adducts (**9**) leads to rupture of the R^2C–CY bond. Subsequent ring closure yields **10**. When Y = O, **10** eliminates COS, producing 2-pyridone. When Y = S, **10** is isolated together with its isocyanate extrusion product, a thiopyran-2-thione (18).



Scheme 10

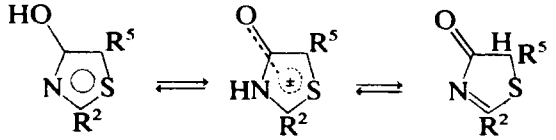
4-Hydroxy-THISs add regioselectively to the C=N bonds of isocyanates and isothiocyanates producing stable adducts (Scheme 11) (19).



Y = O, S
R = Ph, acyl

Scheme 11

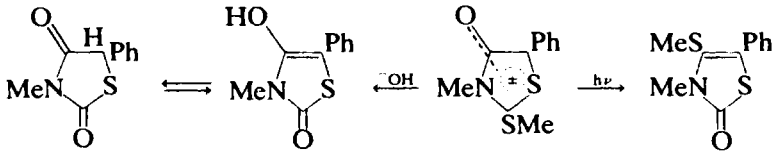
Interestingly, 4-hydroxythiazoles (**11**) react like the 4-hydroxy-THISs with alkynes and alkenes (Scheme 12) (20), further demonstrating the usefulness of 4-hydroxythiazole derivatives for the preparation of 2-pyridones and thiophenes.



11

Scheme 12

Irradiation of a 2-methylthio-4-hydroxythiazolium hydroxide inner salt (**12**) leads to exchange of the carbon atoms located in the 2 and 4 positions, probably *via* a thiirenium ion (Scheme 13) (5).



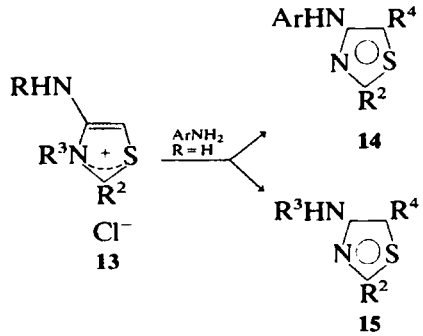
12

Scheme 13

The methylthio group in **12** can be replaced with OH. Subsequent deprotonation affords a 2,4-dioxothiazole (5).

III. 4-AMINOTHIAZOLIUM HYDROXIDE INNER SALTS

4-Aminothiazolium hydroxide inner salts (**1**) (X = NR) are only known as the derived hydrochlorides (**13**) or acylated hydrochlorides. The former react with arylamines to give 4-arylaminothiazoles. The ratio between **14** and **15** depends on the reaction conditions, a fact accounted for by a mechanism involving ring opening to a diaminocyanomethylthiomethane, followed by recyclization by nucleophilic attack of one of the amino nitrogens on the nitrile carbon. Subsequent ring opening and cyclization with elimination of amine yields the final product (Scheme 14) (21).



Scheme 14

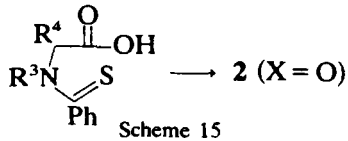
Photolysis of 4-aminothiazolium salts in aqueous solution may cause ring opening, probably via a thiirane, to give α-cyano-β-aminovinyl-disulfide or α-acylacetamidine derivatives (22).

IV. 4-MERCAPTO- OR 4-ALKYLIDENETHIAZOLIUM HYDROXIDE INNER SALTS

4-Mercapto- or 4-alkylidenethiazolium hydroxide inner salts (**1**) (X = S or CRR') have not been described.

V. 5-HYDROXYTHIAZOLIUM HYDROXIDE INNER SALTS

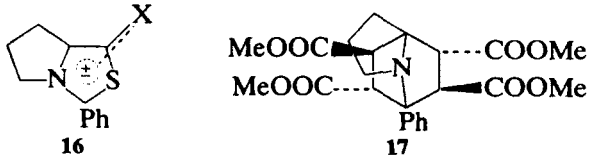
5-Hydroxythiazolium hydroxide inner salts (**2**) (X = O) have been synthesized by an improved acetic-anhydride-triethylamine-catalyzed cyclization of *N*-substituted *N*-thiobenzoylalanines (Scheme 15) (23).



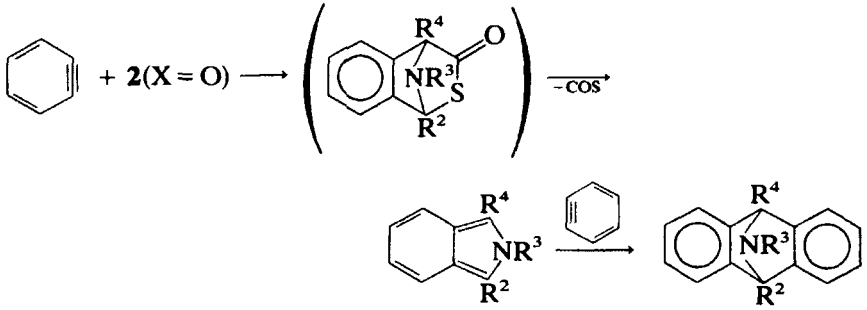
Scheme 15

The reasonable stable products are characterized by an ir-absorption near 1615 cm^{-1}. The 4-protons resonate near 6.2 ppm in the ^1H NMR spectrum (23). ^{13}C NMR spectra exhibit a carbonyl atom signal near 173 ppm, whereas C-4 resonates near δ 108; these positions are characteristic of other mesoionic ring carbon atoms (24). In the mass spectra, decomposition with loss of CO, rupture of the 1,5 and 2,3 bonds with elimination of $R^3NC_2R^4O$; and cleavage of the 1,2 and 3,4 bonds with elimination of C_2R^4OS is observed (11)

5-Hydroxy-THISs react with electron-deficient alkynes to give nonisolable adducts that extrude carbonyl sulfide, affording pyrroles (23). Compound **16** (X = O) seems particularly reactive (Scheme 16) (25). The cycloaddition to benzyne yields isoindoles in low yield. Further cycloaddition between isoindole and benzyne leads to an iminoanthracene as the main product (Scheme 17). The cycloadducts derived from electron-deficient alkenes are stable (23, 25) unless highly strained. Thus the two adducts, **18a** (R = H, R′ = COOMe) and **18b** (R = COOMe, R′ = H), formed from **7**, both extrude furan and COS under the reaction conditions producing the pyrroles (**19**, R = H or COOMe) (Scheme 18). Similarly, the cycloadduct formed between **16** (X = O) and dimethylfumarate

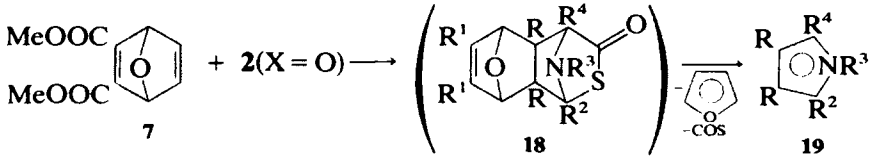


Scheme 16



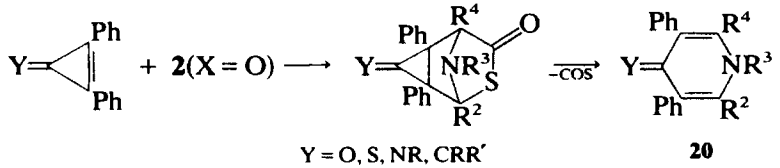
Scheme 17

is unstable, eliminating COS and reacting with a second molecule of dimethylfumarate to give **17** as the final product (17).



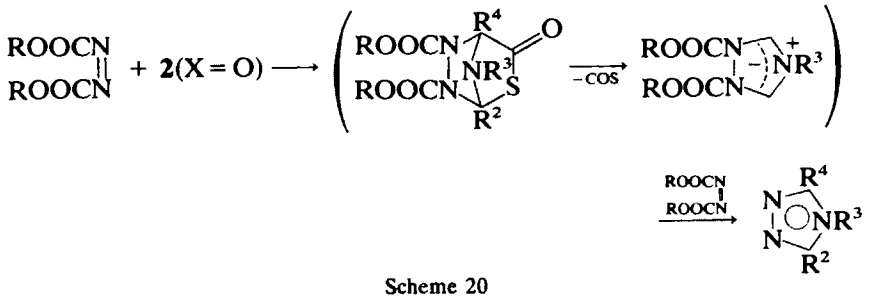
Scheme 18

In contrast to the 4-hydroxy isomers, the thermally stable 5-hydroxy-THISs add to the C=C bond of cyclopropenylidenes (4, 18, 27, 28). The adducts eliminate carbonyl sulfide, and the strained bond breaks resulting in ring-expansion with formation of pyridin-4-ones, -thiones, or -imines, or 4-alkylidenedihydropyridines (**20**, X = O, S, NR, or CRR') (Scheme 19).



Scheme 19

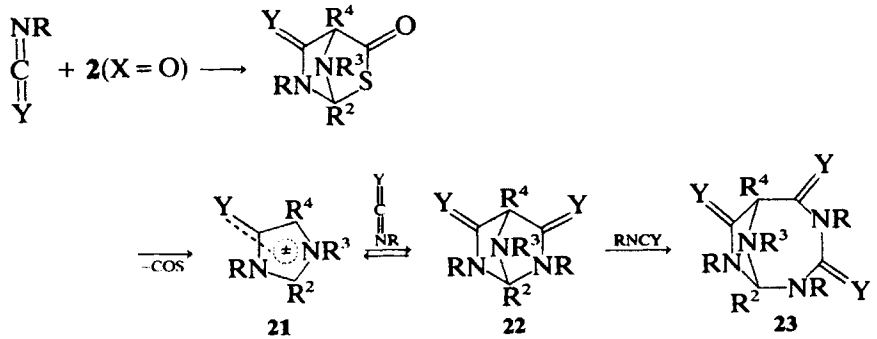
5-Hydroxy-THISs react with diethoxycarbonylazine producing a 1,2,4-triazole via addition, elimination of carbonyl sulfide (29), and subsequent loss of the ester groups (Scheme 20) (30).



Scheme 20

5-Hydroxy-THISs add regioselectively to the C=N bonds of isocyanates or isothiocyanates. The initially formed cycloadducts eliminate carbonyl sulfide with formation of 4-hydroxy- or 4-mercaptoimidazolium hydroxide inner salts (**21**) (Scheme 21). 4-Hydroxyimidazolium hydroxide

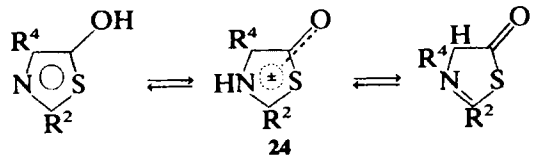
inner salts and not too highly substituted 4-mercapto analogs may undergo further reaction with excess of the heterocumulene, normally affording cycloadducts such as **22** as the final products (23). An equilibrium between **21** and **22** seems to exist, favoring **21** with increasing strain in **22** (26). The strained **22** ($Y=O$, $R_3R_4=(CH_2)_3$) react differently, adding a further molecule of isocyanate to give **23** as the final product (26).



Scheme 21

Acylisocyanates or isothiocyanates undergo cycloaddition with 5-hydroxy-THISs under so mild conditions that isolation of the initial adducts becomes possible (23). In cycloaddition reactions the 5-hydroxy-THISs can be replaced by their precursors (23).

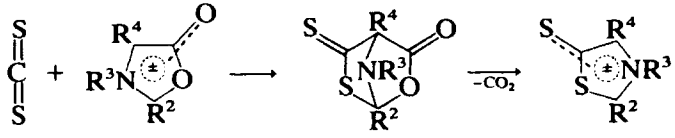
Again, it is noteworthy that 4-substituted 5-hydroxythiazoles (**24**) react like 5-hydroxy-THISs with alkynes to give pyrroles and sometimes with alkenes to give *exo*-cycloadducts (Scheme 22). In the latter case other processes compete with the cycloaddition, becoming dominant when **24** is treated with azo-compounds, enamines, or heterocumulenes (31).



Scheme 22

VI. 5-MERCAPTOTHIAZOLIUM HYDROXIDE INNER SALTS

5-Mercaptothiazolium hydroxide inner salts (**2**) (X = S) are prepared from 5-hydroxy-oxazolium inner salts and CS_2 (2, 25). The oxazolium inner salts may advantageously be replaced with their precursors, which are *N*-arylacylalanins (Scheme 23).

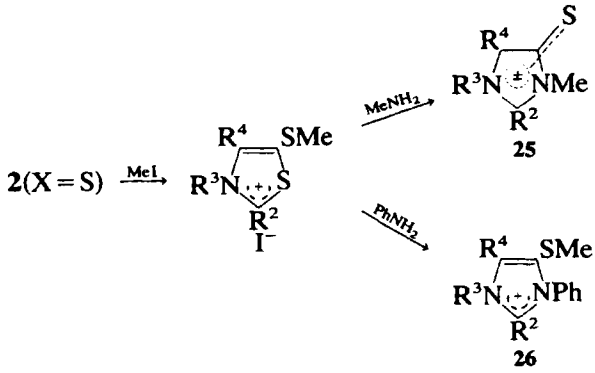


Scheme 23

1,3-Dipolar reactivity of 5-mercapto-THISs has only been demonstrated for **16** (X = S), which, like its oxygen analog, produces with dimethylfumarate, **17**, and with phenylisothiocyanate, **21** (25). Compound **16** (X = S) does not react with other typical dipolarenophiles (25).

5-mercapto-THISs are protonated or alkylated on the exocyclic sulfur atom with simultaneous disappearance of a characteristic long-wave absorption in the ultraviolet region (32, 33). These are stronger for **2** (X = S) than for its 4-aza derivative (33).

The 5-methylthiothiazolium salts react with methylamine to give 4-mercaptoimidazolium hydroxide inner salts (**25**) and with aniline to give **26** (Scheme 24) (32).



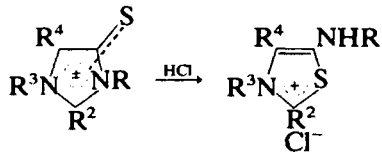
Scheme 24

5-Mercapto-THISs react with dimethoxycarbonylacetylene, producing tetramethoxycarbonylthiophene by an unknown mechanism (29).

VII. 5-AMINOTHIAZOLIUM HYDROXIDE INNER SALTS

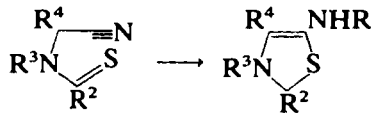
5-Aminothiazolium hydroxide inner salts (**2**) (X = NR) are only known as *N*-phenyl (29) or acyl derivatives, (6, 34) or as hydrochlorides (35).

4-Mercapto-imidazolium inner salts have been reported to rearrange under the influence of hydrochloric acid, producing 5-aminothiazolium chlorides (Scheme 25) (36). Their *N*-acylated derivatives are obtained by cyclization of *N*-thiobenzoyl alkylaminoacetonitriles, effected with acyl or sulfonyl halides (Scheme 26) (34, 35).



R = Alkyl

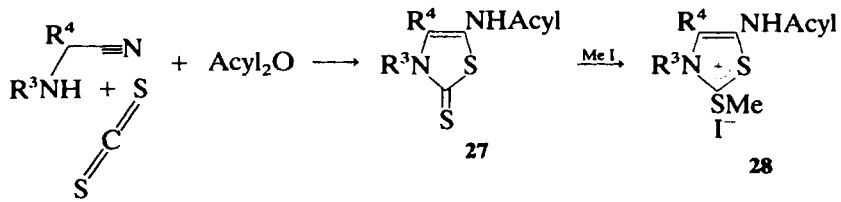
Scheme 25



R = H, Acyl, Sulfonyl

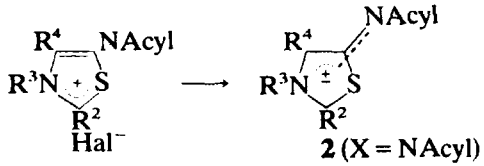
Scheme 26

2-Methylthio-5-aminothiazolium salts (**28**) are accessible through methylation of thiazolethiones (**27**), which are, in turn, obtained from alkylaminoacetonitriles and carbondisulfide (Scheme 27).



Scheme 27

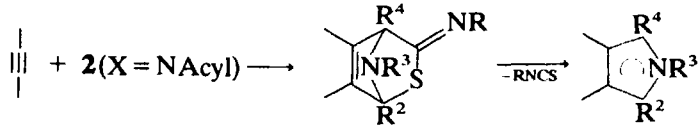
The 5-amino-THISs are very strong bases (35). The hydrochlorides, therefore, have not yet been deprotonized successfully. However, the decreased basicity of the *N*-acylated derivatives makes these readily accessible from their hydrochlorides (Scheme 28).



Scheme 28

The 5-acylamino-THISs are devoid of carbonyl absorptions above 1600 cm^{-1}, suggesting that their oxygen atom adopt a considerable part of the negative charge of the system (6). A normal carbonyl band appears on protonation, also accompanied by a hypsochromic shift in ultraviolet absorption (6). H-4 of 5-acyl-amino-THISs resonates near 7.4 ppm in the ^1H NMR spectrum (6). Three fragmentation modes of the molecular ion of these mesoions have been observed (6): rupture of the 2,3 and 1,5 bonds with formation of an R^2CS^+ ion, rupture of 1,2 and 3,4 bonds with formation of R^2CNR^{3+}, and cleavage of the 2,3 and 4,5 bonds giving rise to R^3NCR^{4+}.

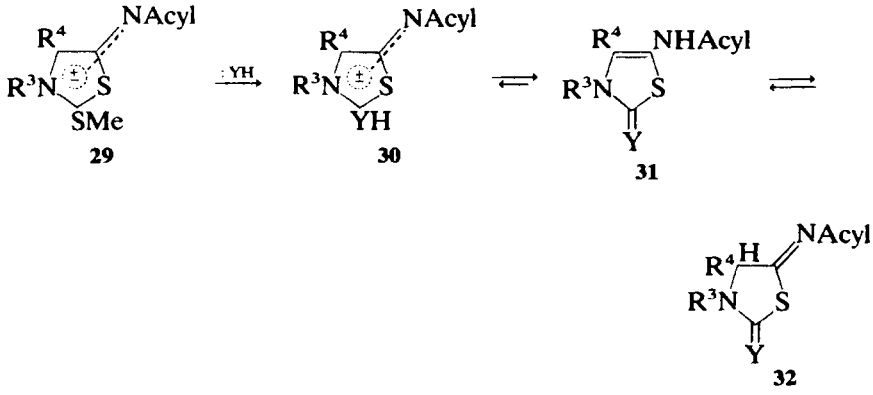
The 5-acylamino-THISs react with alkynes in a way already exemplified for 5-hydroxy-THISs. Pyrroles are formed under elimination of isothiocyanate (Scheme 29) (37). 5-Acylamino-THISs are readily brominated in the 4-position (21).



Scheme 29

2-methylthio-5-acylaminothiazolium hydroxide inner salts (**29**) and nucleophiles :YH react with replacement of the methylthio group

(Scheme 30) (6). Infrared spectra of the products possess a normal amide carbonyl absorption, indicating that the products are not present on the dipolar form (**30**) but rather as the neutral Δ^4-thiazoline tautomer (**31** or **32**) (6).



:YH = $^-$SH, $^-CH(CN)_2$, Piperidine in MeOH, $^-$OH, $MeNH_2$

Scheme 30

5-Benzoylamino-THISs seem to rearrange on photolysis (38).

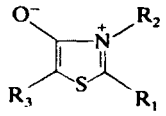
VIII. 5-ALKYLIDENETHIAZOLIUM HYDROXIDE INNER SALTS

5-Alkylidenethiazolium hydroxide inner salts (**2**) (X = CRR') have not yet been described.

Besides being useful precursors to pyrroles; pyridine-2-ones; -4-ones, -4-thiones, and -4-imines; 4-alkylidene-dihydropyridines; thiophenes; 1,2,4-triazoles; thiapyrane-2-thiones, isoquinoline-3-ones; isobenzothiophenes; and 4-mercaptoimidazolium hydroxide inner salts, mesoionic thiazoles are potentially useful in the construction of molecules with herbicidic (39), central nerve stimulating, and antiinflammatory properties (40, 41). Application in dye synthesis has likewise been reported (42).

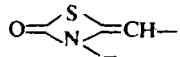
IX. TABLES OF COMPOUNDS

TABLE VIII-1



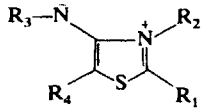
R_1	R_2	R_3	m.p.	Ref.*
H	Me(EtO)CH–	$pClC_6H_4$–	—	20
H	MeO_2CCH= $C(CO_2Me)$–	p-ClC_6H_4–	—	20
Me	Ph	Ph	172–3	43, 44 u
Me	Ph	p-ClC_6H_4–	180	8, 45
Me	Ph	p-$O_2NC_6H_4$–	280	8, 45
Ph	Ph	H	113–5 (dec.)	3, 10, 11 sm, 19, 25, 44, 46
Ph	$PhCH_2$–	Ph	163	43, 44 u, 45
Ph	$PhCH_2$–	p-ClC_6H_4–	168–70	8, 45
Ph	$PhCH_2$–	p-$O_2NC_6H_4$–	210	8, 45
Ph	Ph	Ac	250–2	3, 10, 44
Ph	Ph	PHCO–	252–3	44
Ph	Ph	Ph	270 (free)	
			167–8 ($HClO_4$)	3, 8, 10, 11 m, 12, 14–17, 43–46
Ph	Ph	p-$MeOC_6H_4$–	250	45
Ph	Ph	p-ClC_6H_4–	300	8 i, 45
Ph	Ph	p-$O_2NC_6H_4$–	273	8, 45
Ph	p-Tolyl	Ac	252	43
Ph	p-Tolyl	Ph	248	43
Ph	p-$MeOC_6H_4$–	Ac	214	43
Ph	p-ClC_6H_4–	H	115–6	3, 10, 11, 43
Ph	p-ClC_6H_4–	Ac	240–2	3, 10
p-ClC_6H_4–	Ph	H	125–6 (dec)	3, 16, 19, 25
p-ClC_6H_4–	Ph	Ph	—	16
p-$O_2NC_6H_4$–	Ph	p-ClC_6H_4–	260	45
p-$O_2NC_6H_4$–	Ph	p-$O_2NC_6H_4$–	242	45
$(Me)_2N$–	Ph	Ac	251–3	47
$(Me)_2N$–	Ph	p-$O_2NC_6H_4$–	287	45
$(Et)_2N$–	Ph	Ac	208	47
$(Bu)_2N$–	Ph	Ac	132–3	41 l, 47
1-pyrrolidinyl	Ph	Ac	298–300	41 l, 47
1-Piperidino	Ph	Ac	214	41 l
1-Morpholino	Ph	H	244	41 l

TABLE VIII-1 (*Continued*)

R_1	R_2	R_3	m.p.	Ref.
1-Morpholino	Ph	Ac	249	47
MeS–	Me	Ph	148	5, 49 x
MeS–	Et		—	42 a
MeS–	H_2N–	Ph Et	179–80	49
MeS–	PhCH=N–	Ph	155–6	49
$PhCH_2S$–	H_2N–	Ph	163–4	49

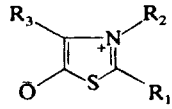
* Reference code *see* p. 2 of Part One.

TABLE VIII-2



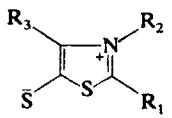
R_1	R_2	R_3	R_4	m.p.	Ref.
Me	Ph	H	H	173(HCl)	50
Me	Ph	Ac	H	228(HCl)	51
$PhCH_2$–	Ph	H	H	190(HCl)	50
Ph	Me	H	H	201(HCl)	50
Ph	Me	Ac	H	215(HCl)	51
Ph	$PhCH_2$–	H	H	192(HCl)	50
				194(HBr)	51
Ph	$PhCH_2$–	H	Ph	176(HCl)	50
Ph	$PhCH_2$–	Ac	H	155(free)	51
				151(HCl)	
				160(HBr)	
Ph	Ph	H	H	207(HCl)	21, 44, 50
				214–8(HCl)	
Ph	Ph	H	Ph	155(HCl)	50
Ph	Ph	Ac	H	198(free)	50, 51
				290(HCl)	
Ph	Ph	PhCO-	H	211–2(free)	50, 37
Ph	Ph	2,4-di$ClC_6H_3OCH_2CO$–	H	—	39 a
Ph	*o*-Tolyl	H	H	(HCl)	21
Ph	*p*-MeO-C_6H_4–	H	H	(HCl)	21
Ph	*p*-ClC_6H_4–	H	H	(HCl)	21
Ph	*p*-ClC_6H_4–	Ac	H	279(HCl)	51
1-Pyrrolidinyl	Ph	Ac	H	295(HCl)	401
1-Piperidino	Ph	Ac	H	265	401
1-Morpholino	Ph	Ac	H	260(HCl)	52
MeS–	Ph	Ac	H	126–8(HI)	52
EtS–	Ph	Ac	H	170(HCl)	52
$PhCH_2S$–	Ph	Ac	H	120(HCl)	52

TABLE VIII-3



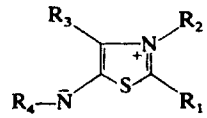
R_1	R_2	R_3	m.p.	Ref.
Ph	Me	H	144–6	11 sm, 23 24 r, 25, 27, 48 53, 54
Ph	Me	Ac	133–5	54–56
Ph	Me	Ph	203–4	4, 15, 17, 28, 29 u, 36
Ph	Me	PhCO–	219–20	54
			220–21	57
Ph	Me	ClHg–	>300	54
Ph	Me	AcOHg–	158–9	54
Ph	Me	$(NC)_2CHC(CN)_2$–	230–2	23
Ph	Me	$(NC)_2C{=}C(CN)$–	275–7	23
Ph		$-CH_2CH_2CH_2-$	148	26, 58, 59, 60
Ph		$-CH_2-S-CH_2-$	145–50	60
Ph	Ph	H	130–1	54
Ph	Ph	Ac	192–3	54
Ph	Ph	Br	163(HBr)	54
Ph	Ph	I	168–9	54
Ph	Ph	ClHg–	187–9	54
p-$MeOC_6H_4$–	Me	H	155–6	11 sm, 23
p-ClC_6H_4–	Me	H	159–61	23, 25, 53
p-ClC_6H_4–	Me	$(NC)_2C{=}C(CN)$–	283–5	23

TABLE VIII-4



R_1	R_2	R_3	m.p.	Ref.
Me	Me	Ph	184–6	29 i,u
Me	Ph	Me	223–6	29 i,u, 36
Ph	Me	Me	190–5	29 i,u
Ph	Me	Ph	184–5	15, 29, 32 33 k, 36
Ph		$-CH_2CH_2CH_2-$	193	26, 58
$-o-C_6H_3CH_2CH_2-$		*p*-$O_2NC_6H_4$–	—	29

TABLE VIII-5



R_1	R_2	R_3	R_4	m.p.	Ref.
Ph	Me	H	H	132–3 ($HClO_4$)	35
Ph	Me	H	Ac	219–20 (free)	25 i,u,r,sm
				243–4 (HCl)	34, 35 i,u,r
Ph	Me	H	PhCO–	261–2 (free)	35
				237–8 (HCl)	35
Ph	Me	H	p-$MeOC_6H_4CO$–	—	34
Ph	Me	H	p-ClC_6H_4CO–	—	34
Ph	Me	H	p-$O_2NC_6H_4CO$–	—	34
Ph	Me	H	m-$O_2NC_6H_4CO$–	—	34
Ph	Me	H	$PhSO_2$–	—	34
Ph	Me	H	p-$MeOC_6H_4SO_2$–	—	34
Ph	Me	Me	H	243–4 (HCl)	6
Ph	Me	Me	Me	228–30 (HCl)	6
Ph	Me	Me	Ph	175–6	6
Ph	Me	Me	Ac–	218–9 (free)	6
Ph	Me	Me	PhCO–	250–1 (free)	6
Ph	Me	Ph	H	206–7(HCl) 302–3($HClO_4$)	35
Ph	Me	Ph	Ph	197–9	36
Ph	Me	Ph	Ac	229(free) 207–8(HCl)	35
Ph	Me	Ph	PhCO–	259(free) 187–8(HCl)	15, 35 i,u,r
Ph	Me	Ph	PhNHCO–	231(HCl) 246(free)	35
Ph	Me	Ph	PhNHCS–	241	35
Ph	Me	Ph	$PhSO_2$–	242–3	35
Ph	Me	Ph	ON–	187	35
Ph	Me	Br	PhCO–	184(HBr) 236(free)	35
Ph	$PhCH_2$–	H	PhCO–	—	34
MeS–	Me	Me	Ac	176	6 u, 61
MeS–	Me	Ph	Ac	212–3	6 u
MeS–	Me	Ph	PhCO–	244–6	6 u
MeS–	i-Pr	H	Ac	179	6, 61

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IX

Cyanine Dyes Derived from Thiazolium Salts

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Hamer's book in this series (1), which reviewed the synthesis of sensitizing dyes, their physical characteristics, and general photographic properties up to 1958, remains the basic encyclopedic source for the study of methine dyes.

More recently, these dyes were the subject of an important chapter by Ficken in Venkataraman's volume published in 1971, "The Chemistry of Synthetic Dyes," which covers supplementary chemical knowledge (2).

Since then, the fundamental physicochemical aspects of the synthesis and properties of cyanines have been exhaustively reviewed by Heseltine and Sturmer in the fourth edition of Mee's treatise (3) and by Sturmer in Weissberger's edition of the "Chemistry of Heterocyclic Compounds" (4). So the purpose of this section dealing especially with thiazolomethine dyes is to give, apart from a complete and recent list of dyes and references, a description of the particularities of their chemistry and chiefly of the reaction mechanisms involved in their synthesis that have remained unknown or have not been discussed until now.

Another objective is to discuss briefly recent and major trends in the field of methine dyes color. Indeed, because of its relatively simple structure, the thiazole ring has been chosen in the past for studying color-structure relations. Using Brooker's "basicity" concepts (5), numerous valuable attempts in different countries succeeded in establishing semiempirical rules for explaining the effects of structural changes on color.

It appears now that, whatever its usefulness, the resonance theory is somewhat inadequate in explaining and predicting either chemical or physical characteristics of dyes compared to more or less sophisticated molecular orbital calculations.

Many patents and studies are still published in the field of thiazolo dyes because the photographic industry is always looking for new sensitizing dyes with improved efficiency and eager to know more about the mechanisms of their action on silver halide.

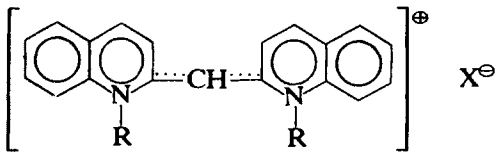
On the other hand, in spite of some interesting tinctorial properties, it does not seem that thiazolo dyes received wide application in the textile industry because they suffer from lack of stability to light and chemical agents.

Recently, however, new interest has developed due to their chemotherapeutic and bacteriostatic usefulness in animal husbandry. They also have been patented as herbicides and plant-growth-regulating agents.

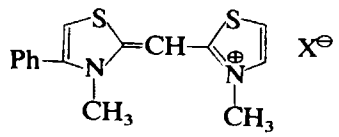
I. NOMENCLATURE

According to general usage, the term "cyanine" designates any cationic dye in which two nuclei of different or same nature are linked by a mono or polymethine chain. When these groups (–CH=) are replaced partially or totally by one or several nitrogen atoms, the cationic dye is called azacyanine.

The name found its origin in the fact that the first dyes known were all derived from quinoline as, for example, 2,2′-cyanine (Scheme 1). In the case of an asymmetrical or symmetrical dye involving one or two nuclei that are different from the quinoline ring, the name of the nucleus becomes the prefix in the name of the dye. So 3,3′-dimethyl-4-phenyl thiazolo cyanine is the dye of structure **1** and 3,1′-dimethyl 4-phenyl thiazolo 2′-cyanine is represented by the formula structure **2** (Scheme 2).



Scheme 1



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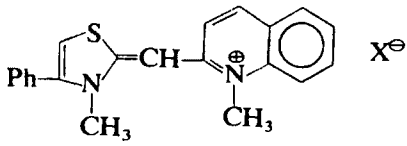


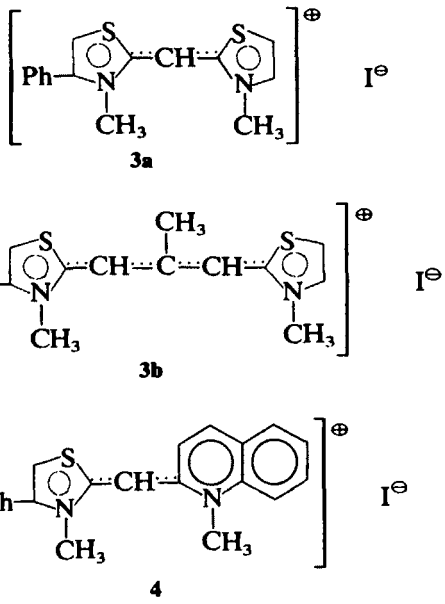
2

Scheme 2

It appears that this nomenclature is ambiguous to the extent that the basic name thiazolocyanine concerns two dyes of different natures that differ only by an index. Moreover, it implies that the positive charge is located on the nitrogen atom of the quinoline ring. In fact, the charge is entirely delocalized on the chromophoric chain (6–10): it cannot be attributed to one particular nitrogen atom of the component nuclei, which on the contrary possess both a relatively negative charge (11). As a consequence, it is difficult to represent the double bond in a given position rather than in the other one. The methine group is better represented by ⁻CH⁻ rather than by –CH=, and each bond possesses its particular value intermediate between a single and a double bond.

Some authors have suggested representing these two dyes as in (Scheme 3), using brackets (12, 13). Consequently, a cationic methine dye is better named in a more logical way by writing successively in brackets the names of the heterocycles involved (not under their dihydro forms) with the position of their attachment, then the length of the methine chain: mono-, tri-, pentamethine (rather than carbo for trimethine, dicarbo for pentamethine). The term cyanine corresponds to a dye of cationic character, since other methine dyes, negatively charged as oxonols, are not designated by the word cyanine.

Applying this rule, the preceding dyes are written (3-methyl-4-phenylthiazole-2)(3-methylthiazole-2)methine cyanine iodide (**3a**) and (3-methyl-4-phenylthiazole-2)(1-methylquinoline-2)methine cyanine iodide (**4**), respectively. Any substituent in the chain is named and its position designated by α, β, or γ, for example, (3-methyl-4-phenylthiazole-2)(3-methylthiazole-2)-β-methyltrimethine cyanine iodide (**3b**).



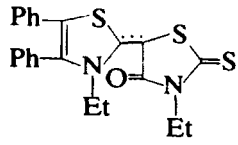
Scheme 3

Merocyanines belong to the class of nonionic methine dyes combining two nuclei, one of which is a ketomethylene of acidic nature such as pyrazolone, rhodanine, oxazolone, thiohydantoin, ...

The linking methine chain includes an even number of methine groups (0, 2, 4). They are commonly named as derivatives of the ketomethylene ring, for example, 3-ethyl-5-(3-ethyl-4,5-diphenylthiazolin-2-ylidene)-rhodanine (**5**) and 4-[4-(3-methyl-4,5-diphenylthiazolin-2-ylidene)-2-butenylidene]-3-methyl-1-*p*-sulfophenyl-2-pyrazolin-5-one (**6**) (Scheme 4).

German or Japanese authors name these dyes (3-ethyl-4,5-diphenylthiazole-2)(3-ethylrhodanine-5)-O-methine neutrocyanine and (3-methyl-4,5-diphenyl thiazole-2)(3-methyl-1-*p*-sulfophenyl-2-pyrazol-5-one-4)tetramethineneutrocyanine, respectively.

Rhodacyanines possess two chromophoric systems. They are at the same time neutrocyanine derivatives, which involves position 5 of the ketomethylene, and methine cyanine, which involves position 2. Following IUPAC's standard nomenclature rules, structure **7** is named 3-ethyl-4-phenyl-2-{4-oxo-3-ethyl-5-[2-(3-ethyl-2,3-dihydro-benzo-1,3-thiazolylidene)ethylidene]-tetrahydro-1,3-thiazolylidene-methyl}-1,3-thiazolium iodide (Scheme 5). It implies that the 4-phenyl thiazole ring having the



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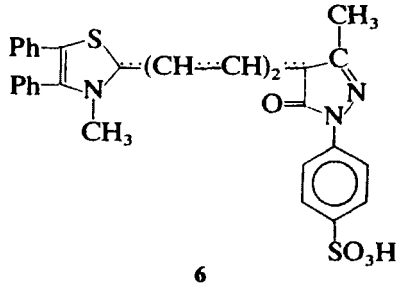

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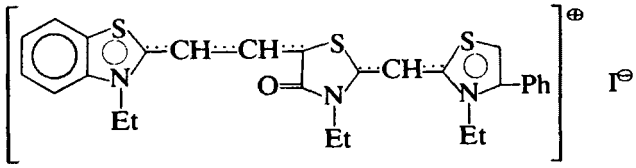
Scheme 4



7

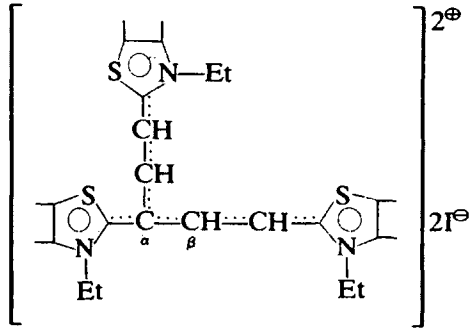
Scheme 5

positive charge plays a prominent part in the dye, although it is not actually possible to locate this charge. The name [(3-ethyl benzothiazole-2)(3-ethyl-4-onethiazole-5)dimethine][3-ethyl-4-phenylthiazole-2]monomethine cyanine, would not possess such an ambiguity in describing the dye.

Likewise, the nomenclature of neocyanines would not present any more difficulties if these suggested rules were followed, but it is not our task to apply them until official nomenclature is modified.

In this last case, the main skeleton considered could be the cationic trimethine cyanine and the third ring with its independent chain could be named as a substituent at the α or $\beta \cdots$ position. When this substituent is of an ionic nature, it could be named after the corresponding ring, for

example, α-(2-vinyl-3-ethylthiazolium-2 iodide)bis-(3-ethyl thiazole-2)-trimethine iodide (**8**) and (α-methylene-3-ethylrhodanine-5)(3-ethyl-4-methylthiazole-2)(3-methylbenzothiazole-2)trimethinecyanine iodide (**9**) (Scheme 6).



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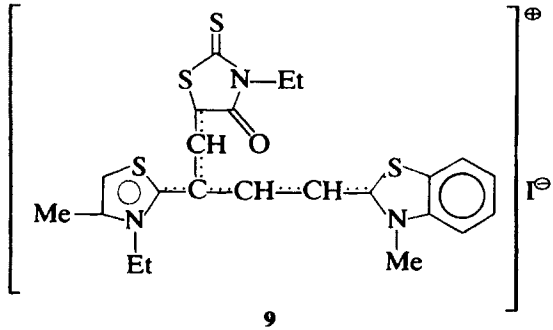

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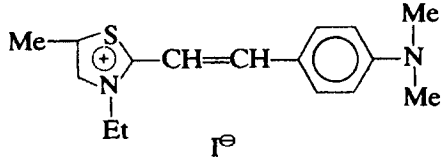
Scheme 6

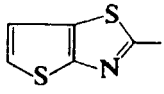
In styryl compounds, a part of the methine chain is replaced by a phenyl group. Their name is based on the nuclei from which they are issued: 3-ethyl-5-methyl-2-(*p*-dimethylaminostyryl)thiazolium iodide (Scheme 7).



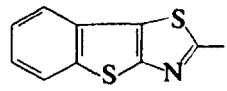
Scheme 7

All dyes of various types that are classified in the tables are derivatives of the thiazole ring with various substituents in positions 2, 3, 4, or 5.

The fused hetero rings of aromatic or pseudoaromatic character on the 4,5 bond as, for example, benzothiazole, naphthothiazole, thieno[2,3*d*]-thiazole, benzthieno[2,3*d*]thiazole, and so forth (Scheme 8), do not appear in the tables.



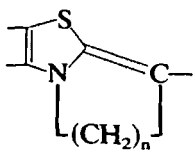
Thieno[2,3-*d*]thiazole



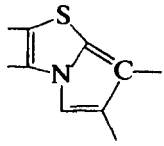
Benzothieno[2,3-*d*]thiazole

Scheme 8

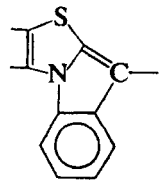
Only the rings shown in Scheme 9 have been indexed.



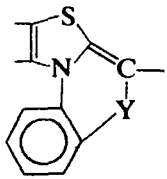
2,3-Polymethylene-thiazole



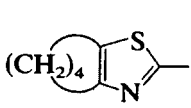
Pyrrolo[2,1-*b*]-thiazole



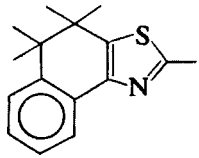
Thiazolo[3,2-*a*]-indole



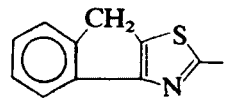
Thiazolo[2,3-*c*]-1,4-benzoxazine (Y = O)



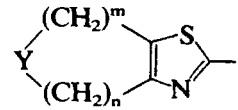
4,5,6,7-Tetrahydro-benzothiazole



4,5-Dihydro-β-naphtho-thiazole



Indeno[1,2-*d*]-thiazole



Dihydropyrano-[4,3-*d*]thiazole (Y = O)

Scheme 9

II. THIAZOLIUM QUATERNARY SALTS*

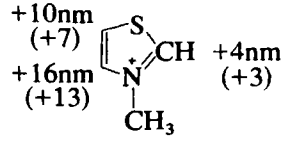
One may find many publications in the literature on the theoretical aspects of thiazolium quaternary salts, because of the biological importance of thiamine and their use as catalysts for benzoin condensation.

* The authors are indebted to Mrs. J. Vitry for her contribution to the compilation of the references for this section.

This section is restricted to the general properties and chemical behavior of quaternary salts chiefly when they are used as dye intermediates (Tables IX-1–3, IX-4abc, IX-5).

Thiazolium salts can be obtained either directly by slight modifications of ring-closure methods, already described for the parent bases, or by classical quaternization of the bases, the detailed mechanism of which have been reported in Chapter III; the quaternization is best represented by a classical SN_2 mechanism, the solvent playing an important part (14) unless the reaction is run without any solvent.

Nishimoto's fractional core charge model introduced in the Pariser-Parr-Pople method allows good correlation between experimental data, calculated characteristics of electronic absorption of thiazolium salts, and oxidation and reduction potentials (15). Quaternization of the nitrogen atom of a thiazole molecule gives a shift of the first band (662, 663). The importance of the bathochromic effect produced by a methyl substituent in different positions of the nucleus depends on the position of the methyl group as shown by the comparison of theoretical increments (in brackets) to the measured ones (Scheme 10) (15). The important hypsochromic shift [4.92 eV (252 nm) to 5.44 eV (229 nm)] observed between absorption of 4-phenylthiazole and 2,3-dimethyl-4-phenylthiazolium has been related to the absence of conjugation between the two cycles as the methyl group on the nitrogen atom prevents the phenyl ring from being coplanar with the thiazole (15, 660).

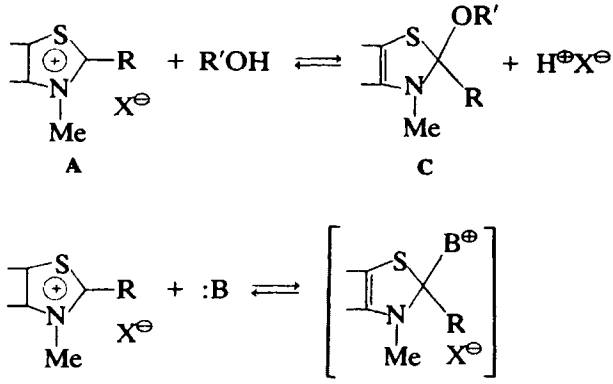


Scheme 10

The mobility of the proton in position 2 of a quaternized molecule and the kinetics of exchange with deuterium has been studied extensively (18–20); it is increased in a basic medium (21–23). The rate of exchange is close to that obtained with the base itself, and the protonated form is supposed to be the active intermediate (236, 664). The remarkable lability of 2-H has been ascribed to a number of factors, including a possible stabilizing resonance effect with contributions of both carbene and ylid structure. This latter may result from the interaction of a *d* orbital at the sulfur atom with the σ orbital out of the ring at C-2 (21).

1. Electrophilic Properties of Thiazolium Salts

The thiazolium ring, as most heterocycloammoniums, is a Lewis acid conferring to the carbon atom in the 2-position the carbocationic property of adding the free pair of a base either organic or mineral that may be the molecule of solvent as ROH (Scheme 11). For many nuclei of suitable acidity, these equilibria can be observed in dilute solution by means of absorption spectra when species **A** and **C** possess different characteristics (24). For example, benzothiazolium and benzoxazolium in methanol and ethanol give at 10^{-4} mole liter^{-1} 8 and 54% of the alkoxy derivatives for the former and 29 and 90% for the latter respectively.

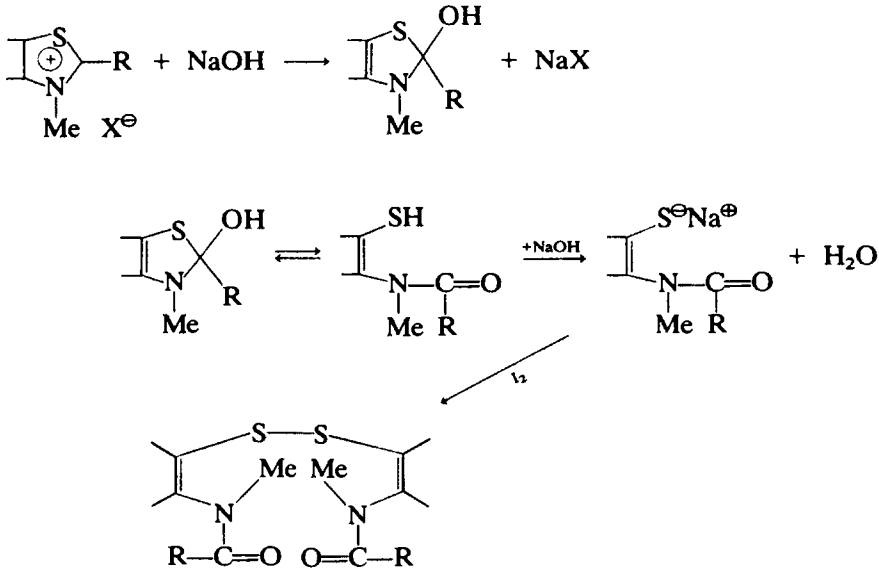


Scheme 11

Besides the well-known lower basicity of ethanol, these data illustrate the greater acidity of benzoxazolium compared with benzothiazolium. The relative pK_a values of the quaternary salts obtained in acetonitrile when treated with tetrabutylammonium hydroxide are 18.3 and 17.6, respectively (25). Those of 2-methyl 4-phenyl thiazolium and 2,4-dimethyl thiazolium are 20.5 and 21.8 under the same conditions (25).

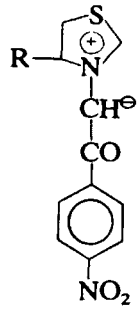
The thiazolium is not acidic enough for observing directly solvation of the molecule (or an hydrolysis and subsequent cleavage of the ring) (24) without adding a base, as it is the case for benzoxazolium or benzothiazolium. With the same dilution (10^{-4} mole liter^{-1}), it is necessary to add sodium ethylate to the solution of 2-methyl-4,5-diphenylthiazolium to observe the equilibrium described above. A new band appears in the UV spectrum at 320 nm that is attributed to the ethoxy derivative by analogy to what has been observed with other benzothiazoliums (26).

In aqueous solution whatever the nature of substituent in position 2 (R = H, alkyl or aryl), a sufficient concentration of NaOH is necessary to cleave the ring after formation of an unstable carbinol in a first step (Scheme 12) (27). The total consumption of alkali amounts to 2 moles per mole (28). The cleavage of the molecule is reversible, since ring closure occurs when adding an acid. The thiol formed can be titrated by an oxidizing agent (29). The kinetics of reversible cleavage were automatically followed by anodic waves measurements of thiols issued from various substituted thiazoliums. Electron-donating groups seem to stabilize the ring for OH attack (30), confirming that cleavage of the unsubstituted ring is easier (31).



Scheme 12

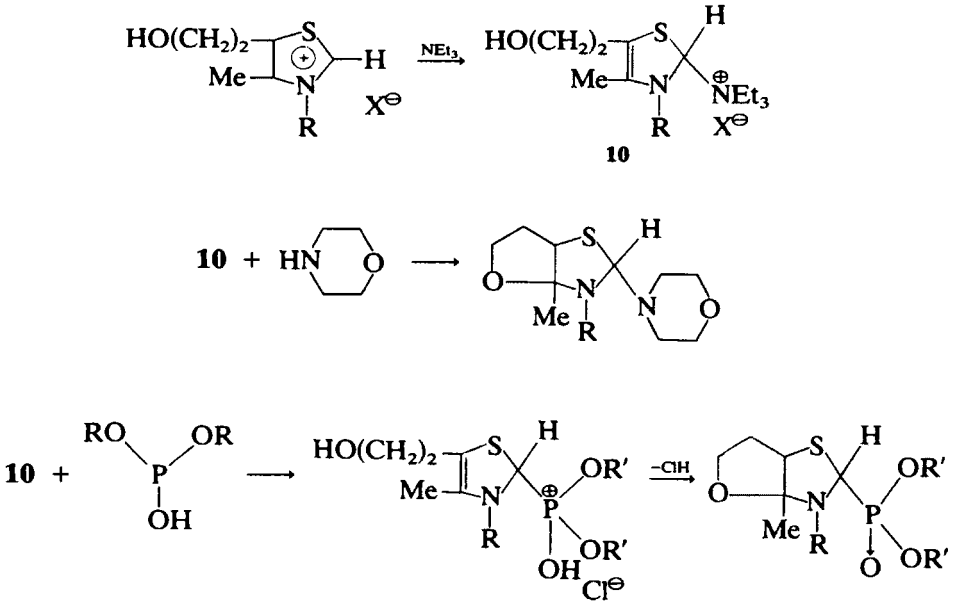
When the nitrogen atom is substituted by a nitrophenacyl group, OH attack gives the betainic zwitterion (Scheme 13), which is soluble in organic solvents (32). The stability of the C-betainic or ylid structure has been explained as an effect of resonance of the negative charge in the molecule (33, 34).



Scheme 13

Chiefly in an hydrophobic medium, a base can extract the proton on position 2 leading to a reactive intermediate (able to give subsequent condensation) that could be an ylid (35, 36) or a carbene (37), though no dimer has ever been isolated as is the case with benzothiazolium (32, 38). Two mechanisms have been proposed for explaining the particular reactivity of thiazolium:

1. Electrophilic reaction can account for the additions of morpholine or phosphonyl (Scheme 14), or

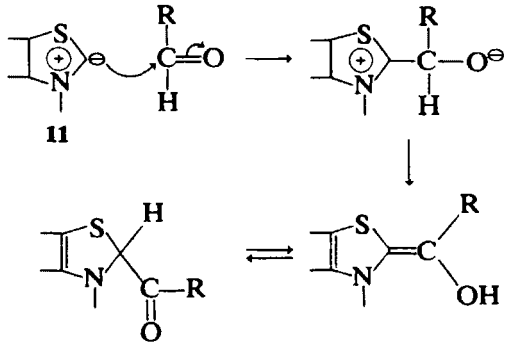


Scheme 14

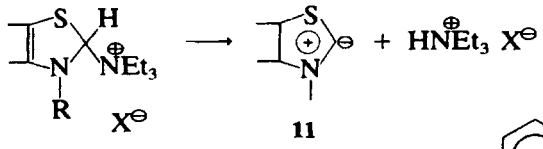
2. Nucleophilic reaction of an ylid, under hydrophobic conditions.

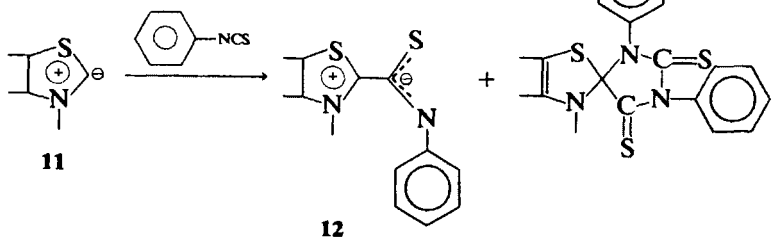
This has been the subject of many investigations starting from thiamine itself or derivatives, with the aim of explaining the role of pyrimidine group in coenzymatic activity.

Adducts from various quaternary salts have been isolated, in reactions with aldehydes, α-ketoaldehydes, dialkylacylphosphonates and dialkylphosphonates, isocyanates, isothiocyanates, and so forth (Scheme 15) (36). The ylid (**11**) resulting from removal of a C_2 proton from 3,4-dimethyl-5-β-hydroxyethylthiazolium iodide by NEt_3 in DMF gives with phenylisothiocyanate the stable dipolar adduct (**12**) that has been identified by its NMR spectrum and reactional product, such as acid addition and thiazolidine obtention via $NaBH_4$ reduction (Scheme 16) (35). It must be mentioned that the adduct issued from di-*p*-tolylcarbodiimide is separated in its halohydrogenated form. An alkaline treatment occasions an easy ring expansion into a 1,4-thiazine derivative (Scheme 17) (35).

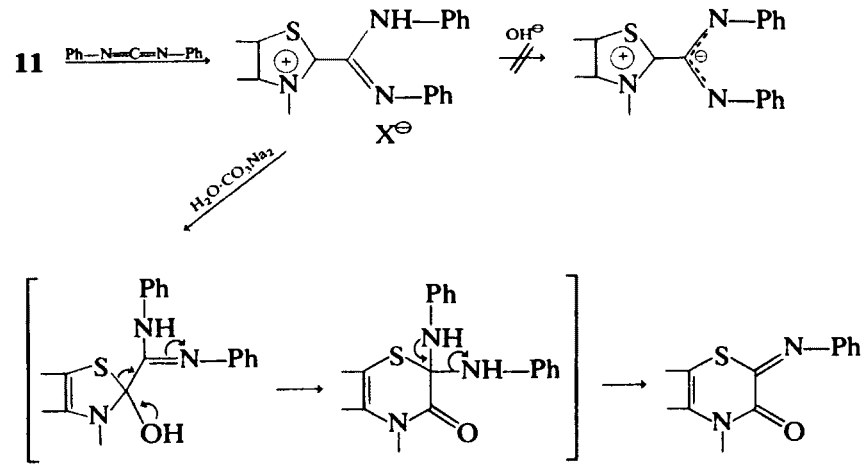


Scheme 15





Scheme 16

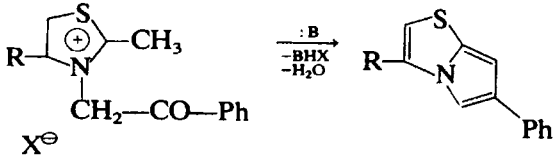


Scheme 17

2. Specific Behavior of 2-Methylthiazolium Salts in Basic Medium

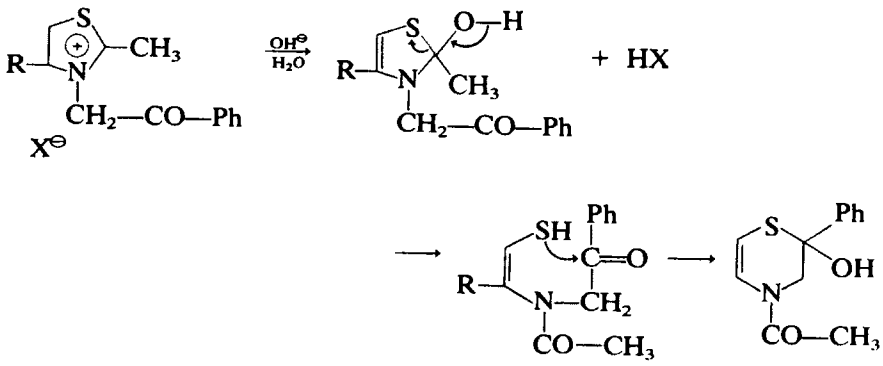
When the substituent on the nitrogen atom is $-\overset{R}{\underset{|}{C}}H-\overset{O}{\overset{||}{C}}-R_2$, R = H, Me, R_2 = Ph, Me, two types of reactions can occur, according to the nature of the medium in which the base is allowed to react:

1. In aprotic conditions acetic anhydride sodium acetate induces formation of a fused ring through an intra molecular condensation. It results in a pyrrolo[2,1-*b*]thiazole (39), which constitutes an interesting intermediate for the synthesis of dyes (Scheme 18) (40).



Scheme 18

2. But when the reaction is carried out in an aqueous solution of sodium hydrogen carbonate, extension of the ring occurs with formation of dihydro-1,4-thiazine derivative (Scheme 19), the structure of which has been established by mean of NMR and infrared spectra (41).



Scheme 19

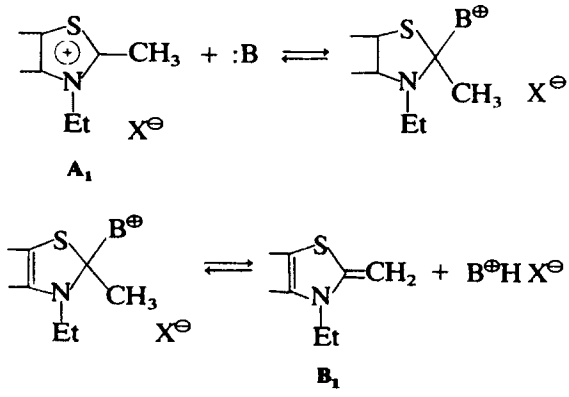
A. *Anhydrobases*

In 1923, Mills introduced thiazole for the first time in the synthesis of methine dyes through a somewhat indirect route. In order to demonstrate the 2,4'-cyanine mechanism of formation by quinoline and quinaldine quaternary salts reacting together, Mills used other pairs of quaternary salts as 2-methylthiazolium with either quinolinium or benzothiazolium (42, 43).

Even if the specific role attributed to benzothiazolium was not confirmed later (24), all these syntheses account for the significant and common behavior of quaternary salts, carbocations giving either symmetrical or asymmetrical reactive anhydrobases. They constitute the main step in cyanine dye formation.

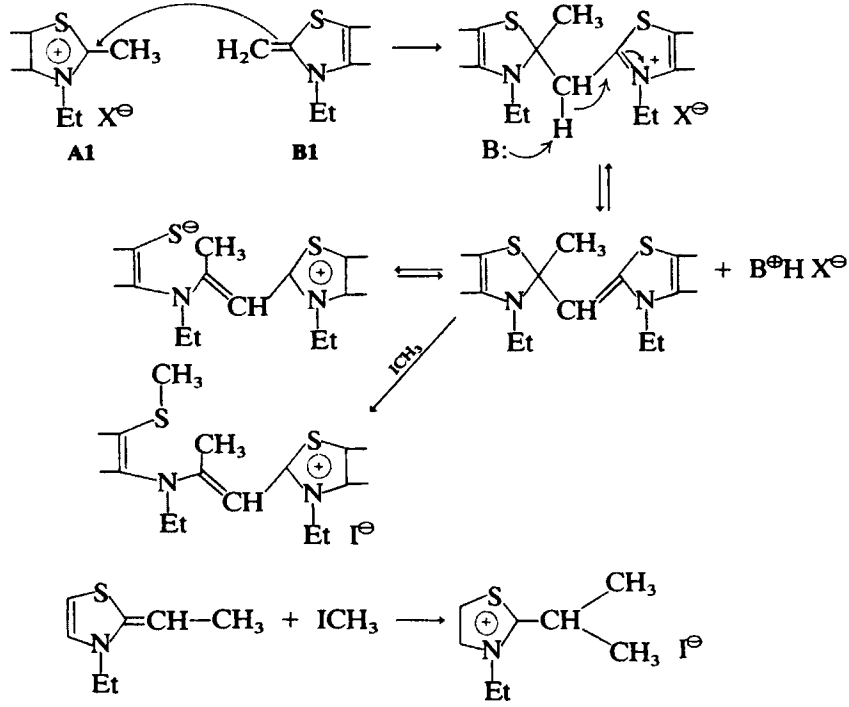
A sufficient concentration of base B is necessary for the removal of a proton of the CH_3 group. In a first step, the equilibrium in Scheme 20 results, in which the monomeric anhydrobase B_1 constitutes the conjugated base of the quaternary salt A_1. As has been shown for other rings (24), the equilibrium depends upon the concentration of the different species and the relative strength of the bases B and B_1, and depends also upon the nature of X.

Many monomeric heterocyclic anhydrobases can be isolated now using specific methods (44), but application of these methods to thiazole ring did not succeed; however, appropriate conditions lead to the separation of a dimer, the structure of which has been established by its NMR spectra and chemical reactivity (26). The most probable mechanism of its formation appears identical with the one previously described in the benzothiazolium series (24). A second molecule of quaternary salt A_1



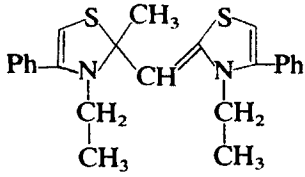
Scheme 20

condenses with the anhydrobase B_1, giving the conjugated acid of the dimer; afterwards, this dimer leads to the anhydrobase through removal of a proton (Scheme 21). This dimer is more stable than B_1 itself.

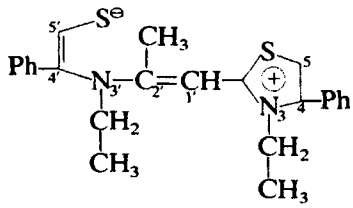


Scheme 21

At first, the dimeric nature of the base isolated from 3-ethyl-2-methyl-4-phenylthiazolium was postulated via a chemical route. Indeed the adduct of ICH_3 on a similar 2-ethylidene base is a 2-isopropylthiazolium salt; in the case of methylene base it is an anilinovinyl compound identified by its absorption spectrum and chemical reactivity (45–47). This dimeric structure of the molecule has been definitively established by its NMR spectrum. It is very similar to the base issued from 2,3-dimethyl-benzothiazolium (48). It corresponds to 2-(3'-ethyl-4'-phenyl-2'-methylenethiazolinilydene)2-methyl-3-ethyl-4-phenylthiazoline (**13**). There is only one methyl signal ($\delta_2 = 2.59$), and two series of signals ($\delta_3 = 1.36$–3.90, $\delta_3 = 1.12$–3.78) correspond to ethyl groups. Three protons attributed to positions 1',5,5' are shifted to a lower field: 5.93, 6.58, and 8.36 ppm. The bulk of the ten phenyl protons is at 7.3 ppm (Scheme 22).



13

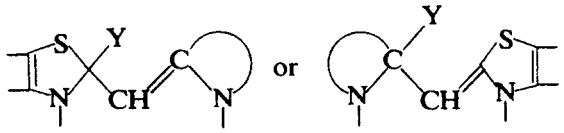


14

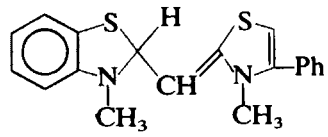
Scheme 22

By comparison with the anhydrobase of 2,3-dimethyl benzothiazolium (48), the following facts can be noted. The shift of the proton 5' signal seems abnormal, the proton signals of 2'-methyl group (2.59 ppm in $CDCl_3$ and CD_3CN/Tetramethylsilane are shifted upfield with respect to the corresponding methyl group (1.66 ppm), and it is the same for the signal of the methine proton 1': 5.93 versus 4.42 ppm. The NMR spectrum accounts better for a zwitterion vinylic structure such as **14**, which also possesses the same absorption spectrum as the identified anilinovinyl quaternary adduct, resulting from ICH_3 action ($\lambda_{max} = 380$ nm) (26).

The zwitterionic opened form, and the closed form, could exist in equilibrium. Anyway, such a molecule is characterized by a methine group joining two rings, one of the starting rings still possessing its methyl-substituted group. Such dimeric structures issued from one same ring may be considered as symmetrical, contrary to asymmetrical ones, where the methine bridge joins two heterocyclic ring of different nature (**15**) such as described for benzothiazole series (Scheme 23) (49). These last derivatives are much more difficult to separate. However they appear to be at the origin of the dyes obtained either in Mill's reaction (42), for example, **16**, or resulting from the action of a basic agent on 2-methylthiazolium.



15 Y = H, Alkyl, Aryl



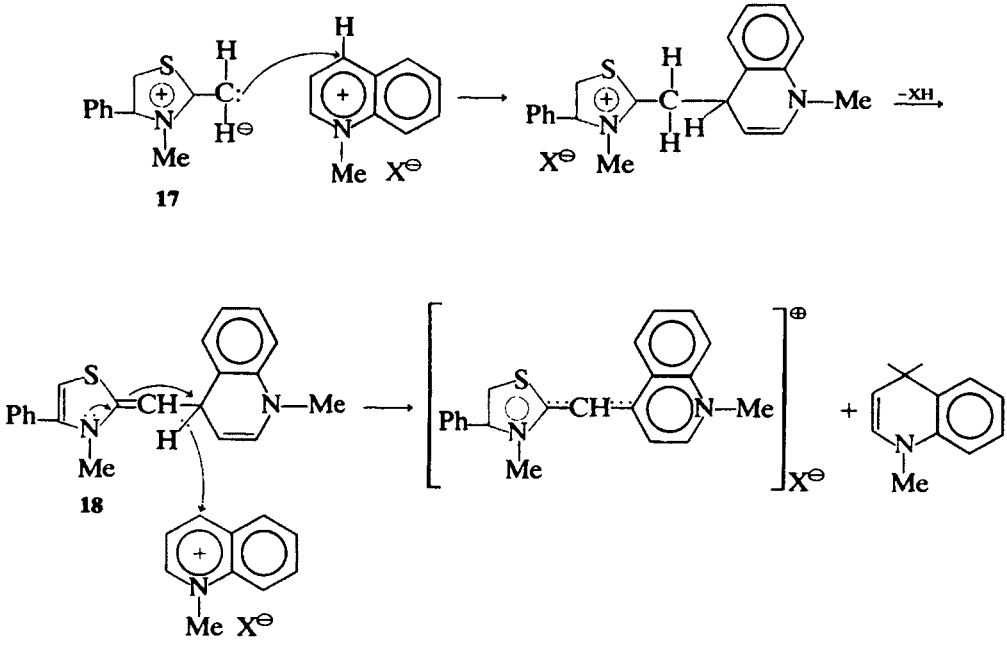
16

Scheme 23

B. *Mechanism of the Thiazolocyanine Formation from Anhydrobases*

This mechanism undoubtedly has a close analogy with the ones described previously in quinoline series, which have received experimental support (54). They can be classified as oxidative synthesis. The dye (3-methyl-4-phenyl thiazole-2)(1-methyl quinoline-4)monomethine cyanine iodide was obtained by condensing the corresponding quaternary salts in alcoholic solution with sodium hydroxide as basic agent (method H) (Scheme 24) In a first step, a proton is extracted from the methyl group by the basic agent B, giving the conjugated base (**17**). It is followed by a nucleophilic attack of the monomeric anhydrobase on carbon-4 of a quinolinium ion, which is the most electrophilic substrate (quinolinium is

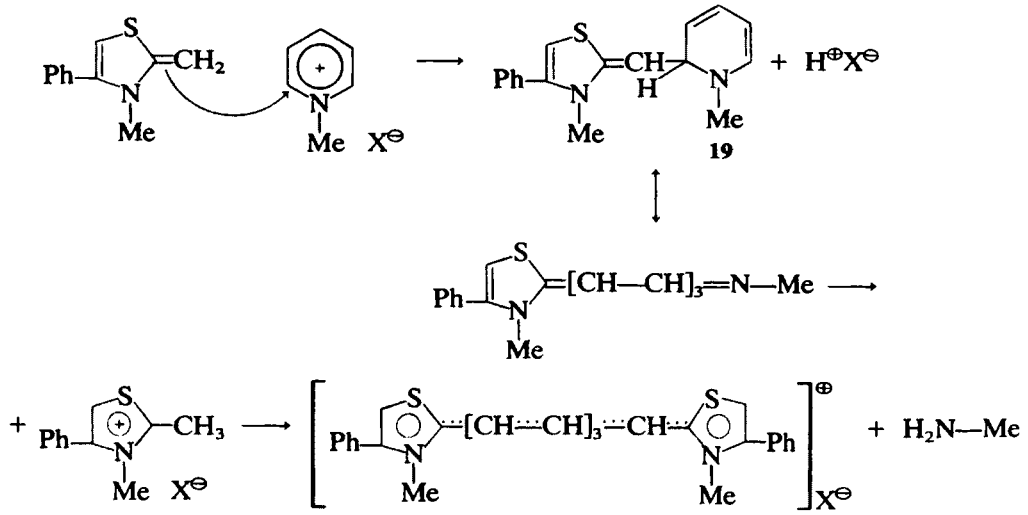
known to undergo nucleophilic attack in position 2 and chiefly in position 4). The conjugated acid loses one proton by action of B to give the reactive unsymmetrical anhydrobase (**18**). In a second step, the hydrogen atom in position 4 of this molecule is transferred in the form of a hydride ion to a second molecule of quinolinium. The former molecule being oxidized, a charge appears on it while the latter is reduced.



Scheme 24

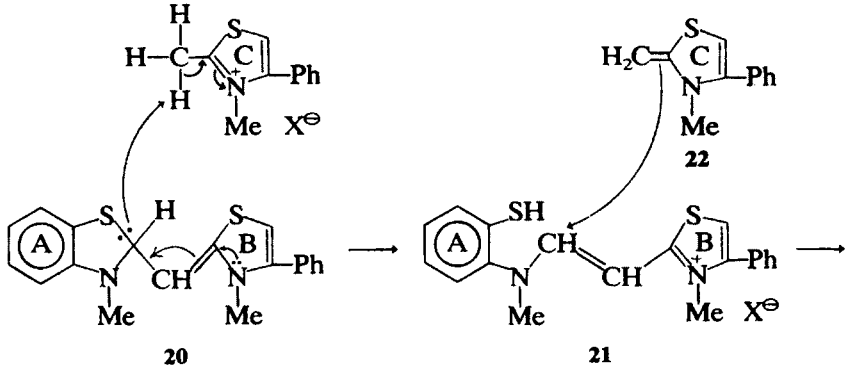
As a whole, 2 moles of quinolinium react with one of thiazolium together with 2 moles of base. This explains the traditional interest of making the condensation with an excess of quinolinium salt in order to get the maximum yield (50, 51).

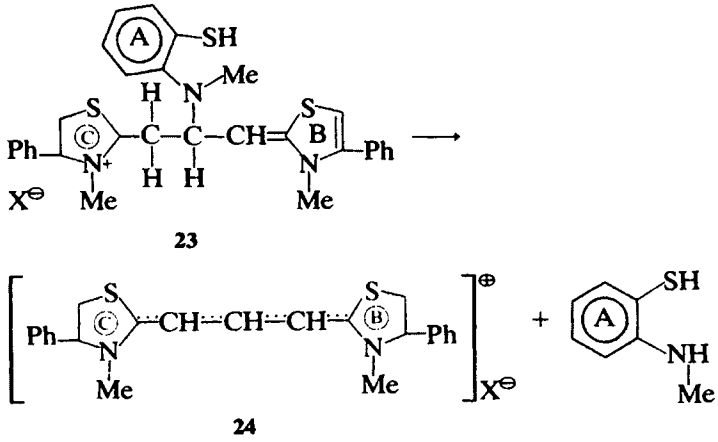
In the case of a pyridinium salt, an indirect proof of the correctness of this mechanism can be found in the presence of a heptamethine thiazolocyanine, together with monomethine, which results unambiguously from **19** by the known opening of the pyridine ring (Scheme 25) (52).



Scheme 25

The asymmetrical anhydrobase (**20**) constitutes the first step of the formation of trimethine thiazolocyanine when a 2-methylthiazolium salt reacts either with a benzothiazolium or its opened form [which is bis-*o*-(formylmethylamino)(diphenyl disulfide] (Scheme 26). In a second step, **20** is protonated by a second molecule of 2-methylthiazolium. It results in cleavage of the benzothiazoline ring, which gives **21** together with the formation of the monomeric anhydrobase (**22**). Cleavage of the C–S bond of **20** can be explained by the important electronic desaturation of the C atom observed in NMR spectrum and the great polarizability of the C–S bond in this type of ring (48).





23

24

Scheme 26

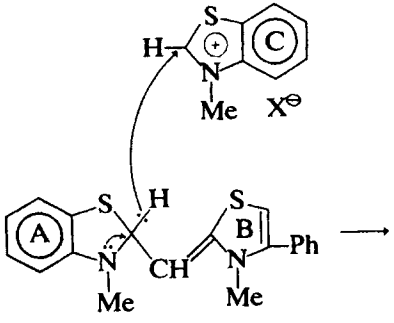
In a third step, the anhydrobase reacts on the carbon which is the most sensitive to nucleophilic attack. The unstable intermediate **23** splits into aminothiophenol and trimethine thiazolocyanine (**24**).

The structure of **20** also explains why the Mill's reaction (43) leads to (3-methylbenzothiazole-2)(3-methyl-4-phenylthiazole)monomethine iodide.

Two probable mechanisms may be involved:

- Hydride ion transfer as in the case of isocyanine (49),
- Possibility of making 2-methyl benzothiazolium either by reaction of the benzothiazolium quaternary salt on the anhydrobase (24) or by reaction of *o*-methylaminothiophenol on the same anhydrobase (26).

The symmetrical dye, bis-(3-methyl-4-phenylthiazole)monomethine cyanine (not mentioned by Mills), has also been identified, and its formation is explained by the enamine character of **20** (Scheme 27).



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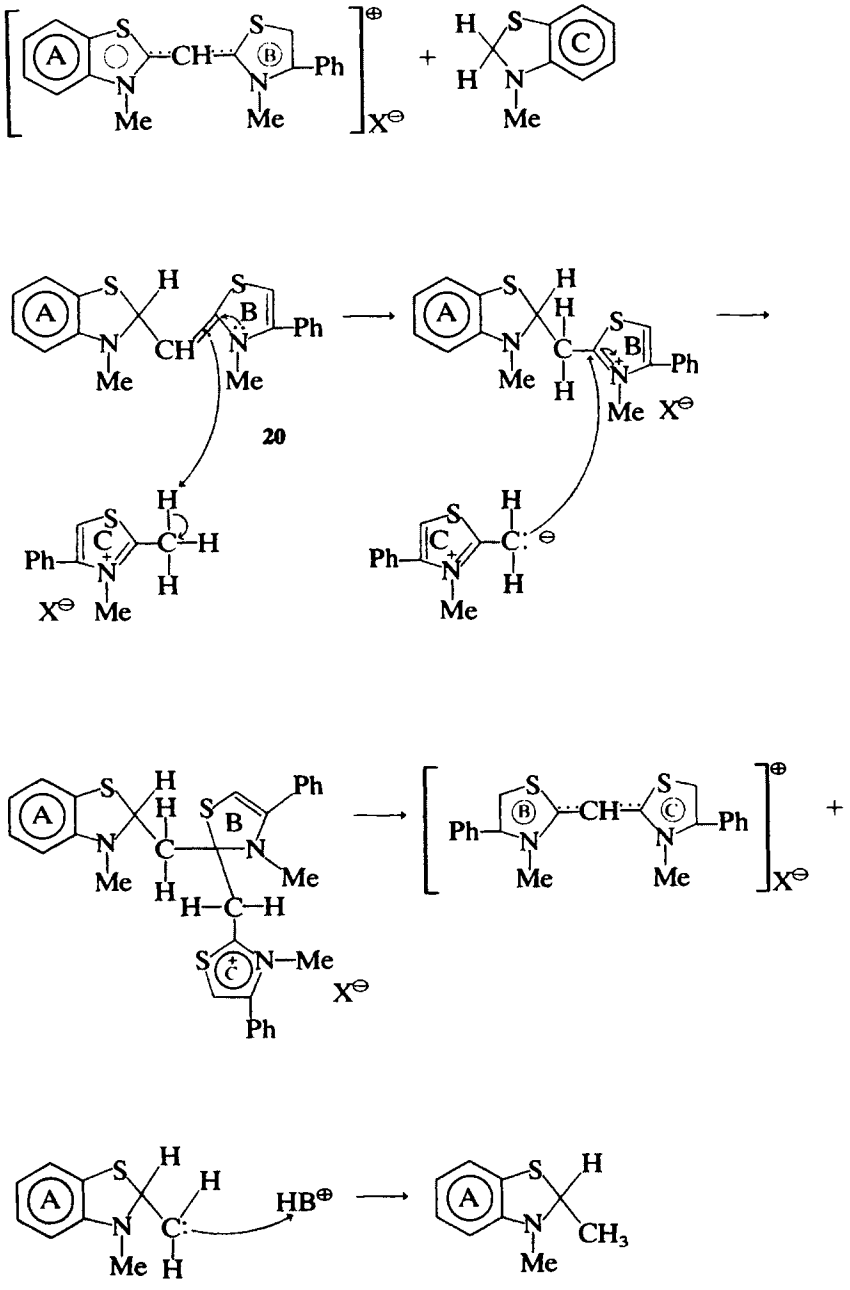
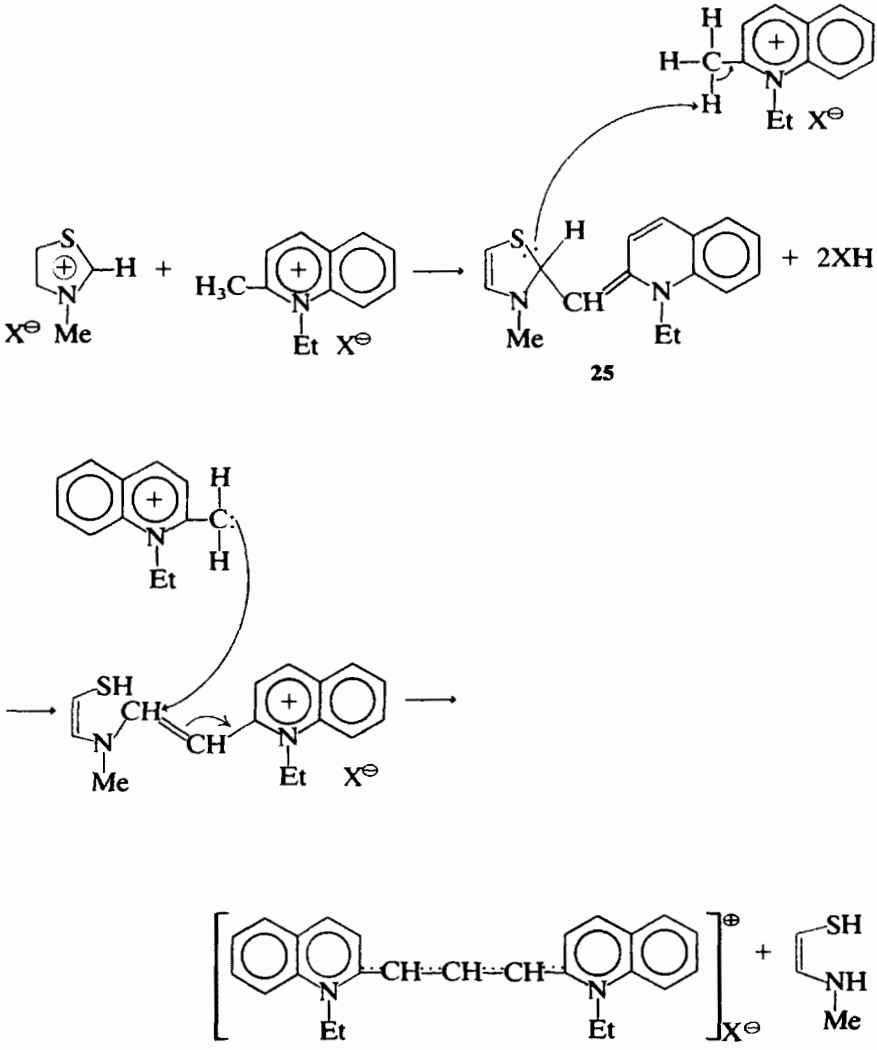
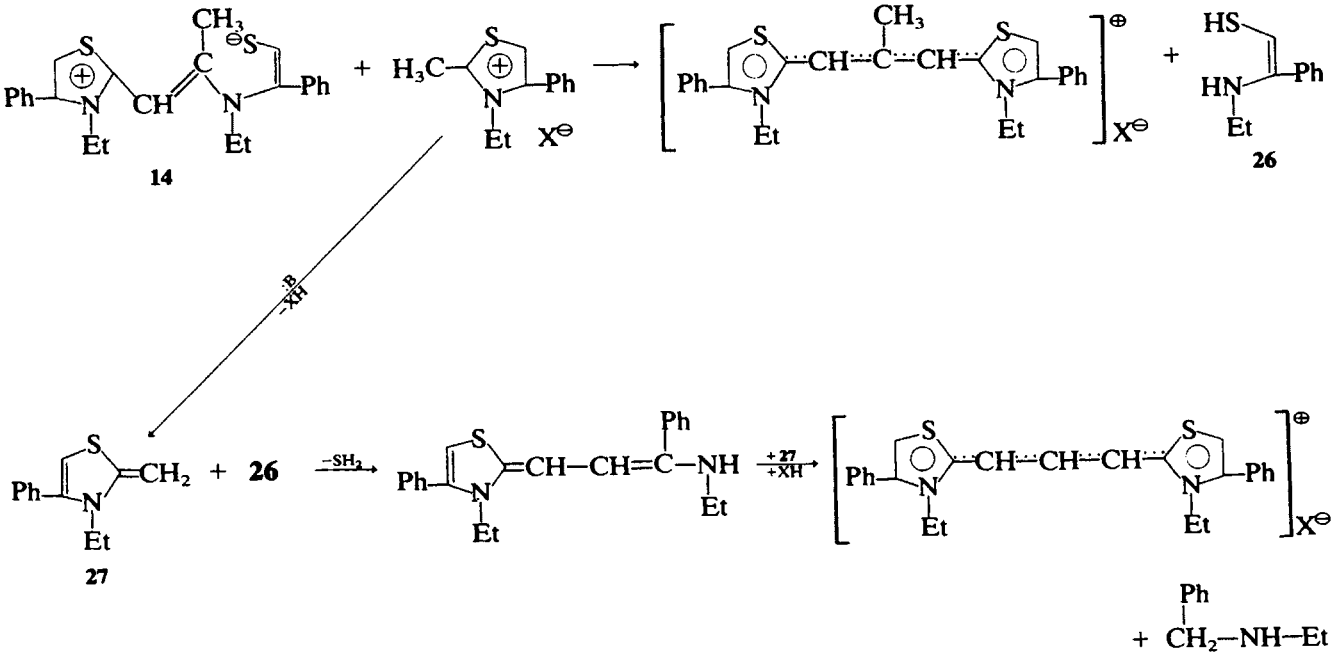


Scheme 27

When a quinaldinium salt and 2-unsubstituted thiazolium are condensed together in the presence of a basic agent, the resulting bis-(methylquinoline-2)trimethine cyanine is issued from the cleavage of the thiazolium ring of the anhydrobase (**25**). It is induced by the $-CH_3$ attack of quinaldinium according to a process already described (Scheme 28).



Scheme 28



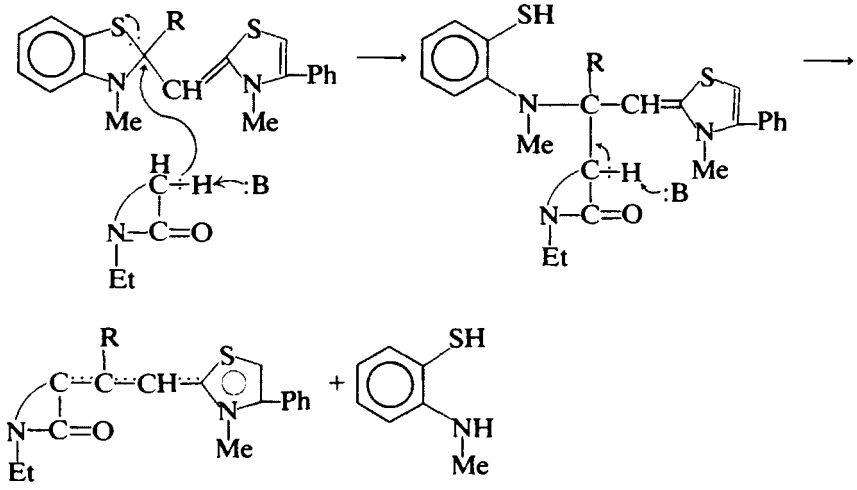
Scheme 29

Due to the structure of the symmetrical anhydrobase, every time a 2-methylthiazolium undergoes the attack of a base, theoretically it can result in two trimethine thiazolocyanines: the mesomethylsubstituted one and the unsubstituted one. For an unexplained reason, it seems that when position 5 of the starting molecule is substituted, only the mesomethyl dye is produced according to the absorption spectrum, 530 nm for the methylmeso and 569 nm for the 4-phenyl substituted derivative (Scheme 29).

As an illustration of the real complexity of Mill's reaction, when two molecules of heterocycloammoniums of different nature, one of them being thiazolium (2-substituted or not), are put together in a basic medium, nine dyes theoretically can be produced (depending on the nature of the substituent in the ring): three thiazolomonomethine cyanines (two symmetrical, one asymmetrical) and six trimethine cyanines (two symmetrical, two symmetrical mesosubstituted, one unsymmetrical, one unsymmetrical mesosubstituted). One cannot separate such a mixture by usual chromatographic means.

C. *Obtention of Neutrocyanine from Anhydrobases*

The nucleophilic carbon of ketomethylene compounds can react with anhydrobases of different species in a basic medium. This reaction presents a narrow similitude with $-CH_3$ attack. The resulting dye, neutrodimethine cyanine either mesomethyl-substituted or not, varies with the nature of the anhydro base (Scheme 30) (53, 54).



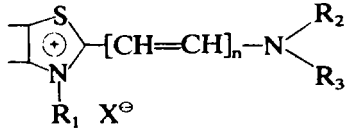
Scheme 30

III. SYNTHESES OF THIAZOLOCYANINES

1. Mononuclear Cyanines

A. *Hemicyanines* (Tables 1111, 1112A,B,C,D, 1113)

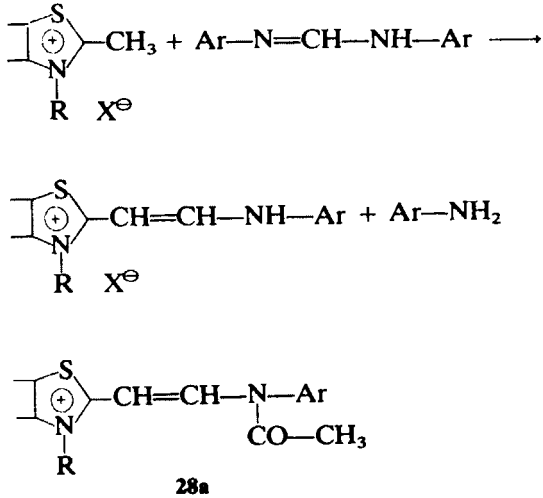
The hemicyanines constitute a particular class among streptocyanines in which one of the two nitrogen atoms belongs to a heterocycloammonium. Thiazolohemicyanine corresponds to the general formula in Scheme 31. When $R_2 = R_3 = H$, the dyes are of aminovinyl type; when $R_2 = H$, $R_3 = Ph$, they are anilinovinyl compounds, and when (–CH=CH) is replaced by a benzene ring, they are aminophenyl.



Scheme 31

Anilinovinyl derivatives condense with methyl or methylene reactive groups of heterocycloammonium or ketomethylene, and are useful intermediates in the syntheses of thiazolotrimethine cyanines and thiazolodimethine neutrocyanine. They are prepared according to the following methods:

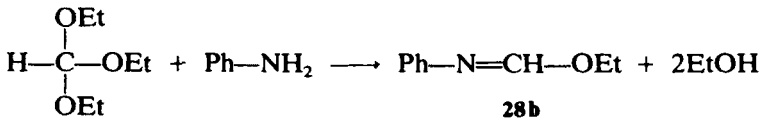
- Melting of a quaternary salt with an arylformamidine (method A, Scheme 32).



28a

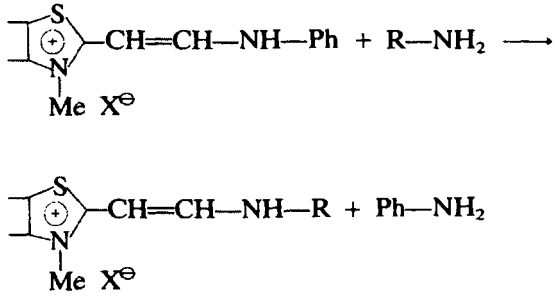
Scheme 32

- Mixing of quaternary salt, aniline, and ethylorthoformate (method B, Scheme 33).



Scheme 33

- Use of ethylisoformanilide (**28b**) (method C).
- Transamination (method D, Scheme 34).



Scheme 34

- Condensation in acetic anhydride involving acetanilidovinyl derivatives (**28a**) (method E, Scheme 32).

The aminophenyl compounds were obtained only by a direct heterocyclization.

B. *Styryl Dyes* (Tables 1121A,B,C,D,E,F,G)

Styryl Dyes result from the condensation of benzaldehyde or *p*-dialkylaminobenzaldehyde with quaternary salts of 2-methylthiazole, either in acetic anhydride or in a solvent with a base as catalyst.

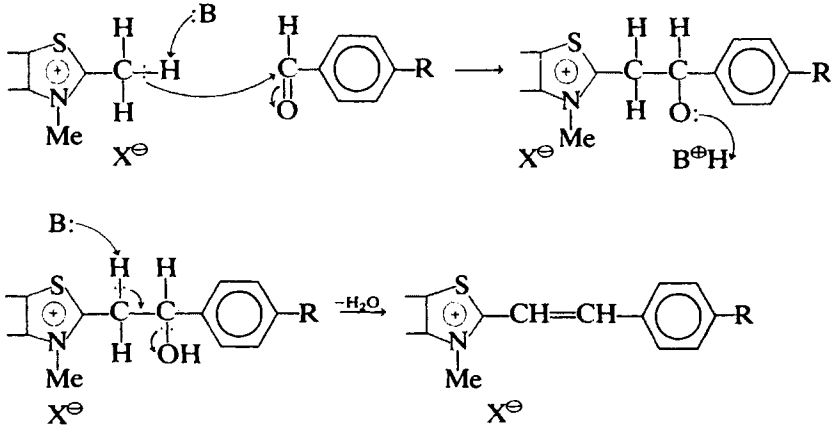
This class of dye has offered in the past two matters of interest. It has been chosen by Mills as the material for demonstrating the mechanism of

the condensation and the role of the anhydrobases issued from quaternary salts by loss of a proton.

It has been used to establish the "basicity" scale of nuclei by means of the deviations calculated from λ_{max}. This "basicity" has in fact a concrete physical sense, corresponding to the pK_a of the heterocycloammonium (25, 55); regarding Mills' views about the role of an active allenic intermediate (56), such compound could never be isolated or even identified (49).

Moreover, the specific role of anhydrobase in this condensation is not confirmed, since separated anhydrobases are not reactive toward aldehydes and the condensation can be made in an acid medium.

The reaction probably must involve two steps, aldolization followed by crotonisation, and depends among other factors on the specific reactivity of the aldehyde and of the methyl, which is influenced both by the nature of the substituents on the ring and by the nature of the anion (Scheme 35) (57, 58, 657)



Scheme 35

The stereo aspect of the condensation has been studied for pyridine derivatives, and according to the nature of solvent, either ethanol or acetic anhydride, a *cis* or a *trans* dye could be obtained (59).

A mesophenyl-substituted trimethine cyanine has been identified as a by-product in syntheses leading to styryl dyes; it is also obtained when the anhydrobase reacts with the styryl dye (26).

C. *Dimethine Cyanines* (Tables 1122A,B)

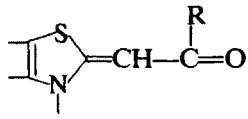
Except in the case of formaldehyde, the electrophilic character of carbon atom of an aliphatic aldehyde is not strong enough to allow its condensation on a CH_3 reactive group. However, such a condensation can occur with an aromatic or pseudoaromatic substance such as benzaldehyde or pyrroloaldehyde, and the λ_{max} of the resulting dimethine dyes have been used in this last case to obtain the "basicity" scale of various rings (16).

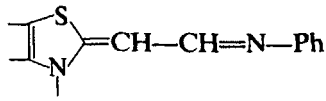
D. *Azastyryl Dyes* (Table 1123)

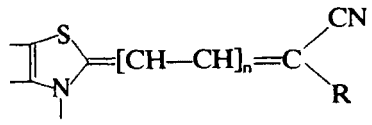
The azastyryl dyes result from the condensation of 2-formylthiazolium salt either on *N,N*-dimethyl-*p*-phenylene diamine or aromatic nitroso derivative.

E. *Nonionic Mononuclear Compounds* (Tables 121, 122, 123)

Very few compounds of this type have been described and appear in the tables of ketomethylene, anilinovinyl bases, and semicyanines (Scheme 36).







Scheme 36

2. Dinuclear Cyanines

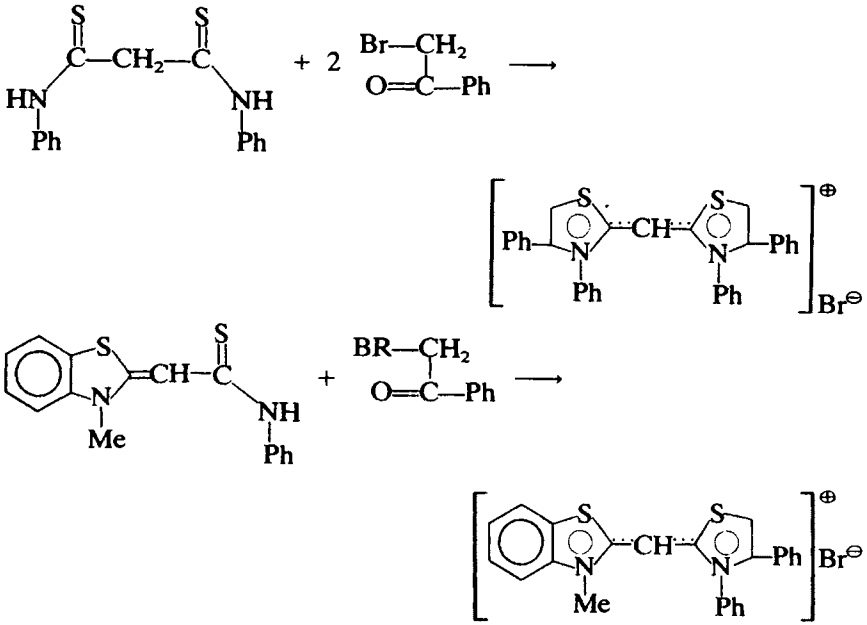
A. *Cationic Dyes*

a. MONOMETHINE THIAZOLOCYANINES (Table 2111)

The general and historical method of formation of monomethine cyanine, which consists of condensing amyl nitrite on a 2-methyl reactive group in acetic anhydride (method A) does not give any result in the case of thiazolium (60). However, sodium nitrite in acetic acid was used to synthesize symmetrical thiazolocyanines (method B). For an unexplained reason, a 2-substituted halogen in a thiazole ring does not possess the reactivity exhibited in the case of other heterocycloammoniums or in the case of other electrophilic reagents such as –SR, $-SO_3^-$, $-SO_3Me$, whatever the nature of the ring may be.

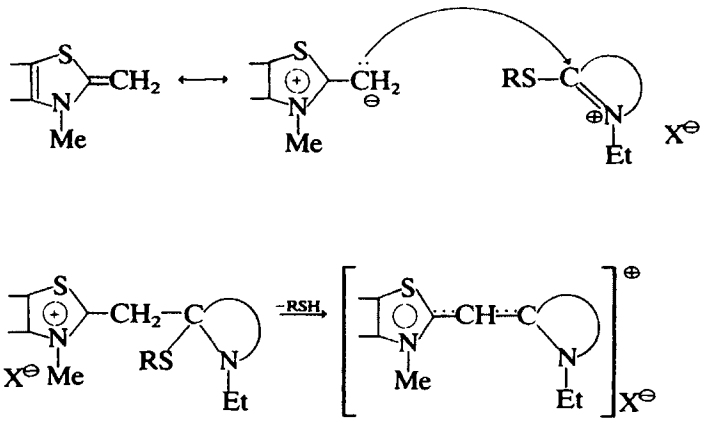
Thiazolomonomethine cyanines result from the condensation of 2 moles of 2-alkylmercaptothiazolium on 1 mole of malonic acid in pyridine (method C) but could not be obtained from this intermediate in acetic anhydride as is the case for other rings (26).

The one-step condensation of phenacyl bromide on dithiomalonanilide (method D) leads to *N*-phenyl thiazolocyanines (Scheme 37).

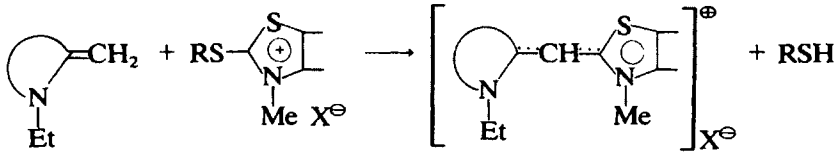


Scheme 37

The unsymmetrical thiazolocyanines (Tables 2112A,B,C,D,E) result from the condensation of an electrophilic reagent such as an heterocycloammonium possessing a substituent leaving group –SR, SO_3^-, $-SO_3Me$, OR) on a reactive methyl group. The reaction can be carried out in the two ways (Schemes 38 and 39). The formation of an anhydrobase constitutes the first step of the reaction. It adds onto the positive carbon atom of the quaternary salt bearing the leaving group, which is eliminated afterwards under the effect of the basic condensation agent. The yields appear to be the same when the anhydrobases are actually isolated, and used in place of the methyl quaternary salts. Any substituents that as carbethoxy are electron withdrawing, and enhance the acidity of thiazolium, facilitate the obtention of anhydrobases. The yields are consequently increased by comparison with an unsubstituted molecule (61, 62).

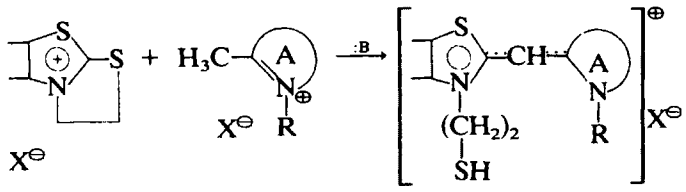


Scheme 38



Scheme 39

The interesting reactions where a free mercapto group is linked to the nitrogen atom of the thiazole (63), after the cleavage of a fused ring, is another illustration of the additive properties of the carbocation (Scheme 40).



Scheme 40

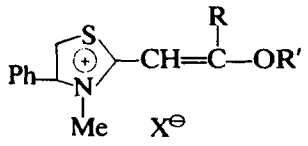
The monomethine cyanines with a methyl group on the chain (Table 2113) are prepared in a basic medium from a 2-alkyl-substituted thiazolium by condensation of an electrophilic reagent.

Few representative dyes of cyanine base (Table 2114) resulting from the condensation of alkylmercapto indolenine on 2-methylthiazolium have been described.

b. TRIMETHINE THIAZOLOCYANINES (Tables 2121A,B,C, 2122A,B,C, 2123A,B, 2124A,B)

SYNTHESES WITH *O*-ESTERS (SYMMETRICAL). Such functionally symmetrical reagents reacting on quaternary salts in pyridine give generally good results for rings for which the *pK* is the more acidic; for the less acidic rings of thiazolium, pyridinium, and quinolinium, except in the case of the very reactive ethyl *o*-formiate, the yields are much lower. That is why the literature gives very few results furnishing at the same time purity, yield, and precise λ_{max}, as is the case with alkyl *o*-acetate or *o*-propionate.

The reason for this relative lack of reactivity of 2-methylthiazolium is probably due to the too-weak nucleophilic character of its carbon-2. For example, any β-alkoxyalcene (**29**) derivatives resulting from the condensation of *o*-ester could never have been isolated, whereas they constitute the essential intermediate step in trimethine syntheses for rings of acidic character (64). However, even if a negative 5-substituent such as ethoxycarbonyl increases the yield (61) by promoting independently the possible formation of the methylene base, it may be stressed that the presence of this base is not the essential condition of the reaction, since the isolated anhydrobase itself is not reactive toward the *o*-ester (Scheme 41).

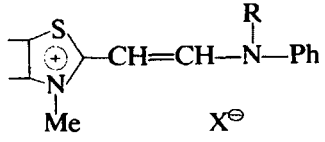


29

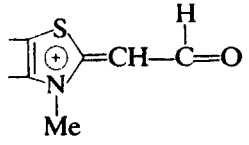
Scheme 41

OTHER ACCESS ROUTES FOR SYMMETRICAL AND UNSYMMETRICAL THIAZOLO DYES. Other functionally symmetrical reagents such as diethoxymethylacetate (method C), ethoxymethylenediethylmalonate (method D), diphenyl formamidine, and ethylisoformanilide condense with 2-methylthiazolium to give the trimethine thiazolo dyes.

Anilino vinyl derivatives of thiazolium (**30**, R = H) or acetanilido (**30**, $R = COCH_3$), as well as formyl methylene **30b** (methods E–G), give asymmetrical dyes when condensed with a methyl reactive group of another species (Scheme 42). Mesosubstituted symmetrical or unsymmetrical thiazolocyanines are obtainable via β-alkylmercaptovinyl thiazolium derivatives (**32**) (methods H and I) (Scheme 43). α or β carbon atoms of the trimethine chain can be substituted by acetyl when a dye is treated with acetic anhydride (method L). The hydrolysis of neocyanines lead to trimethine cyanine by fractional elimination of a composant chain (method K).

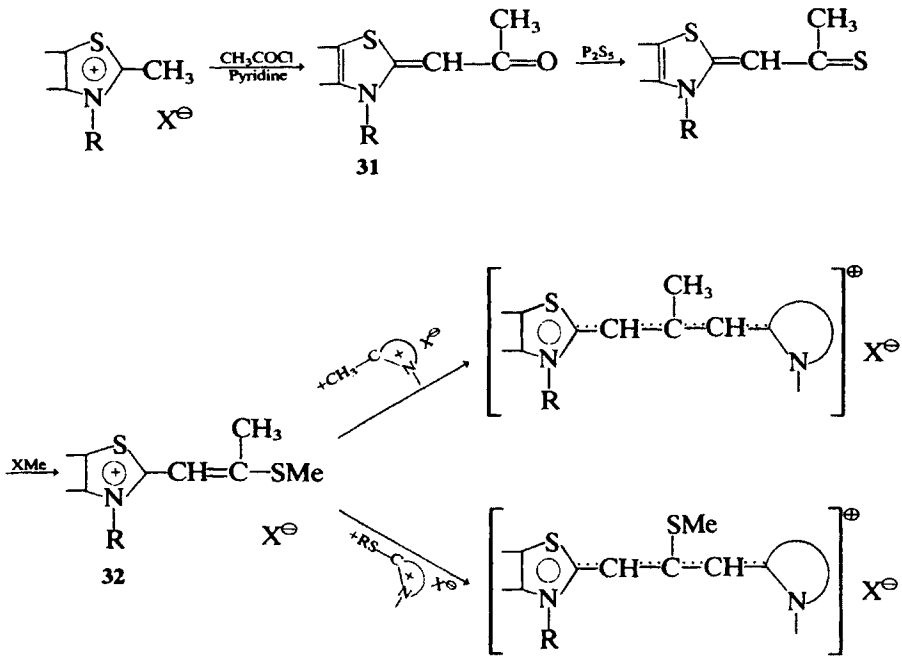


30



30b

Scheme 42



Scheme 43

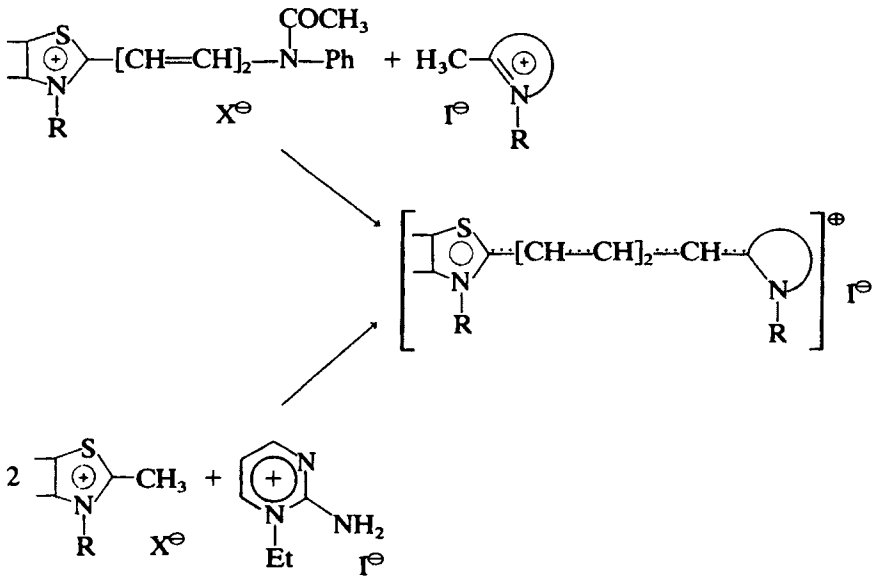
c. PENTAMETHINE THIAZOLOCYANINES (Table 213)

The three methine carbons of the chain can be provided by 1,3,3-triethoxypropene (method C) or β-anilinoacroleinanil, vinylog of diphenyl formamidine issued from the condensation of aniline on tetraalkoxypropane (method A).

Two steps take place in the synthesis, as in the case of trimethine dyes. The first intermediate is a 2-anilinobutadienyl thiazolium, which then reacts with a second mole of 2-methylthiazolium salt or another molecule of a different ring according to the desired product: either a symmetrical or asymmetrical dye (method B).

The ring fission of pyrimidinium gives good results when this salt is condensed with 2-methylbenzothiazolium; the yield obtained is very poor with 2-methylthiazolium (method D) (545).

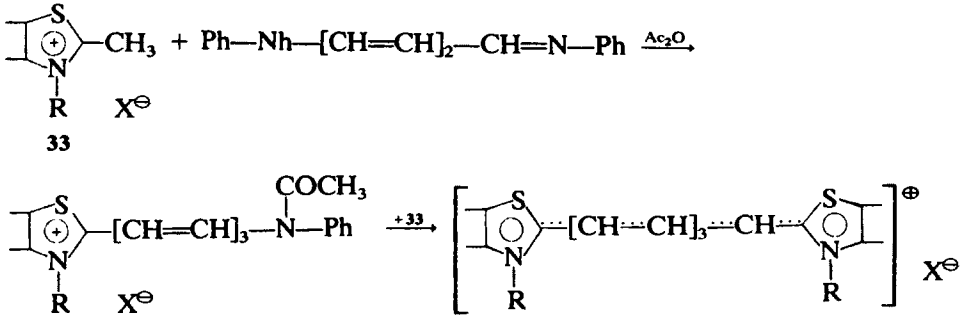
Low yield in pentamethine thiazolocyanine results also from the fission of the pyridine ring in the presence of 2-chloro-3,3-dimethylindolenine (544). Explanations of this unusual reaction have been given (Scheme 44) (67).



Scheme 44

d. HEPTAMETHINE THIAZOLOCYANINES (Table 214)

The five carbon atoms of the methine chain are brought by glutaconic aldehyde (method A) or by the dihydrochloride of its dianilide (method B). Both are issued from the fission of the pyridinium ring when a strong electron-attracting substituent group is fixed on the nitrogen atom; the reaction can be performed in one or two steps whether a symmetrical or unsymmetrical dye is concerned, the intermediate being anilino-1,3,5-hexatrienylthiazolium or its acetyl derivative (method C) (Scheme 45).



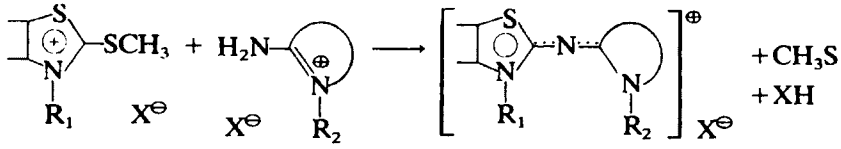
Scheme 45

e. CHAIN-BRIDGED THIAZOLOCYANINES (Tables 2151, 2152A,B,C,D)

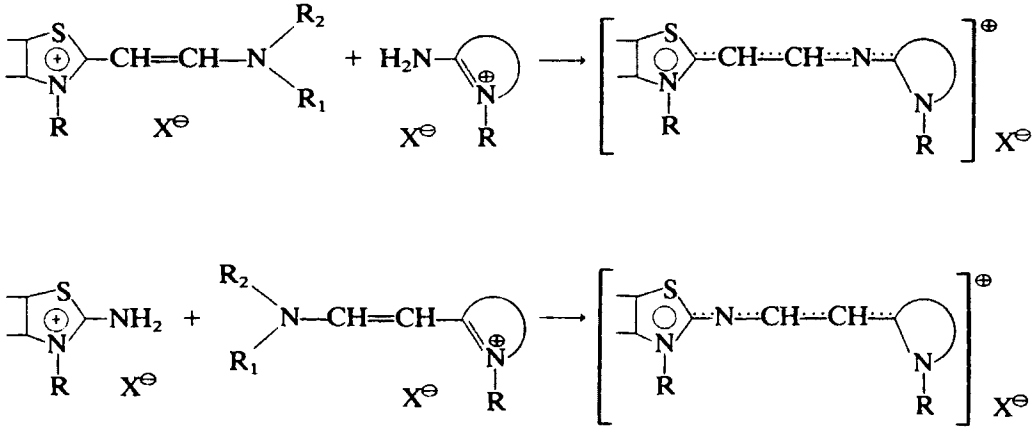
The methine chain is obtained by reacting ethyl *o*-formate (method A) or ethylisoformanilide (method B) with a bis quaternary salt of bis-(2-thiazolyl)butane. Concerning dyes with fused thiazolo rings: pyrrolo[2,1b]thiazole, thiazolo[2,3a]indole, thiazolo[2,3c]1,4-benzoxazine, the α carbon directly linked to the carbon 2 of the thiazole ring is also responsible for the classical syntheses giving trimethine or pentamethine dyes.

f. AZACYANINES

MONOAZATHIAZOLOCYANINES (Tables 2171A,B). The same reactive intermediates and the same conditions as in the case of thiazolomethine dyes are used in the synthesis of this class of dyes, except that the CH_3 group is replaced by a -NH group (Schemes 46 and 47). No β-azatrimethine thiazolocyanine has been described, in spite of an access method applied with success to other rings (65).



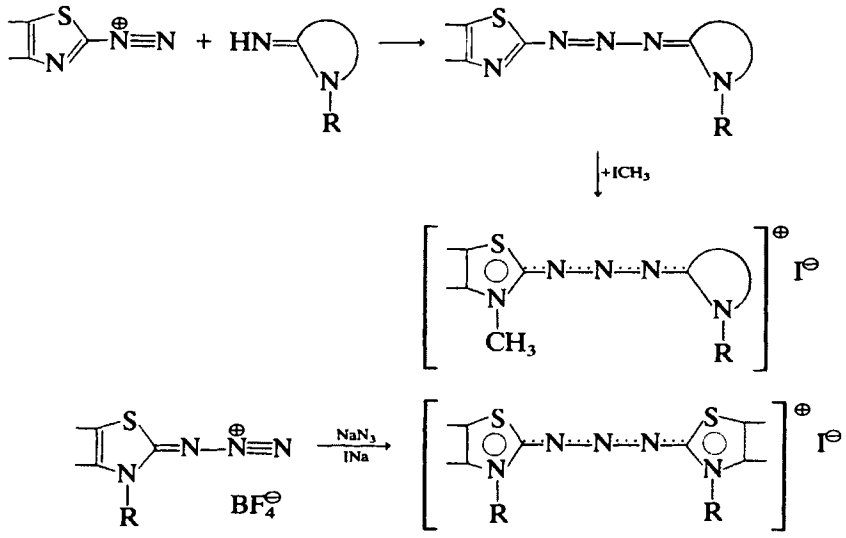
Scheme 46



Scheme 47

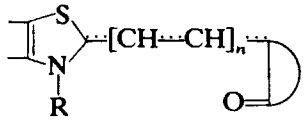
α,γ-DIAZATRIMETHINE THIAZOLOCYANINES (Table 2172).

TRIAZATHIAZOLOCYANINES (Table 2173). Triazathiazolocyanines are obtained by the methods in Scheme 48.



Scheme 48

B. *Neutrocyanines* (or Merocyanines) (Scheme 49)

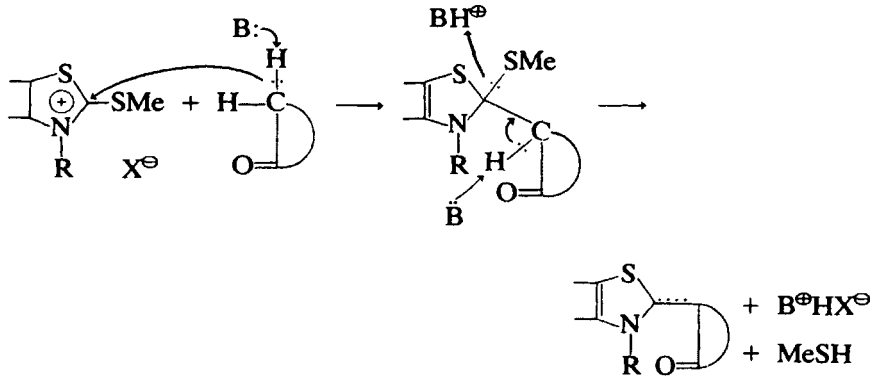


$n = 0, 2, 4, 6$

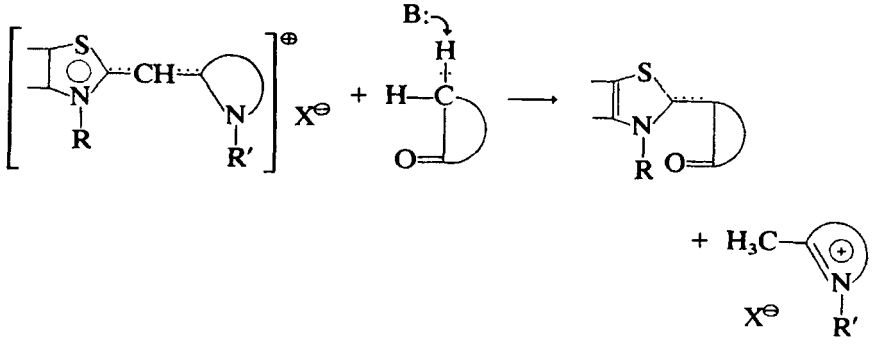
Scheme 49

a. ZEROMETHINE CYANINES (Table 221)

Zeromethine cyanines result from the reaction of the electrophilic reagent thiazolium salt having a leaving group –SR, $-SO_3^-$, or $-SO_3Me$ on carbon-2 with any ketomethylene compounds that are nucleophilic reagents (Scheme 50). The same mechanism is operating when a ketomethylene compound react on an unsymmetrical monomethine thiazolocyanine with elimination of the hetero ring, which is the more basic (Scheme 51) (26, 67).



Scheme 50

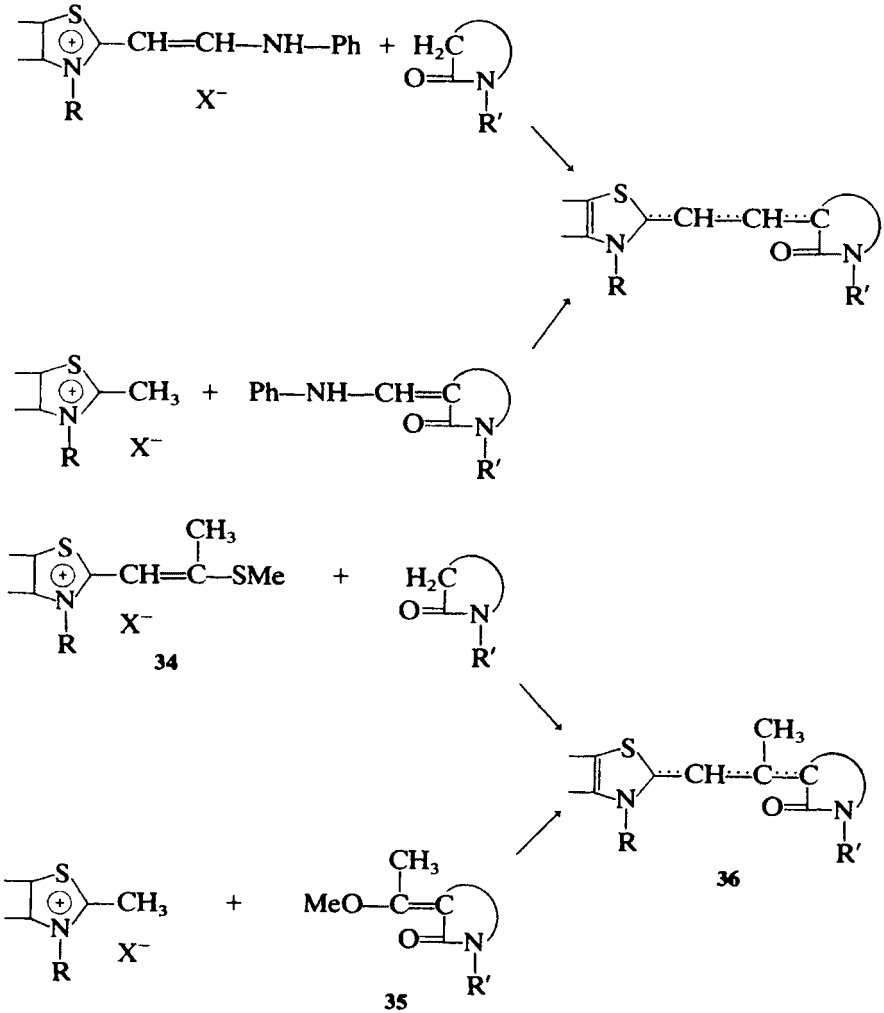


Scheme 51

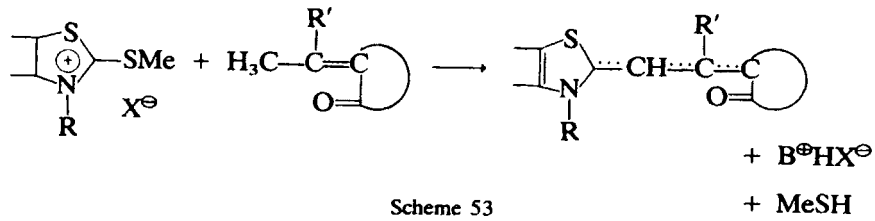
b. DIMETHINE NEUTROCYANINES (Tables 222A,B,C,D,E)

Two different access routes are used, whether the leaving group is carried on thiazolium derivatives such as anilinovinyl (method A), acetanilidovinyl (method B), formyl methylene, or thioformylmethylene or on the ketomethylene compound (method C). The use of acid anhydride together with pyridine has been patented (method E).

The choice of the intermediate depends on the reactivity of the ring. For a pyrazolone (**34**) rather than **35** is used; it is the reverse for rhodanine (Schemes 52 and 53).

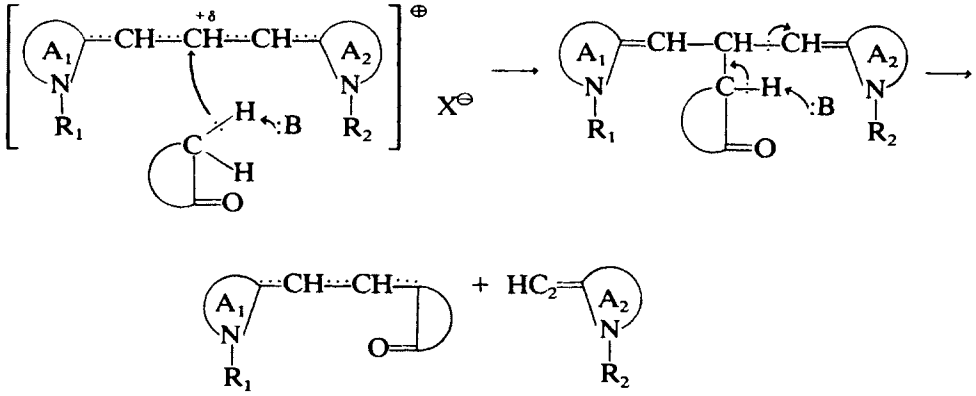


Scheme 52



Scheme 53

The electronic structure of a trimethine asymmetrical cyanine, controls the attack of a ketomethylene (Scheme 54). There is a condensation of the nucleophilic carbon on the electrophilic central carbon atom of the methine chain, leading to a neutrodimethine cyanine and simultaneously elimination of the more basic nucleus.

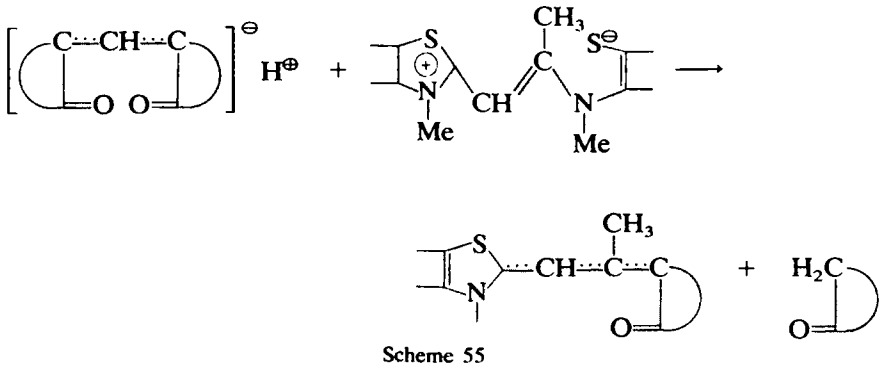


Scheme 54

For example, when *N*-ethylrhodanine is condensed with (quinoline-4)(4-methylthiazole-2)trimethine cyanine or (pyridine-2)(4-methylthiazole-2)trimethine cyanine, the yields obtained for neutrothiazolodimethine dye are 25 and 75%, respectively (53).

The easier elimination of pyridine compared to quinoline-4 may be related to the pK_a value of 4-methylthiazole, which is between those of lepidine and 2-picoline (25, 55). This reaction explains also why a neutrodimethine cyanine is obtained with such good yields when reacting together a quaternary salt, ketomethylene, and *o*-ester in a basic medium. As the reaction proceeds, the trimethine cyanine is attacked by the ketomethylene. The resulting 2-methyl quaternary salt is transformed into trimethine cyanine, consuming the totality of the ketomethylene (1, p. 512; 661). The mesosubstituted neutrodimethine cyanine is practically pure.

The condensation of a thiazolium with an oxonol dye in a basic medium is another example of the combination of electrophilic and nucleophilic reagents (Scheme 55). With a nonopening ring, the obtained neutrodimethine cyanine is not mesosubstituted (68).

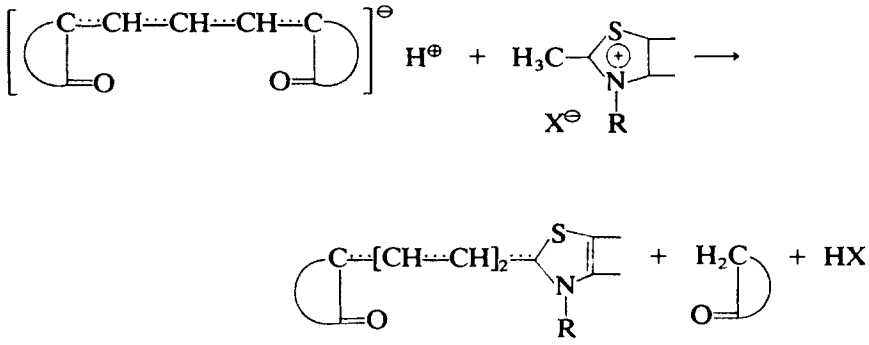


Scheme 55

c. TETRAMETHINE NEUTROCYANINES (Table 223)

Two access routes are also used with the vinylog derivatives of previous compounds, for example, either 2-(4-anilinobutadienyl)thiazolium with a ketomethylene, or 4-(4-anilinobutadienylidene)ketomethylene with 2-methylthiazolium.

The cleavage of thiazolopentamethine cyanine and also neocyanine results in a tetramethine neutrocyanine together with neutrodimethine cyanine (26). 2-Methylthiazolium reacts with a trimethine oxonol dye and gives a neutrotetramethine dye (Scheme 56) (26).



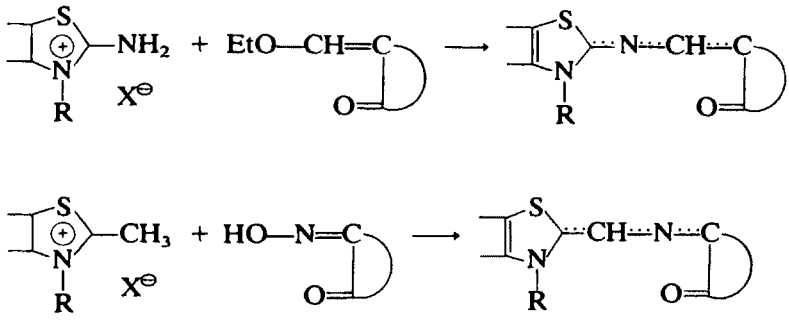
Scheme 56

d. HEXAMETHINE NEUTROCYANINES (Table 224)

Hexamethine neutrocyanines are obtained by heating 2-(6-acetanilido-1,3,5-hexatrienyl)-4-arylthiazolium with ketomethylene and sodium acetate in acetic anhydride (69).

e. AZANEUTROCYANINES (Table 225)

According to the position of nitrogen, the leaving substituent may be brought either by ketomethylene (5-ethoxymethylene) (method A) reacting on an aminothiazolium or by an amino derivative of this ketomethylene reacting on a 2-methylthiazolium (method B) (Scheme 57).



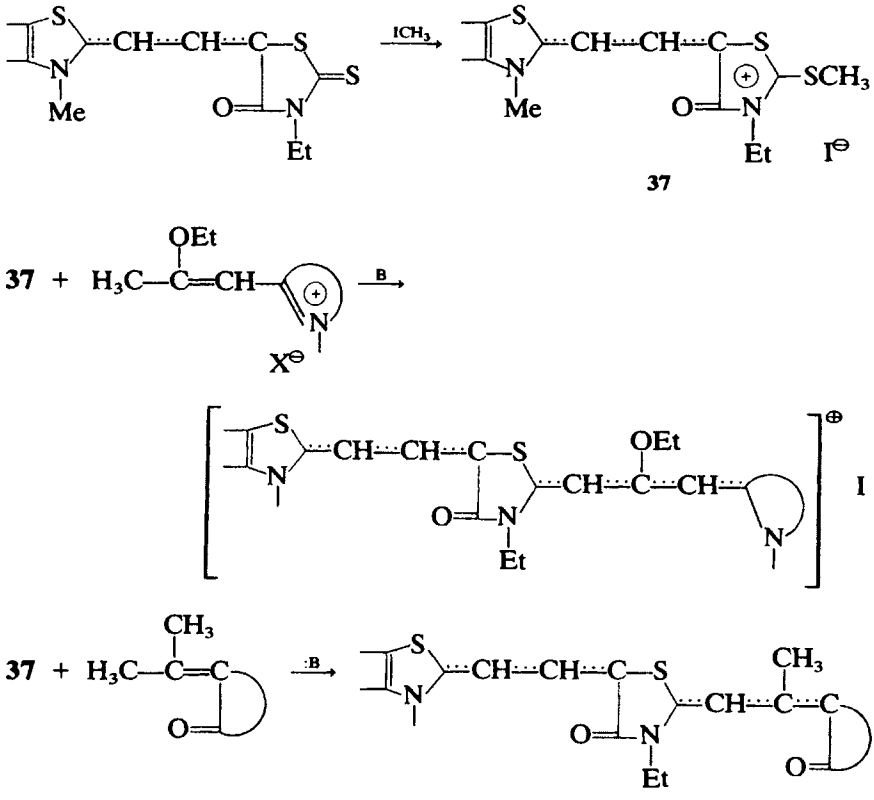
Scheme 57

3. Trinuclear Dyes

Among the dyes described in patents or literature listed in Tables 311, 312A,B,C,D, 313, 315A,B, 322A,B,C, the two following classes appear the more important, both from a theoretical and practical point of view.

A. *Rhodacyanines* (Tables 3141A,B,C,3142,A,B)

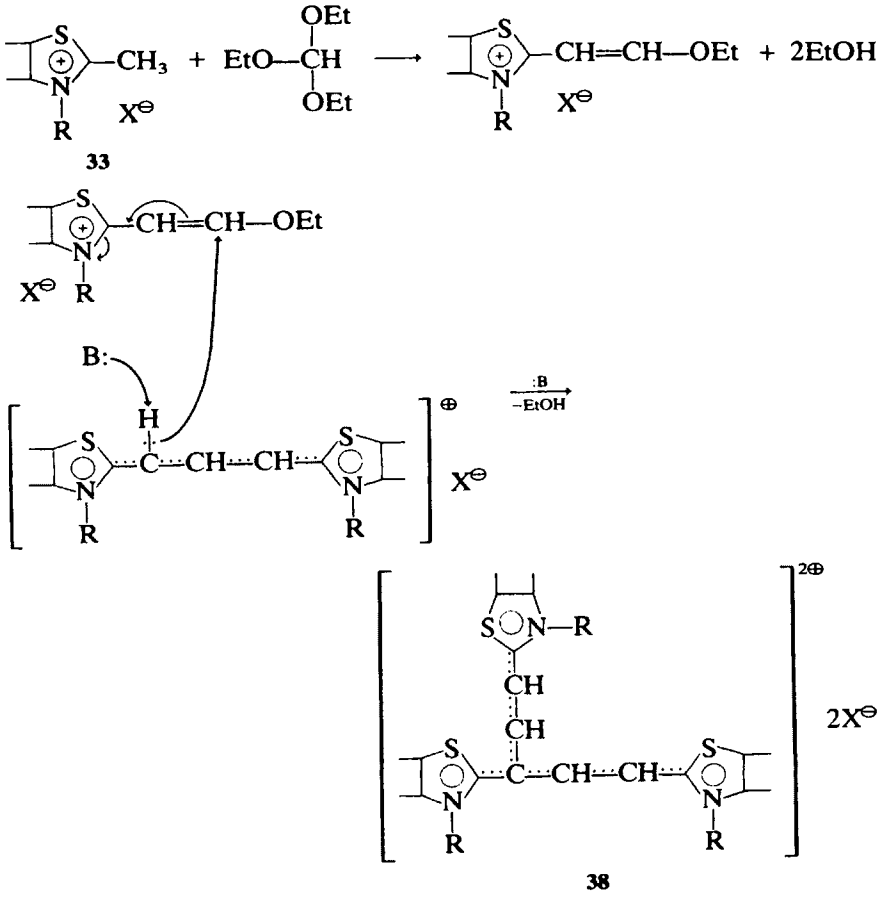
These dyes possess two independent chromophoric chains of even methine (neutro) and uneven methine (cyanine) fixed on a central ketomethylene nucleus. The methylene reactive group is first used for the neutrocyanine synthesis in position 5, the quaternization of which can ensure a subsequent polymethine synthesis in position 2 of a cationic dye by ordinary means (Scheme 58). As indicated, this quaternized neutrocyanine (**37**) may as well give another neutrocyanine.



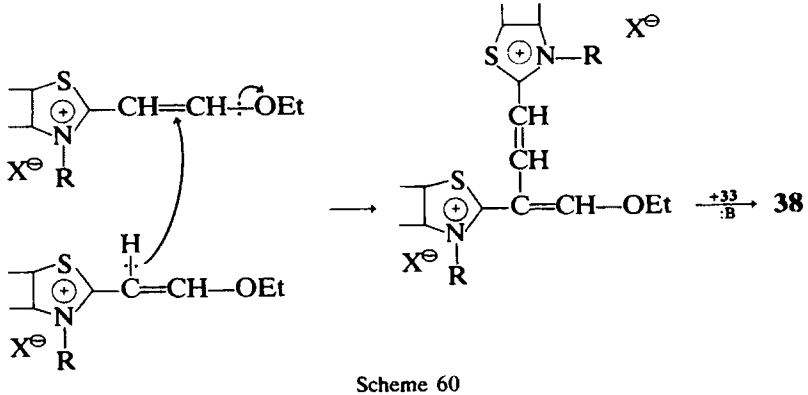
Scheme 58

B. *Neocyanines* (Tables 321A,B)

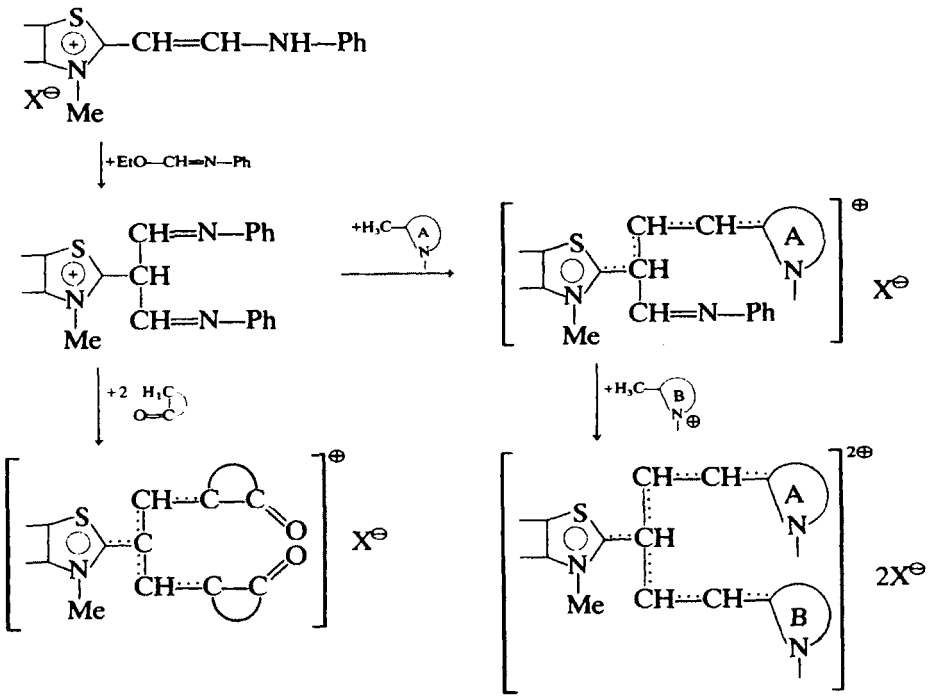
When a reactive methyl group of a heterocycloammonium reacts with ethyl *o*-formate in a solvent, the result of the condensation depends both on the basicity of the quaternary salt and on the nature of the solvent. For example, 2-methylbenzothiazolium in cresol gives chiefly neocyanine, whereas the same reaction performed in pyridine gives trimethine cyanine with a nearly quantitative yield. In the case of 2,4-dimethylthiazolium and cresol, ethyl-*o*-formate is not reactive; if pyridine is used, the reaction gives a low yield of trimethine thiazolocyanine plus neocyanine. Reducing the basicity of the ring by negative substituent as carbethoxy groups in positions 4 and 5 increases the yield of trimethine thiazolocyanine, simultaneously with the disappearance of neocyanine. But the interpretation of this reaction as far as the relative ratio of the two dyes is concerned should take into account the fact that neocyanines derived from benzothiazole decompose readily in a pyridine alcohol mixture,



Scheme 59



Scheme 60



Scheme 61

giving trimethine cyanines. So if in some experiments no neocyanine was found does not mean that it is not produced in the course of the reaction, but only that it is too unstable in the medium. The formation of neocyanines can be interpreted by the two following probable mechanisms, both starting from the very reactive β-alcoxyalcene derivative (64) and which are supported by the electronic state on the methine chain:

1. This derivative condenses either on itself (64) or on the anhydrobase, giving the trimethine dye. Indeed, the nucleophilic α-carbon of the dye—the proton is labile and can be replaced (70, 71)—is liable to add onto the electrophilic β-carbon of the alcene derivative. The neocyanine results from elimination of a molecule of ethanol.

2. Two moles of β-alkoxyalcene can condense on each other by means of their α- and β-carbon atoms. The resulting intermediate reacts on the anhydrobase by elimination of a molecule of ethanol resulting in a neocyanine formation (Schemes 59 and 60). Both monoanilino and bis-anilino derivatives resulting from the condensation of dimethylformamide have been isolated. They are capable of furnishing various condensations on either ketomethylene or another reactive nucleus (Scheme 61).

4. Tetranuclear Dyes

Examples of different kinds of dyes obtained by usual synthesis starting from bis-thiazolium salts are listed in Tables 41A,B,C, 42, 43A,B,C, 44.

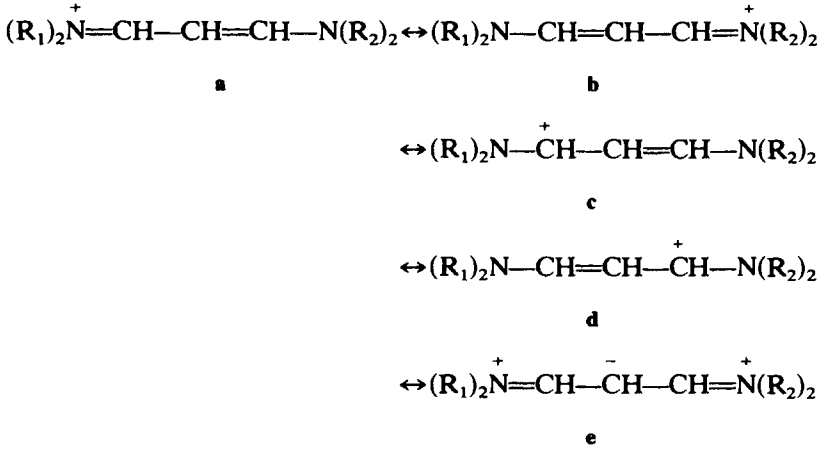
IV. STRUCTURE AND COLOR

Since the very beginning of chemistry, many efforts have been devoted to find out basic relationships between the characteristics of absorption spectra and the molecular structure of dyes.

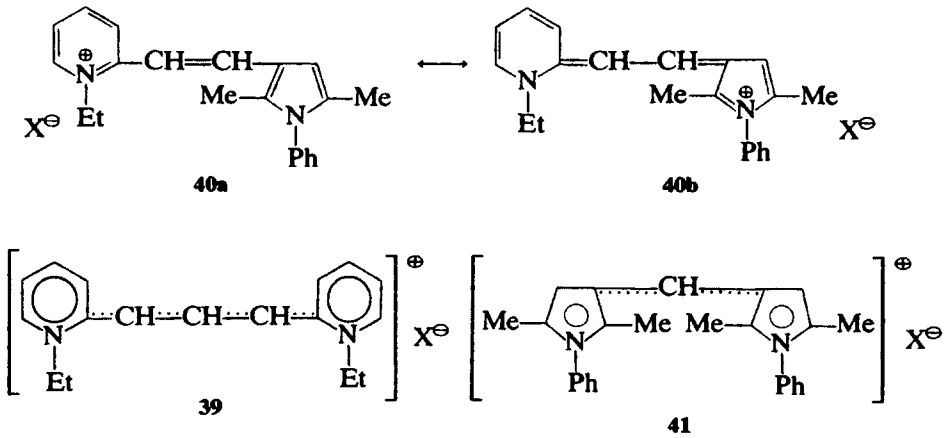
Among the authors whose contribution has been important in the past, either by their experimental work or by their theoretical approach, the names of Koenig, Hamer, Fischer, Brooker, Kiprianov, Sklar, Schwarzenbach, Eistert, Dimroth, and Platt are well familiar to scientists having an interest in the field of methine dyes, as well as more recently those of Kuhn, Wizinger, Scheibe, Hünig, Van Dormael, Dähne, and Fabian.

1. Resonance Theory and Concept of "Basicity"

Most of the qualitative relationships between color and structure of methine dyes based on the resonance theory were established independently during the 1940's by Brooker and coworkers (16, 72–74) and by Kiprianov (75–78), and specific application to thiazolo dyes appeared later with the studies of Knott (79) and Rout (80–84). In this approach, the absorptions of dyes belonging to amidinium ionic system are conveyed by a group of contributing structures resulting from the different ways of localization of the $2n$ π electrons on the $2n-1$ atoms of the chromophoric cationic chain, rather than by a single formula:



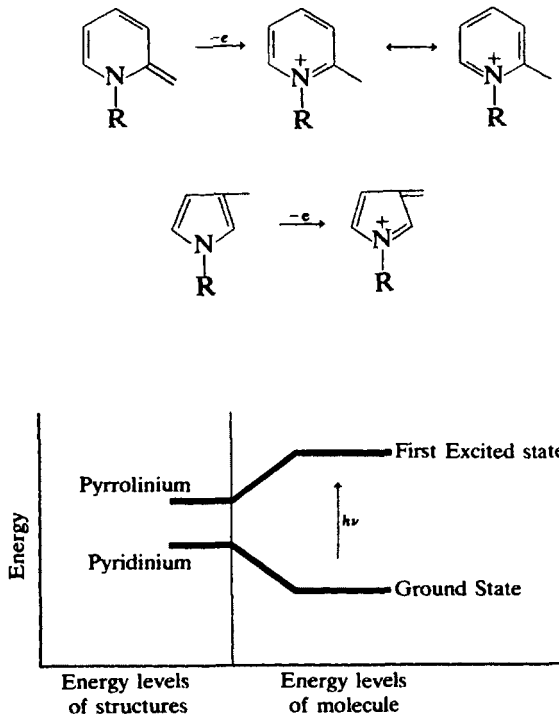
All the structures (a to e) contribute to the dye molecule, both in the ground and excited states. From their interaction, it results that in the ground state, there will be relatively greater contribution from the low-energy extreme structures; higher-energy intermediate structures play a greater part in the excited state. The effect of the absorption of light would be related to the change of the relative contribution of the structures involved in the resonance hybrid in favor of those of higher energy resulting in some displacement of positive charge away from the nitrogen atom to the carbons of the conjugated chain (Scheme 62) (5, 72).



Scheme 62

Dye **40a** is considered by Brooker as a "structural hybrid" of symmetrical dyes **39** and **41** for the reason that five carbon atoms separate the two nitrogen atoms of the terminal groups. If the pyridine and pyrrole rings were to possess the same energy, the λ_{max} of unsymmetrical dye should be the arithmetic mean of the λ_{max} of both symmetrical dyes: 562 and 448 nm. The observed λ_{max}, 426 nm, lies at shorter wavelength, and the difference called "deviation" is attributed to the difference in the energies of the extreme structures, related to the electron-donating abilities or "basicities" of the terminal groups (Scheme 63) (5, 72). According to resonance theory, the pyridinium structure involving two possible charged structures must be more important or stabilized than pyrrolium, implying just one positive design. A pyridine nucleus accommodating more easily a positive charge is more "basic" than pyrrole. The **40b** arrangement is not stabilized by resonance to the same extent as the

pyridinium one, and its energy will be higher as indicated by Brooker (5). Associating all the heterocyclic nuclei able to form methine dyes with either a pyrrole of *p*-dimethylamino phenyl group, Brooker obtained a scale of relative increasing "basicities" in which indole is the least basic and benzimidazole the most basic nucleus, thiazole rings (4-H, 4-Me, 4-Ph substituted)taking place at the end of this table between quinoline and pyridine rings (72, 16). A similar classification was made for the acidic electron-accepting terminal groups, that is, ketomethylene compounds in merocyanine series (72).



42

Scheme 63

"Vinylogous" shift of about 100 nm in symmetrical dyes, convergent and nonconvergent series, and solvent effects, have also been successfully interpreted by Brooker's and Kiprianov's conceptions.

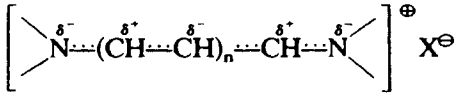
2. Limit of the "Basicity" Concept

Deviation includes, in fact, the summation of steric and electronic effects, and basicity is somewhat a useful predictor for properties of complex dyes (solvent sensitivity, isomeric forms of trinuclear dyes) and gives also semiquantitative data for color structure relation: λ_{max}, (atomic) charge density, redox properties.

But however useful this concept may have been, the formalism of resonance on which it is based is not well adapted to the quantitative electronic description of polymethine dyes. The choice of the limiting structures and the estimations of their relative weight and energy appear arbitrary in many cases, and moreover, according to Moffit (85), the ready acceptance with which qualitative symbolism has been used to operate the splitting of the extreme energy levels in the resonance hybrid is liable to propagate an undesirable misunderstanding (e.g., **42**). Equally, no proof has been given concerning this assertion that the absorption of light should be accompanied by some movement of the positive charge away from the nitrogen onto the carbon of the conjugated chain (5). Strict interpretation of the resonance model for an excited-state dye is only partially parallelled by molecular orbital results. Although positive π charge does accumulate on the chain methine carbons as a result of excitation, excess electrons migrating toward the ends of the chromophore do not appreciably change the charge on the nitrogen atoms, but rather changes the charges on other atoms, for example, carbons of the terminal groups. A more serious objection results from the observation that when rings other than pyrrole in dimethine cyanines or dimethylaminophenyl in styryl dyes are taken as reference to establish or verify the scale of "basicity," the deviations so obtained are dispersed and lead to another order of "basicity" that cannot be interpreted. Striking examples have been given by the use of pyranothiazole and thiapyranothiazole nuclei as reference (86, 87). On the other hand, Brooker's concept of basicity implying a strictly one-electron process could not be confirmed by the experimental determination of polarographic reduction potentials of the quaternary salts from which dyes are issued (25). On the contrary, some correlation exists between "deviations" and properties deriving from a two-electron process, for example, the linear relationship between the pK_a of quaternary salts (25) or the pK_a of symmetrical trimethine cyanines (658) with deviation attached to the nuclei. The deviation has also been related to the Hammett's σ coefficient (88, 89).

3. Modern Conception

The theory of resonance and Valence Bond method appear now inadequate to give an entirely satisfactory structural and energetic description of a methine dye molecule and to predict either its peculiarities or physicochemical characteristics. Following the pioneering theoretical work of Forster (90), Herzfeld and Sklar (91), and of Mulliken (92), Kuhn (6–8) used the free-electron model to calculate the molecular orbital structure of polymethine cation dyes. The conclusion is that all such dyes possess the same conjugated system in which the net positive charge is delocalized, being distributed alternatively into positive and negative partial charges on the carbons of the chain (Scheme 64).



Scheme 64

The nitrogen ending atoms being more electronegative possess a π electronic density greater than that of the carbon atoms directly linked to them.

Finally, Huckel's method allowed the calculation of transition energies (93, 95, 96), and as the access to computers of large capacity becomes more common, the Pariser–Parr–Pople type of treatment within the π framework (11, 97–99) or CNDO in all-valence electron methods (100, 101) allows the predictions of not only λ_{max}, but also the influence of geometrical isomerism on full spectra (666), the energy for each transition, its oscillator strength, polarization vectors, and other physicochemical properties such as dipole moment, basic strength, oxidation, and reduction polarographic potentials, as well as ^{13}C (10) and proton nuclear magnetic resonance (94).

As a consequence of the alternative distribution of an even number ($2n$) π electrons on an odd number ($2n-1$) carbon atoms, centers of the methine chain susceptible to nucleophilic attack are effectively the even carbons atoms starting from nitrogen, as it has been proven experimentally (103), particularly with a ketomethylene giving a neutrocyanine compound (53, 67).

The charge distribution may be symmetrical when the system possesses similar nitrogen atoms and identical or unsymmetrical nuclei approaching more or less a polyene-like bond state when the nuclei are of different

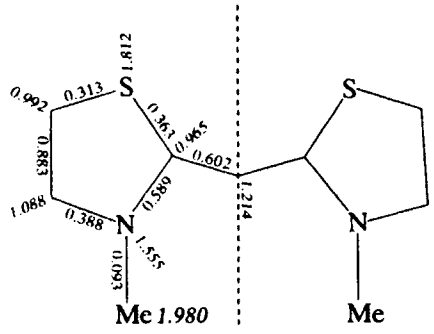
nature. Accompanying the alternative charge distribution, it has been established that the NMR chemical shift τ of the methine protons presents corresponding strong alternation (102), and equalization of bond length has been confirmed by X-ray structural analysis (104).

Likewise, quantum mechanical calculation succeeds in giving a theoretical explanation of some facts that the resonance theory could not explain, for example, why bis(pyridine-2)monomethine cyanine and bis(pyridine-4)monomethine cyanine possess the same lowest energy transition contrary to the 2,2′- and 2,4′-quinoline monomethine dyes, together with a molecular coefficient extinction lower than that of the 4,4′-quinoline dye (11). Calculation shows also that there is no theoretical reason for observing a relationship between λ_{max} and pK_a in a large series of dyes with different nuclei as it has been postulated, even if limited observations and calculations in short homogeneous series could lead to this conclusion (105).

The ground-state electronic diagrams of some thiazolo dyes have been calculated with the use of theoretical model of fractional core charge model applied to PPP method (659).

The correspondence between calculated and experimental values for the λ_{max} of the monomethine dyes, 404 nm for 410 nm, 404 nm for 412 nm, are satisfactory but this does not imply that **43** and **44** possess the same first ionization potential and the same electronic affinity simultaneously.

Considering Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital (providing that solvation energies are equal) **44** might be a better reducer than **43** (Schemes 65–68).

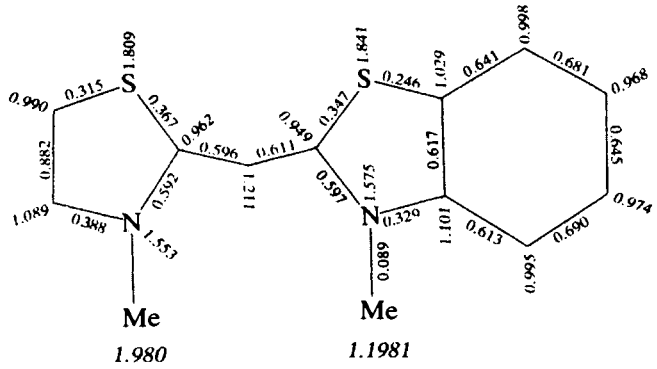


π Charge density
π Bond order in ground state

Ground state electronic diagram
(Fractional core charge model within PPP framework)

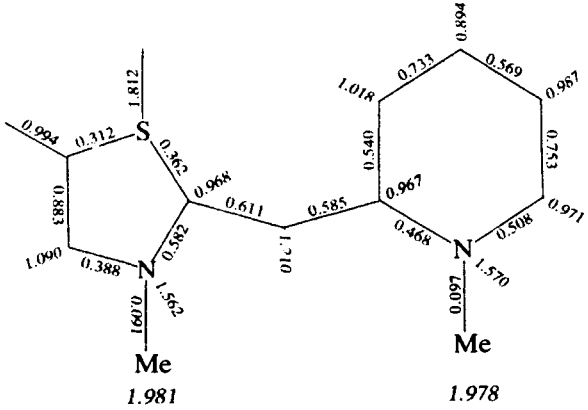
43

Scheme 65

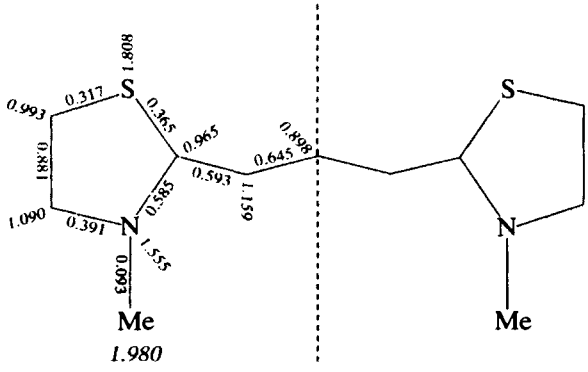


44

Scheme 66



Scheme 67



Scheme 68

Calculation can also explain why in some thiazole dyes vinylene shift of the first two homologs is larger than the shift between higher members of the series, and also why wavelengths of absorption of nonsymmetrical dyes as calculated by the mean value rule differ from experimental data (667). This deviation is caused by an interannular no-bond SS-interaction in the monomethine ion.

The remarkable solvatochromism found in neutrocyanines was extensively studied. It has been the subject of a long and severe controversy as to its origin (106).

It seems now established by NMR spectroscopic investigations that a change can take place in electronic structures and atomic configuration of the dyes depending on the polarity of the solvent. Parameters describing the transition from one single bond to more double bond character vary according to the nature of the solvent (107).

The relations between structure and electrochemical potential are an important aspect in the study of dyes, since effective sensitizers require both the correct absorption wavelength and suitable electrochemical potentials.

Although the reduction process is not always a reversible one, oxidation and reduction potential values can be sometimes related to the Hückel energies of the highest and lowest filled molecular orbital of the dye (108).

Investigations on thiazolodyes in the infrared region 1600 to 1400 cm^{-1} have shown that each vinylog gives rise to a characteristic pattern of resonant conjugated stretching modes, exhibiting a low frequency shift as the conjugated length increases (109).

4. Absorption and Substituents

A. *Influence of Substituents in the Nuclei*

Whatever their nature may be, phenyl or alkyl, the substituents of the thiazole ring in position 4 or 5 give a bathochromic shift (110, 111) of the absorption of a symmetrical trimethine thiazolocyanine compared to an unsubstituted dye. For a given substituent, this shift is greater for position 5 than for 4 (112).

The "basicity" of a 4-phenyl-substituted thiazole is less than the corresponding methyl-substituted thiazole (16) and the pK_a values of quaternary salts are in the same order (25).

Several hypotheses have been advanced in order to explain these results. Any substituent in position 4 produces a twist of the molecule resulting from a steric hindrance between this substituent and the group fixed on the nitrogen atom (113, 114).

The delocalization could be higher through the sulfur atom in the case of a substituent in position 5 (112).

Unquaternized dyes, substituted by styryl groups in positions 4 and 5, have been used to prevent steric hindrance (115).

Electron-donating or -withdrawing properties of a substituent on the 4 and 5 positions have also been used in order to modulate the "basicity" in the hope to observe either hypsochromic or bathochromic shift (110).

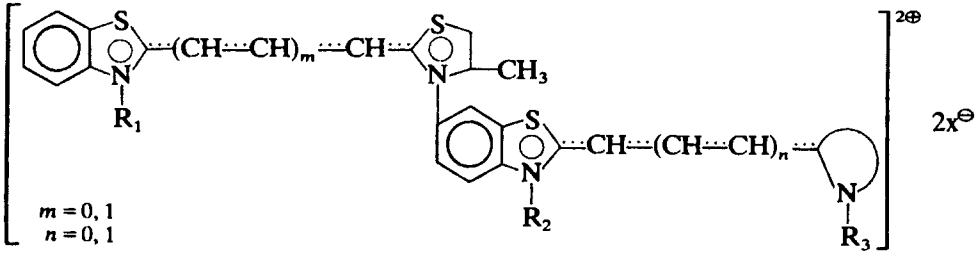
In every case a bathochromic shift that is greater for asymmetrical than for symmetrical dyes has only been observed.

Until now, no final conclusion seems to have been reached as to the origin and amplitude of the phenomenon. The nature of the alkyl group fixed on the nitrogen atoms does not influence the position of λ_{max}, but substituents of different kinds produce, for trimethine thiazolocyanine as well as styryl derivatives (116), a bathochromic shift in the order:

$$\text{Et} < \text{Ph} < \text{2-pyridyl} < \text{2-thiazolyl} < \text{2-benzothiazolyl}$$

whereas the reverse effect is observed for neutrorhodathiazolocyanine, the same substituents giving an increasing hypsochromic shift (117).

In tetranuclear dyes such as in Scheme 69 with two independent chromophoric chains, providing the chains are of different length, the absorptions maxima lie at the same λ as each of the component cyanine; but chains of equal lengths produce a shift of the two λ, one toward longer



Scheme 69

wavelength, the other toward shorter wavelength relative to the parent dye (118).

B. *Substituents on the Chain*

An alkyl group in the chain of a monomethine thiazolocyanine prevents the molecule from being planar. It gives a bathochromic λ_{max} shift of 40 nm and a decrease of the oscillator strength (26), as is the case for other methine dyes.

The λ_{max} of mesomethyl-substituted trimethine thiazolo dyes is shifted by 30 nm toward shorter wavelength. The shift is only of 20 to 25 nm for an ethyl group, whereas phenyl has no effect.

According to the nature of nuclei in the case of asymmetrical dyes, it has been shown that the influence of substituents in the meso position is neither identical nor in the same direction.

The meso carbon atom should present a carbenium ($C^{\delta+}$) structure with a low π electron density in the ground state, in the excited state this carbon possesses the carbeniate structure ($C^{\delta-}$) with a high π electron density (119). An electron-donating group in such a position should stabilize the ground state and rise the excited state to the highest level; hypsochromic shift results as a whole.

Any electron-attracting group, $-NO_2$, $-CN$, $-Ac$, or $-CO_2Et$, on the α-carbon of the methine chain of a thiazole dye gives a bathochromic shift (120). A reverse effect is observed for an alkoxy group.

Color and redox properties of a dye are related to the two molecular orbitals of ε_{LV} and ε^*_{HF}. They are both sensitive to the nature and position of the substituent. A perturbation of both orbitals occurs generally, but in some cases the effect is much more important for one of them.

The λ_{max} of bridged dyes such as thiazoloindole symmetrical and unsymmetrical trimethine dyes are shifted toward shorter wavelength compared to the corresponding *N*-phenylthiazolocyanine. This hypsochromic shift corresponds to an electron-donating substituent in the α-position of the chain when steric hindrance is absent (121).

A rigidized molecule obtained when the two α-carbons of the trimethine chain are linked by a dimethylene bridge cannot be planar. According to the resonance concept, its "stability" increases as a bathochromic effect of 41 nm is observed (122). The λ_{max} of the bistyryl dye obtained by the substitution of the β-proton in the chain of a styryl dye by a dialkylamino group is nearly the same as for the parent styryl dye (123).

* ε_{LV} = energy of the lowest vacant orbital; ε_{HF} = energy of the highest filled orbital.

C. *Nitrogen Atoms Replacing Methine Groups of the Chain*

A great number of monoaza or polyaza, either symmetrical or unsymmetrical, mono trimethine thiazolocyanines have been synthesized in order to verify or to obtain semiempirical rules, more or less based on the resonance theory, concerning the relation between the color of a thiazolo dye and the number and place of nitrogen atoms in the chromophoric chain. For example, Forster's rule applies to ionic dyes and stipulates that the λ_{max} will increase with the decreasing tendency of chromophoric atoms lying between the two auxochromes to take up the characteristic charges (90).

Knott's rule concerns the importance of the place of the nitrogen atom replacing a methine carbon in the conjugated chain; when the atom is separated from the active auxochromic atoms by an odd number of conjugated atoms, the shift is bathochromic. It is hypsochromic when there is an even number. The importance of the shift could establish a measure of $\pm M$ effect of various heterocyclic nuclei (79, 124). Many papers have been published, and examples have been given to verify these rules (79–84).

V. USES OF DYES

1. Photography

The use of sensitizing dyes in photography has been the subject of many studies and constitutes still now, one of the most studied areas in specialized periodic publications (125, 126) or in textbooks (88, 127). It can be ascertained that one hundred years after Vogel's discovery of spectral sensitization, the basic mechanisms of action of dyes on their silver halide support still remain not fully understood. However, the theoretical reasons explaining why among many other dye families practically only cyanine methine dyes appear to be spectral sensitizers (128) are better known.

Sensitizers as well as desensitizers form a reversal oxidoreduction system with silver halides, according to both pH and *p*Ag of the photographic emulsion. But besides the specific influence of the emulsion, the efficiency of a sensitizing dye depends on many other factors such as its adsorption, its spectral absorption, the energetic transfer yield, the dye aggregate to the silver halide, and finally on its desensitizing property in

the spectral region where it is not a sensitizer by itself. Effective sensitizers require both the correct absorption wavelength and suitable electrochemical potential.

Since there do not exist generally accepted test methods to measure the efficiency of a dye, the tables do not mention any characteristic of the efficiency and spectral domain of dyes, as they are sometimes found in patents or the literature. Sensitizing power decreases as the chain length increases, and desensitizing and fogging properties have been related to the increase of the ground-level energy (129) together with electron affinity and basicity (130, 131). Experimentally it has been proved that thiazolo carbocyanines become desensitizers when a quinoline ring is fused to the thiazole one. Electron-accepting substituents such as a NO_2 group on the nucleus, or nitrogen in polymethine chain can confer strong desensitizing properties to the dyes depending on their position and number (132).

Generally an efficient sensitizing dye requires a planar molecular or nearly planar, and so, any steric factor preventing the chromophoric conjugated system from being in a plane leads to an important loss of the sensitizing power. Even if the assistance of the computer allows now the design of new molecules of dyes with appropriate characteristics, practical testing is still necessary for their discrimination as sensitizers. 4-Phenylthiazolo dyes are known to be desensitizers (111), though 4,5-diphenyl-substituted trinuclear dyes have been patented as red sensitizers for color photography (133). In general, methine thiazolo dyes are considered to be lacking efficiency; nevertheless some have been patented as supersensitizers. Used with some dyes of other classes, they produce an increase of the intensity and an extent of the sensitization by a suradditive effect. Other physical properties are taken into account for selecting specific sensitizers:

- Easiness of their incorporation by means of their solubility in various media,
- Nonwandering in order to prevent the dyes from migrating from a layer to the next one in multilayer coatings.
- Easy removal during the development process in order to avoid residual and unwanted color stain.

Styryl derivatives have been patented as sensitizers (76) and other methine dyes for sensitization in direct photothermographic material (134).

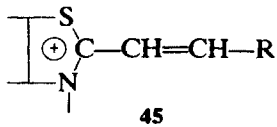
2. Textile Dyes

Thiazoloazatrimethine dyes, as generally basic dyes, possess a good affinity for acrylic fibers. It seems that the light fastness of trimethine thiazolo dyes can be increased by the progressive replacement of methine groups by nitrogen atoms, and an excellent fastness to light is reported to be displayed by three nitrogen atoms in the chromophoric chain (66).

3. Pharmaceutical Uses

A great number of various substituted aminophenyl derivatives of thiazolium, and their organic or metallic complexes, have been patented as weed-killers or regulating growth factors of plants (135–138).

The bactericidal and enzymatic action of dyes, particularly of vinyl derivatives of 3,4,5-substituted thiazolium, for example, **45** (Scheme 70) (139), have been systematically studied to know more about the basic mechanisms involved (140).



45

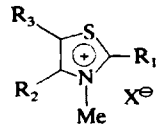
Scheme 70

Many methine cationic dyes, styrylic (141), pyrrolic, or amino-substituted (142) derivatives of thiazolium, possess interesting anthelmintic properties (143). This last class has been used as accelerators of the catabolism and activators of cellular exchanges (144).

Mention must be made of the use of *o*- or *p*-hydroxystyryl thiazolo dyes as indicators for protolytic titrations in nonaqueous media (145), and of the hypotensive action of some neotrinuclear thiazolo cyanines in experiments on animals (146).

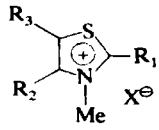
VI. LIST OF THIAZOLIUM SALTS

TABLE IX-1. 3-METHYLTHIAZOLIUM SALTS



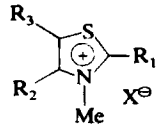
R_1	R_2	R_3	Anion	m.p. (°C)	Ref.*
H	H	H	I^-	159	147
H	H	H	OTs^-	—	20 r, 28 k, 148 l, 149 k, 150 h
Me	H	H	Cl^-	—	20 r
Me	H	H	I^-	—	149 k, 151
Me	H	H	OTs^-	185	28 k, 150, 152–154
Et	H	H	I^-	—	149 k, 154 k
n-Pr	H	H	I^-	—	154
i-Bu	H	H	I^-	—	154
Neopentyl	H	H	I^-	—	154
i-Pr	H	H	I^-	—	149 k, 154
t-Bu	H	H	I^-	—	149 k, 154
$CMe(OH)CONH_2$	H	H	I^-	152	155
$CPh(OCH_2CH_2OH)_2$	H	H	I^-	190–2	156
CH=CHNHPh	H	H	OTs^-	—	157
C[NH(*p*-tolyl)]: N(*p*-tolyl)	H	H	I^-	196–7	158
	H	H	I^-	210	159 u
Ph	H	H	Cl^-	—	160
p-$(Me)_2NC_6H_4$	H	H	I^-	220	137
p-$(Me)_2NC_6H_4$	H	H	Cl^-	—	161 h
p-$(Me)_2NC_6H_4$	H	H	OTs^-	—	162 l
SMe	H	H	I^-	—	159, 163, 164 k
H	Me	H	Br^-	155–7	18 ir, 19, 21kr, 23 k
H	Me	H	Cl^-	—	28 k, 150, 165, 166
H	Me	H	I^-	119–20	156, 167–169
H	Me	H	OTs^-	148	20 r, 21
H	CH_2-4′-thiazolyl	H	I^-	162-3	170
H	CH_2-4′-thiazolyl	H	$2I^-$	240	170
H	*t*-Bu	H	OTs^-	140	20 u
H	Ph	H	Cl^-	—	160 i
H	H	Me	Cl^-	—	150, 160, 172
H	H	Me	I^-	67, 1–8, 3	28 k, 171
H	H	Me	IO_4^-	75, 1–6	171
H	H	Me	OTs^-	69	20

TABLE IX-1 (*Continued*)



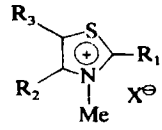
R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
H	H	COOEt	I^-	153	173
H	H	Ph	Cl^-	—	160
H	H	Ph	I^-	—	172
Me	Me	H	Cl^-	235	147
Me	Me	H	I^-	—	20 r,u, 28 k, 150 k, 151, 169, 174–177, 178a,
Me	Me	H	OTs^-	159	179a
Me	Ph	H	I^-	202	150, 174, 180–182, 183 a, 184 a, 185 a, 186, 187 k
Me	p-ClC_6H_4	H	I^-	—	187
Me	p-BrC_6H_4	H	I	—	181, 183, 185, 188
Me	p-$NO_2C_6H_4$	H	I^-	186	184, 185, 187 k
Me	m-$NO_2C_6H_4$	H	I^-	—	187 k
Me	p-$MeOC_6H_4$	H	I^-	197–8	183 a, 184, 185
Me	p-$EtOC_6H_4$	H	I^-	204	183 a, 185
Me	2-Naphthyl	H	I^-	220	189
Me	5-Acenaphthenyl	H	I^-	186	189
Me	NH_2	H	I^-	235	190
CH_2OH	Me	H	I^-	—	191 r,u
CH(Me)OH	Me	H	Br^-	166–7.5	165
CH(Me)OH	Me	H	I^-	149–50	165, 192 u
CH(Me)OH	Me	H	NO_3^-	133–4	192 u
CH(Me)OP(O)(OMe)O^-	Me	H	Inner salt	—	166
$CH(Me)OP(O)OEt)_2$	Me	H	Br	—	166
CHPh(OH)	Me	H	I^-	165–7	193
(CH(Ph)OP(O)(OMe)O^-	Me	H	Inner salt	—	166
$CH(Ph)OP(O)OEt)_2$	Me	H	Br^-	—	166
$CMe(OH)_2$	Me	H	I^-	—	194, 195 k
CH=CHNHPh	Me	H	I	248	176
CH=CHN(COMe)Ph	Ph	H	I	162–3	181, 182, 183 a, 184
CH=CHN(COMe)Ph	p-BrC_6H_4	H	I	174–5	183, 188 u
CH=CHN(COMe)Ph	p-$EtOC_6H_4$	H	I^-	188	183 a
Acetyl	Me	H	I^-	137–8	168 u, 192, 194, 195 k
Benzoyl	Me	H	I^-	159–60	156, 196
Ph	Me	H	I^-	—	197
p-$Me_2NC_6H_4$	Me	H	Cl^-	—	161, 162
p-$Me_2NC_6H_4$	Me	H	I^-	165	137
p-$Me_2NC_6H_4$	Me	H	OTs^-	—	138, 198
p-$Me_2NC_6H_4$	n-Pr	H	I^-	198	162
NH_2	Ph	H	I^-	—	181, 182
NH_2	p-$MeOC_6H_4$	H	I	—	181

TABLE IX-1 (*Continued*)



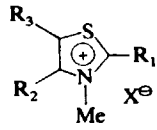
R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
NH_2	*p*-$EtOC_6H_4$	H	I^-	—	181
$NH(CH_2)_6NH$-2-(3,4-di-Me-thiazolyl)	Me	H	$2I^-$	202	199
$NH(CH_2)_4NH$-2(3,4-di-Me-thiazolyl)	Me	H	$2I^-$	236	199
$NH(CH_2)_2NH$-2-(3,4-di-Me-thiazolyl)	Me	H	$2I^-$	265	199
SCH_3	Me	H	I^-	—	163, 164
SCH_3	Ph	H	I^-	—	200
Me	H	Me	OTs^-	121	20, 28 k, 153
Me	H	*t*-Bu	OTs^-	141	20
Me	H	Ph	I^-	—	153
Me	H	Br	I^-	243	157 u
Me	H	OEt	I^-	109–10	201
Me	H	NH_2	I^-	—	157
CH_2Ph	H	$NHCOCH_3$	I^-	265	202
t-Bu	H	Me	OTs^-	101	20
Styryl	H	Ph	OTs^-	90–9	203 l
Styryl	H	OEt	I^-	170	201
CH=CHNHPh	H	Me	I^-	—	204
CH=CHNHPh	H	Br	OTs^-	—	157
Ph	H	Ph	OTs^-	230–3	205
Ph	H	2-Naphthyl	OTs^-	210–2	203 l
p-Biphenylyl	H	Ph	OTs^-	238–40	203 l
N,N,N-trimethyl-*p*-aniliniumyl	H	Ph	OTs^-	238–40	203 l
p-FC_6H_4	H	Ph	OTs^-	157	203 l
p-ClC_6H_4	H	Ph	OTs^-	192–4	203 l
m-IC_6H_4	H	Ph	OTs^-	172–4	203 l
o-IC_6H_4	H	Ph	OTs^-	210–3	203 l
1-Naphthyl	H	Ph	OTs^-	151	203 l
2-Thienyl	H	Ph	OTs^-	173–6	203 l
$NHCOCH_3$	H	CH_2NMe_2	I^-	209	206
$NHCOCH_3$	H	CH_2NEt_2	I^-	173	206
$NHCOCH_3$	H	CH_2-piperidinyl	I^-	200	206
$NHCOCH_3$	H	CH_2-Morpholinyl	I^-	198	206
SMe	H	Me	I^-	—	164
SMe	H	NH_2	I^-	150	207
SMe	H	$NHCOCH_3$	I^-	212	157, 207
H	R_1	R_1	$MeSO_4^-$	—	208
H	Me	Me	OTs^-	135	20, 28 k, 150
H	Me	Et	I^-	130.5–1.5	209
H	Me	$(CH_2)_2Cl$	I^-	165	210, 211 l
H	Me	CH_2CH_2OH	I^-	—	35, 158, 167, 212 l, 213 p, 214, 215 m, 216

TABLE IX-1 (*Continued*)



R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
—	Me	CH_2CH_2OH	Ylide	—	35, 212
H	Me	CH_2OH	Cl^-	—	217 f
H	Me	CHOHMe	I^-	164.5	218
H	Me	Acetyl	I^-	168	218
H	Me	COOEt	I^-	—	167
H	Alkyl	CH_2CH_2OH		—	219
Me	Me	Me	I^-	117–18	220
			OTs^-	149	20 r,u, 28 k, 150, 221
Me	Me	COOH	I^-	—	222
Me	Me	CO_2^-	Betaine	190–1	222
Me	iBu	Me	I^-	121–3	220
Me	CH_2Ph	Me	I^-	—	220
Me	Spiro[4,5]decano[6,7-*d*]		I^-	205–7	223
Me	Ph	Me	I^-	181	220
				111–13	224 a
Me	Ph	Ph	I	208	186, 225
Me	Ph	Ph	OTs^-	—	187 k, 226
Me	Ph	*p*-ClC_6H_4	I^-	130	186
Me	Ph	*p*-$NO_2C_6H_4$	I^-	95	186
Me	Ph	OPh	OTs^-	—	227
Me	*p*-Biphenylyl	*p*-Biphenylyl	I^-	226	228
Me	*p*-ClC_6H_4	Ph	I^-	134	186
Me	*p*-BrC_6H_4	O(p-BrC_6H_4)	OTs	—	229 a
Me	*p*-$MeOC_6H_4$	OPh	OTs^-	—	229 a
Me	2,4-$(MeO)_2C_6H_3$	*p*-ClC_6H_4	I^-	93	186
Me	2-Naphthyl	2-Naphthyl	I^-	227	228
Me	2-Furyl	COOEt	Me-SO_4	—	230 a
CH_2OH	Me	CH_2CH_2OH	I^-	—	191
C(NH-*p*-MeC_6H_4) =N-*p*-MeC_6H_4	Me	CH_2CH_2OH	I^-	194–6	35, 158
C(SH)=NPh	Me	CH_2CH_2OH	Cl^-	206–9	35
$C(S^-)$=NPh	Me	CH_2CH_2OH	Zwitterion	135–6	35
$C(S^-)$=NPh	Me	$(CH_2)_2OCSNHPh$	Zwitterion	175–6	35
$C(S^-)$=N-*p*-ClC_6H_4	Me	CH_2CH_2OH	Inner salt	168–9	35
$C(S^-)$=N-*p*-$NO_2C_6H_4$	Me	CH_2CH_2OH	Inner salt	180–1	35
Ph	Ph	SMe	I^-	—	231
Ph	Ph	SO_3^-	Betaine	303–4	232
p-$Me_2NC_6H_4$	R′	R″		—	161 l, 198
p-$R_2NC_6H_4$	R	R	X^-	—	137, 198
p-$R_2NC_6H_4$	R	R	I^-	—	198
p-$R_2NC_6H_4$	R	R	OTs^-	—	198
p-$Me_2NC_6H_4$	Me	Me	Cl^-	—	162
p-$Me_2NC_6H_4$	Me	Me	I^-	229	137
p-$Me_2NC_6H_4$	Me	Me	OTs^-	—	198
p-$Me_2NC_6H_4$	Me	Et	I^-	154–6	162
p-$Me_2NC_6H_4$	Me	*n*-Bu	I^-	134	162

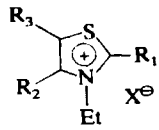
TABLE IX-1 (*Continued*)



R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
p-$Me_2NC_6H_4$	Me	*n*-Octyl	I^-	102	162
p-$Me_2NC_6H_4$	Me	*i*-Pr	I^-	135	162
p-$Me_2NC_6H_4$	Et	Me	I^-	203	162
p-$Me_2NC_6H_4$	Et	*n*-Pr	I^-	149	162
p-$Me_2NC_6H_4$	*n*-Pr	Et	I^-	125	162
p-$Me_2NC_6H_4$		$-(CH_2)_4-$	I^-	233–4	138
p-$Me_2NC_6H_4$		$-(CH_2)_4-$	Cl^-	—	162
p-$Me_2NC_6H_4$		$-(CH_2)_4-$	OTs^-	—	162
p-$Me_2NC_6H_4$		$-(CH_2)_5-$	I^-	190	162
p-$Me_2NC_6H_4$	Ph	Me	I^-	159–60	162
NH_2	Me	Me	$MeSO_4^-$	145	233
NH_2	Me	Br	X^-	—	234 p
NH_2	Me	I	X^-	—	234 p
NHAc	Me	CH_2NMe_2	I^-	202–4	206
NHAc	Me	CH_2NEt_2	I^-	167	206
NHAc	Me	CH_2-piperidinyl	I^-	197	206
NHAc	Me	CH_2-morpholinyl	I^-	217	206
$N(Me)_2$	Me	Ph	Br^-	—	235
SMe	Me	Me	I^-	—	164
SMe	Ph	NH_2	$CH_3SO_4^-$	123	202

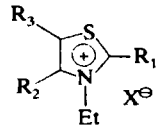
• Reference code, *see* p. 2 of Part One. References in italics refer to papers describing experimental conditions for synthesis.

TABLE IX-2. 3-ETHYLTHIAZOLIUM SALTS



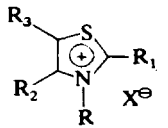
R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
H	H	H	I^-	—	236 r
Me	H	H	I^-	—	237, 238
CH=CHN(COMe)Ph	H	H	I^-	—	238
NH_2	H	H	I^-	—	239
H	Me	H	Br^-	170–1	19, 240 l
H	Me	H	I^-	—	241, 242
Me	Me	H	I^-	—	237, 243–248
Me	COOEt	H	OTs^-	—	157
Me	Ph	H	I^-	175.5–6.5	237, 238
Me	*p*-Xenyl	H	I^-	222	189
Me	*p*-HOC_6H_4	H	I^-	—	249
Me	*p*-$CF_3SO_2C_6H_4$	H	I^-	—	250
Me	1-Azulenyl	H	OTs^-	—	189
Me	1-Naphthyl	H	I^-	217–18	189
Me	2-Naphthyl	H	I^-	187	189
Me	2-Pyrryl	H	OTs^-	—	251
Me	2-Furyl	H	OTs^-	—	230
Me	2-Benzofuryl	H	I^-	—	230 a
Me	2-Benzofuryl	H	OTs^-	—	230 a
Me	2-Benzothiazolyl	H	I^-	202	252
Me	NH_2	H	I^-	205	190
p-Dimethyl aminostyryl	*p*-Sulfophenyl	H	Betaine	283–5.5	253
CH=CHNH-(2,5-xylyl)	Me	H	I^-	232	243
CH=CHNH-(*p*-BrC_6H_4)	Me	H	I^-	234	243
CH=CHNH-(*p*-$MeOC_6H_4$)	Me	H	I^-	165	243
CH=CHNH-(*o*-$MeOC_6H_4$)	Me	H	I^-	251	243
CH=CHNH-(*p*-$EtOC_6H_4$)	Me	H	I^-	181	243
CH=CHNH(5-Cl-2-pyridyl)	Me	H	I^-	211	243
CH=CHNH-2-(5-Br-pyridyl)	Me	H	I^-	256	254 l
CH=CHNH-2-(5-I-pyridyl)	Me	H	I^-	274	243
I	Me	H	I^-	171	255
Me	H	COOMe	OTs^-	—	157
Me	H	3-Me-4-$MeOC_6H_3$	I^-	198–202	256, 257
Me	H	3-Ph,4-$MeOC_6H_3$	I^-	—	256
Me	H	3,4$(MeO)_2C_6H_3$	I^-	193–7	256, 257
Me	H	3,4$(EtO)_2C_6H_3$	I^-	—	256

TABLE IX-2 (*Continued*)



R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
Me	H	2,3-$Me_2$4-$MeOC_6H_2$	I^-	—	256
Me	H	2,5-$Me_2$4-$MeOC_6H_2$	I^-	—	256
Me	H	3,5-Me_2,4-$MeOC_6H_2$	I^-	—	256
Me	H	2-Naphthyl	I^-	210	228
Me	H	5-Acenaphthyl	I	—	228
Me	H	2-Benzofuranyl	I	—	256
Me	H	2-Benzothiazolyl	I^-	265	252
Me	H	$NHCOCH_3$	OTs^-	—	157 u
Et	H	COOEt	OTs^-	—	157
SC_2H_5	H	$NHCOCH_3$	I^-	—	258
H	Me	Me	I^-	—	259
H	Me	CH_2CH_2OEt	I^-	—	259
Me	Me	Acetyl	I^-	—	157
Me	CH_2Ph	Me	I^-	135	220
Me	Ph	Me	OTs^-	—	260
Me	Ph	Ph	I	184	225, 261, 262,
Me	Ph	Ph	$EtSO_4^-$	—	263, 264, 265
Me	*p*-$MeOC_6H_4$	Ph	OTs^-	—	229
Me	–spiro(4,5)decano{6,7-*d*}–		I^-	188–92	223
CH=C(CH_3)Cl	Ph	Ph	Cl^-	119–20	266
SMe	Me	Me	Br^-	—	267
SMe	–CH_2–CH_2–		Cl^-	—	267

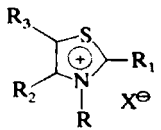
TABLE IX-3. 3-ALKYL- AND 3-ARYLTHIAZOLIUM SALTS



R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
n-Pr	H	Me	H	Br^-	139–41	19
n-Pr	Me	Me	H	Br^-	—	268
n-Bu	H	Me	H	Cl^-	—	242
n-Bu	Me	Me	H	I^-	—	176, 269
n-Bu	CH=CHNHPh	Me	H	I^-	180	176
n-Bu	CH=CHNH-2-(5-I-pyridyl)	Me	H	I^-	178	269
n-Heptyl	Me	Me	H	I^-	—	248
n-Heptyl	CH=CHNH-2-(5-Br-pyridyl)	Me	H	I^-	—	2541
$(CH_2)_3COOH$	H	Me	CH_2CH_2OH	Cl^-	—	270
$(CH_2)_3CO_2Et$	H	Me	CH_2CH_2OH	Cl^-	—	2701
$(CH_2)_3COOEt$	H	Me	$(CH_2)_2OCOMe$	Br^-	—	2701
$(CH_2)_3SO_2NH_2$	Me	Me	H	Br^-	224	262, 271
i-Amyl	Me	Me	H	I^-	—	176, 268
$(CH_2)_2CONH_2$	H	Me	CH_2CH_2OH	Cl^-, HCl	156–8	272
$(CH_2)_2CONHEt$	H	Me	CH_2CH_2OH	Cl^-, HCl	150–5	272, 2731
$(CH_2)_2CONHCHMe_2$	NH_2	H	H	Cl^-	—	274
$(CH_2)_2CONEt_2$	NH_2	H	H	Cl^-	—	274
$(CH_2)_2COOH$	NH_2	H	H	Cl^-	149–50	275 i
$(CH_2)_2COOH$	NH_2	H	H	Betaïne $1H_2O$	164–5	274

$(CH_2)_2COOH$	NH_2	Me	H	Betaïne $0.5\ H_2O$	165	275
$(CH_2)_2COOMe$	NH_2	H	H	Cl^-	—	274
$(CH_2)_2Ph$	H	Me	H	Br^-	196	276
$(CH_2)_2NH_2$	H	Me	H	Cl^-	—	277 f
$(CH_2)_2NH_2$	H	Me	CH_2CH_2OH	Cl^-, HCl	—	273 f
$(CH_2)_2N(Et)_2$	H	Me	CH_2CH_2OH	Cl^-	—	217 f
2-Phtalimidoethyl	H	Me	H	Br^-	238	277, 278
$(CH_2)_2NO_2$	H	Me	H	Cl^-	—	277 f
$(CH_2)_2COOMe$	H	Me	H	Br^-	—	217 f
p-Chlorocymoxyethyl	Me	Me	H	Br^-	214	279
Hexahydrobenzyl	H	Me	H	Cl^-	—	242
$CH_2CH(CHO)Br$	H	Me	CH_2CH_2OH	Br^-	60	280
$CH_2CH(OH)Ph$	H	Me	H	Br^-	182.5–3	19, 281
$CH_2CH(OCO$-cyclohexyl)Ph	H	Me	H	Br^-	—	281
$CH_2CH(OCO$-cyclohexyl)Ph	C[CH(O)Ph](Ph)(OH)	Me	H	Br^-	—	281
Allyl	H	Me	H	Br^-	132–40	19, 27, 152
Allyl	Me	Me	H	Br^-	—	152, 176
Allyl	CH=CHNHPh	Me	H	Br^-	—	176
Allyl	CH=CHNH-(3,5-diMeC_6H_3)	Me	H	Br^-	190	176
CH_2COCH_3	Alkyl	H	H	—	—	39
$CH_2COCHBr_2$	H	CH_3	CH_2CH_2OH	Br^-	—	280
3-Bromo-3-phtalimido-acetonyl	H	Me	CH_2CH_2OH	Br^-	142	280
$CH_2COCOOH$	H	Me	CH_2CH_2OH	Br^-	—	280
CH_2COPh	H	H	H	Br^-	227–9	19, 32
CH_2COPh	Alkyl	H	H	X^-	—	39, 282
CH_2COPh	Me	H	H	Br^-	—	41
CH_2COPh	H	Me	H	OH^-	91–2	271
CH_2COPh	H	Me	H	Br^-	—	32

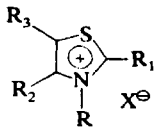
TABLE IX-3 (*Continued*)



R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
CH_2COPh	Me	Me	H	Br^-	159–60	283
CH_2COPh	Et	Me	H	Br^-	—	283
CH_2COPh	NH_2	Me	H	Br	—	284
CH_2COPh	Me	Me	Me	Br^-	203–4	283
$CH_2CO(p\text{-}BrC_6H_4)$	Me	H	H	Br^-	—	41
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	H	H	Br^-	226	32
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	H	H	Betaïne	158	32
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	Me	H	Br^-	260–1	285 1
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	Me	H	Betaïne	136–7	27
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	Me	CH_2CH_2OH	Br^-	222	285 1
$CH_2CO(p\text{-}NO_2C_6H_4)$	H	Me	COOEt	Br^-	205	285 1
CH_2-2-furoyl	NH_2	Me	H	Br^-	174	286
CH_2-2-(5-Br-furoyl)	NH_2	Me	H	Cl^-	223	286
CH_2-2-(5-NO_2-furoyl)	NH_2	H	H	Br^-	208–10	286
CH_2-2-(5-NO_2-furoyl)	NH_2	Me	H	Br^-	253–5	286
$CH_2CONHSO_2CH_3$	Me	Me	H	Br^-	228	262, 271
CH_2COOH	NH_2	H	H	Betaïne	247	287, 288
CH_2COOH	H	Me	CH_2CH_2OH	Cl	—	289, 290, 291
CH_2COOH	H	Me	CH_2CH_2OH	OH^-	178–9	289, 290, 291
CH_2COOEt	NH_2	H	H	Cl^-	196	287, 288
CH_2COOEt	Me	Me	H	Cl^-	200	287, 288
CH_2COOEt	NH_2	Me	H	Cl^-	180–1	287, 288
CH_2COOEt	H	Me	CH_2CH_2OH	Cl^-	—	270, 289, 290

$CH_2COOCH_2SO_3H$	Me	Me	H	Br^-	—	292
CH_2Ph	H	H	H	Br^-	—	293
CH_2Ph	Me	H	H	—	—	294
CH_2Ph	$CMe(OH)CONH_2$	H	H	Br^-	151	155
CH_2Ph	Br	H	H	Br^-	—	295 n
CH_2Ph	H	Me	H	Cl^-	148	18 i,r, 19, 152, 165, 197, 217, 240 l, 242, 276, 296–300, 301 x
CH_2Ph	H	Me	H	Br^-	—	
CH_2Ph	H	Ph	H	Br^-	—	19
CH_2Ph	Me	Me	H	Br^-	—	197, 276
CH_2Ph	Me	Me	H	Cl^-	202	152, 294, 300
CH_2Ph	CH_2Ph	Me	H	Cl^-	170	197, 276
CH_2Ph	CH_2Ph	Me	H	Br^-	—	197, 276
CH_2Ph	CHOHMe	Me	H	Br^-	159–160	165
CH_2Ph	C(NH-*p*-tolyl) =N-*p*-tolyl	Me	H	Br^-	225–6	158
CH_2Ph	Octylamino	H	Me	Cl^-	186–9	302
CH_2Ph	H	Me	Me	Cl^-	180	300
CH_2Ph	H	Me	CH_2CH_2OH	Cl^-	141–3	212 e, 215 m, 217 f, 303, 304, 305, 306
CH_2Ph	H	Me	CH_2CH_2OH	Br^-	—	
CH_2Ph	H	Me	CH_2CH_2OCOPh	Br^-	—	166, 307
CH_2Ph	H	Me	COOEt	I^-	186	303, 308
CH_2Ph	$CH(Me)OP(O)(OEt_2)$	Me	CH_2CH_2OBr	Br^-	—	166, 307 k
CH_2Ph	$CH(Ph)OP(O)(OEt_2)$	Me	CH_2CH_2OBr	Br^-	—	307 k
CH_2Ph	C(NH-*p*-tolyl) =N-*p*-tolyl	Me	CH_2CH_2OH	Br^-	193–4	35, 158
CH_2Ph	$C(NPh)S^-$	Me	CH_2CH_2OH	Zwitterion	153–4	35
CH_2Ph	$C(N\text{-}p\text{-}ClC_6H_4)S^-$	Me	CH_2CH_2OH	Zwitterion	132–4	35
$CH_2\text{-}p\text{-}PhC_6H_4$	Me	Me	CH_2CH_2OH	Cl^-	184–6	309
$CH_2\text{-}p\text{-}ClC_6H_4$	Me	Me	CH_2CH_2OH	Cl^-	128–31	309
$CH_2\text{-}o\text{-}ClC_6H_4$	Me	Me	H	Cl^-	190	298
$CH_2\text{-}p\text{-}NH_2C_6H_4$	Me	H	H	Cl^-	188	294 k, 310

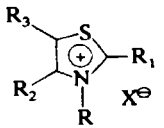
TABLE IX-3 (*Continued*)



R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
CH_2-*p*-$NH_2C_6H_4$	H	Me	H	Cl^-	183–6	294, 310
CH_2-*p*-$NH_2C_6H_4$	Me	Me	H	Cl^-	186–7	294, 310
CH_2-*p*-NH_2-C_6H_4	H	Me	CH_2CH_2OEt	Cl^-	172–3	310
CH_2-*m*-NH_2-C_6H_4	Me	H	H	Cl^-	228–8.5	294, 310
CH_2-*m*-$NH_2C_6H_4$	H	Me	H	Cl^-	226–7	294, 310
CH_2-*m*-$NH_2C_6H_4$	Me	Me	H	Cl^-	228–9.5	294, 310
CH_2-*m*-$NH_2C_6H_4$	H	Me	CH_2CH_2OEt	Cl^-	—	310
CH_2-*o*-$NH_2C_6H_4$	Me	H	H	Cl^-	164–5	294, 310
CH_2-*o*-$NH_2C_6H_4$	H	Me	H	Cl^-, HCl	212	294, 298, 311, 312
CH_2-*o*-$NH_2C_6H_4$	H	Me	H	Cl^-	—	277 e, 278, 313
CH_2-*o*-$NH_2C_6H_4$	H	Me	H	I^-	237	310
CH_2-*o*-$NH_2C_6H_4$	Me	Me	H	Cl^-	161–2	294, 310
CH_2-*o*-$NH_2C_6H_4$	H	Me	Me	Cl^-, HCl	—	310–312
CH_2-*o*-$NH_2C_6H_4$	H	Me	CH_2CH_2OH	Cl^-	—	310, 314
CH_2-*p*-$NO_2C_6H_4$	Me	H	H	Cl^-	196–9	276, 285 l, 310
CH_2-*p*-$NO_2C_6H_4$	Br	H	H	Br^-	—	310
CH_2-*p*-$NO_2C_6H_4$	Me	Me	H	Cl^-	71–20	310
CH_2-*p*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	Cl^-	166–7	276, 285 e
CH_2-*p*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	Br^-	150	276
CH_2-*p*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	I^-	120–1	212 l, 285 l
CH_2-*p*-$NO_2C_6H_4$	H	Me	CH_2CH_2OAc	Br^-	178	276
CH_2-*p*-$NO_2C_6H_4$	H	Me	COOEt	Cl^-	—	285 e
CH_2-*p*-$NO_2C_6H_4$	H	Me	COOEt	I^-	160–1	285 e

CH_2-*p*-$NO_2C_6H_4$	C(NH-*p*-tolyl) =N-*p*-tolyl	Me	CH_2CH_2OH	Br^-	191–192	158
CH_2-*m*-$NO_2C_6H_4$	Me	H	H	Cl^-	149–51	310
CH_2-*m*-$NO_2C_6H_4$	H	Me	H	Cl^-	192–2.5	310
CH_2-*m*-$NO_2C_6H_4$	Me	Me	H	Cl^-	212–3	310
CH_2-*m*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	Cl^-	152–3.5	2121, 310
CH_2-*o*-$NO_2C_6H_4$	Me	H	H	Cl^-	176–7	310
CH_2-*o*-$NO_2C_6H_4$	H	Me	H	Cl^-	198	278, 297, 298,
CH_2-*o*-$NO_2C_6H_4$	H	Me	H	Br^-	204	310–313, 315
CH_2-*o*-$NO_2C_6H_4$	Me	Me	H	Cl^-	199–201	310
CH_2-*o*-$NO_2C_6H_4$	H	Me	Me	Cl^-	203–4	311, 312
CH_2-*o*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	Cl^-	207–8	2121
CH_2-*o*-$NO_2C_6H_4$	H	Me	CH_2CH_2OH	Cl^-	203–5	297, 310, 312, 313–315
CH_2(2-benzimidazolyl)	H	H	H	Cl^-	—	3161
CH_2(2-benzothiazolyl)	H	Ph	Ph	OTs^-	—	317 a
CH_2CN	H	Me	CH_2CH_2OH	—	132–3	212
CH_2-*N*-creatinyl	H	Me	CH_2CH_2OH	Br^-	—	318
i-Pr	H	4-Me	H	I^-	136–7	19
i-Pr	SMe	H	$NHCOCH_3$	OH^-	83	207
i-Pr	SMe	H	$NHCOCH_3$	I^-	182–3	207
$CH(CH_3)(C_6H_5)$	Me	Me	H	ClO_4^-	162	319
$CH(CH_2COOH)COOH$	H	Me	CH_2CH_2OH	Betaïne	161–2	270, 289–291
$CH(CH_2COOH)COOH$	H	Me	CH_2CH_2OH	Cl^-	—	270, 289–291
$CH(CH_2COOH)COOH$	H	Me	CH_2CH_2OH	Br^-	—	270
$CH(CH_2COOH)COOH$	H	Me	CH_2CH_2OH	OH^-	167	270
$CH(CH_2CO_2Et)CO_2Et$	H	Me	CH_2CH_2OH	Cl^-	—	270, 290, 291
				Br^-	—	270
$CH(CH{=}CH_2)Ph$	NH_2	Ph	Ph	Cl^-	—	320
$CH(CO$-*p*-$NO_2C_6H_4)$ N(CHO)Ph	H	H	H	Betaïne	172	32
$CH(CO$-*p*-$NO_2C_6H_4)$ N(CHO)Ph	H	Me	H	Betaine	194–5	32
$CH{=}CHCH_2Ph$	NH_2	Ph	Ph	Cl^-	—	320

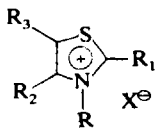
TABLE IX-3 (*Continued*)



R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
Ph	SMe	H	H	I^-	—	163
Ph	H	Me	H	I^-	241	147, 152, 241
Ph	Me	Me	H	I^-	—	147, 152, 238, 241, 244
Ph	Me	Me	H	ClO_4^-	180	321
Ph	Me	Ph	H	Br^-	149	120
Ph	Me	*p*-Xenyl	H	I^-	240	189
Ph	CH_2COMe	Ph	H	Br^-	—	120
Ph	CH_2CN	Ph	H	Br^-	237	120, 322
Ph	Ph	Me	H	ClO_4^-	205	323
Ph	Ph	Me	H	I^-	222	323
Ph	Ph	*p*-HOC_6H_4	H	Br^-	—	249
Ph	SMe	Me	H	I^-	—	163
Ph	SEt	NHCOMe	H	HCl	170	324
Ph	SCH_2Ph	NHCOMe	H	HCl	120	324
Ph	Me	H	Ph	ClO_4^-	—	325
Ph	Me	H	*p*-$MeOC_6H_4$	ClO_4^-	—	325
Ph	Me	Me	Me	Br^-	133	120
Ph	CH_2COMe	Me	Me	Br^-	232	120
Ph	Ph	COMe	OH	OH^-	170–2	326
Ph	Ph	OEt	Ph	—	—	327
Ph	Ph	$OCOCH_3$	Ph	—	—	327
p-MeC_6H_4	SCH_3	H	H	I^-	—	163

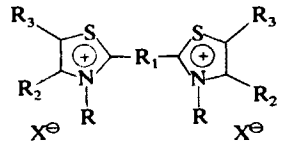
p-MeC_6H_4	CH_2CN	Ph	H	Br^-	231	322
p-MeC_6H_4	SCH_3	Me	H	I^-	—	163
o-MeC_6H_4	H	Me	H	I^-	230	298
o-MeC_6H_4	Me	Me	H	I^-	217–18	147
o-MeC_6H_4	Me	Me	H	ClO_4^-	172	147
o-MeC_6H_4	CH_2CN	Ph	H	Br^-	235	322
p-$EtOCOC_6H_4$	NHNH-*p*-MeC_6H_4	Ph	H	Br^-	177	328
p-$EtOCOC_6H_4$	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	180–1	328
p-Biphenylyl	Me	Me	H	I^-	—	238
p-ClC_6H_4	CH_2CN	Ph	H	Br^-	198	322
p-ClC_6H_4	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	214	328
p-BrC_6H_4	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	221	328
o-MeCONH-C_6H_4	H	Me	H	Cl^-	222	298
p-$Me_2NC_6H_4$	Me	Me	H	ClO_4^-	—	244
p-$Me_2NC_6H_4$	Ph	NH_2	H	Cl^-	176	329
p-$NO_2C_6H_4$	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	193	328
2,4,6-$(NO_2)_3C_6H_2$	Me	H	H	Cl^-	126	330
p-$MeOC_6H_4$	SMe	H	H	I^-	—	163
p-$MeOC_6H_4$	Me	Me	H	ClO_4^-	—	244
p-$MeOC_6H_4$	CH_2CN	Ph	H	Br^-	212	322
p-$MeOC_6H_4$	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	191	328
p-$MeOC_6H_4$	SMe	Me	H	I^-	—	163
o-$MeOC_6H_4$	CH_2CN	Ph	H	Br^-	220	322
p-$EtOC_6H_4$	NHNH-*p*-MeC_6H_4	Ph	H	Br^-	139	328
p-$EtOC_6H_4$	NHNH-*p*-$NH_2SO_2C_6H_4$	Ph	H	Br^-	196–8	328
p-$EtOC_6H_4$	NHNH-*p*-$NaSO_3C_6H_4$	Ph	H	Br^-	170–2	328
1-Naphthyl	Me	Me	H	ClO_4^-	—	244
2-Naphthyl	Me	H	Ph	ClO_4^-	—	325
2-Pyridyl	SMe	R_2	R_3	ClO_4^-	—	331
5-(6-NH_2-4-Me-pyrimidinyl)	H	Me	H	Cl^-, HCl	254–5	332
5-(6-NH_2-4-Me-pyrimidinyl)	H	Me	CH_2CH_2OH	Cl^-, HCl	250	332

TABLE IX-3 (*Continued*)



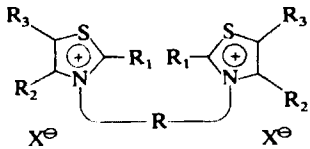
R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
5-(6-NH_2-4-Et-pyrimidinyl)	H	Me	H	Cl^-, HCl	252-3	332
5-(6-NH_2-4-Et-pyrimidinyl)	H	Me	CH_2CH_2OH	Cl^-, HCl	220	332
5-(2,6-diNH_2-4-Me-pyrimidinyl)	H	Me	H	Cl^-, HCl	315	332
5-(2,6-diOH-4-Me-pyrimidinyl)	H	Me	H	Cl^-	306	332
2-Benzimidazolyl	H	H	H	Cl^-	—	316 e
2-Benzimidazolyl	H	H	H	$SO_4^=$	—	316 e
2-Benzimidazolyl	H	H	H	$CO_3^=$	—	316 e
2-Benzimidazolyl	H	H	H	$ClC_2H_4CO_2^-$	—	316 e
2-(1,5,6-triMe-7-CF_3-benzimidazolyl)	Me	H	H	Cl^-	—	316 l
2-Thiazolyl	SMe	R^2	R^3	ClO_4^-	—	331
3-Acetylimino	Me	Me	H	ylide	—	333

TABLE IX-4A. 2,2'-BIS-THIAZOLIUM SALTS



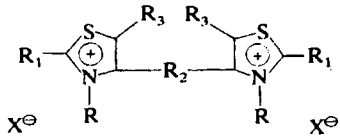
R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
Me	$(CH_2)_4$	Me	H	OTs^-	216	334
Me	$(CH_2)_4$	Me	H	ClO_4^-	268	334
Me	$(CH_2)_4$	Ph	H	I^-	272	334
Et	$(CH_2)_4$	Ph	H	I^-	243	334
Et	$(CH_2)_4$	Et	H	ClO_4^-	278	334
Pr	$(CH_2)_4$	Ph	H	I^-	201	334
Bu	$(CH_2)_4$	Ph	H	I^-	212	334
CH_2COPh	$(CH_2)_4$	H	H	Br^-	142–3	335

TABLE IX-4B. 3,3'-BIS-THIAZOLIUM SALTS



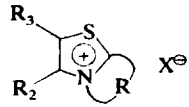
R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
3,3'-$(CH_2)_2$	Me	Me	H	Cl^-	300	336 a
3,3'-$(CH_2)_2$	Me	Ph	H	Cl^-	—	336 a
3,3'-$(CH_2)_2$	*p*-Me_2N-styryl	Ph	H	I^-	281	336
3,3'-$(CH_2)_3$	Me	Me	H	Cl^-	300	336
3,3'-$(CH_2)_3$	Me	Ph	H	Br^-	—	336
3,3'-$(CH_2)_3$	Me	Ph	H	Cl^-	—	336
3,3'-$(CH_2)_5$	H	Me	H	Br^-	244	337
3,3'-$(CH_2)_5$	Me	Me	H	Br^-	195	337
3,3'-$(CH_2)_5$	H	Me	Me	Br^-	—	337
3,3'-$(CH_2)_5$	Me	Me	Me	Br^-	167	337
$(CH_2)_2O(CH_2)_2$	H	H	H	I^-	188	338
$(CH_2)_2O(CH_2)_2$	H	H	H	OH^-	—	338
$(CH_2)_2O(CH_2)_2$	Me	H	H	I^-	175	338
$(CH_2)_2O(CH_2)_2$	Me	H	H	OH^-	—	338
$(CH_2)_2O(CH_2)_2$	H	Me	H	I^-	65	338
$(CH_2)_2O(CH_2)_2$	H	Me	H	OH^-	—	338
$(CH_2)_2O(CH_2)_2$	H	H	Me	I^-	180	338
$(CH_2)_2O(CH_2)_2$	H	H	Me	OH^-	—	338
C_6H_4 (*m*)	Me	Me	H	ClO_4^-	—	339

TABLE IX-4C. 4,4'-BIS-THIAZOLIUM SALTS



R	R_1	R_2	R_3	Anion	m.p. (°C)	Ref.
Me	H	CH_2	H	I^-	162–3	170
Me	H	CH_2	H	$2I^-$	240	170

TABLE IX-5. 2,3-POLYMETHYLENE THIAZOLIUM SALTS



R	R_2	R_3	Anion	m.p. (°C)	Ref.
$(CH_2)_3$	Me	H	ClO_4^-	130–2	340, 341
$(CH_2)_3$		$-(CH_2)_4-$	Cl^-	—	341
$(CH_2)_3$	Ph	H	ClO_4^-	187	341
$(CH_2)_3$	Ph	Ph	IO_4^-	—	340, 342
$(CH_2)_3$	Ph	Ph	ClO_4^-	—	340, 342
$(CH_2)_4$	Me	H	ClO_4^-	196	340–342
$(CH_2)_4$	Ph	H	ClO_4^-	190–1	342
$(CH_2)_4$	Ph	H	I^-	212	342
$(CH_2)_4$	Me	Me	ClO_4^-	170–1	342
$(CH_2)_4$	Ph	Ph	I^-	210	340–342
$(CH_2)_5$	Me	H	ClO_4^-	154	341
$(CH_2)_5$	Ph	H	I^-	176–7	341
$(CH_2)_5$	Me	Me	ClO_4^-	104	341
$(CH_2)_5$	Ph	Ph	I^-	217–8	340–342

VII. CLASSIFICATION AND LIST OF THIAZOLOCYANINE DYES

1. MONONUCLEAR CYANINES

11. **Cationic dyes**

111. *Hemicyanines*

1111. Aminovinyl compounds

1112. Anilinovinyl compounds

1113. Aminophenyl compounds

112. *Dimethine compounds*

1121. Styryl dyes

1122. Dimethine cyanines

1123. Azastyryl compounds

12. **Non-ionic mononuclear compounds**

121. *Ketomethylene compounds*

122. *Anilinovinyl base*

123. *Semicyanines*

2. DINUCLEAR CYANINES

21. **Cationic cyanines**

211. *Monomethine cyanines*

2111. Symmetrical

2112. Unsymmetrical

2113. Substituents on the chain

2114. Cyanines bases

212. *Trimethine cyanines*

2121. Symmetrical unsubstituted

2122. Unsymmetrical unsubstituted

2123. Symmetrical substituted on the chain

2124. Unsymmetrical substituted on the chain

213. *Pentamethine cyanines*

214. *Heptamethine cyanines*

215. *Chain-bridged cyanines*

2151. Chain-bridged

2152. Between chain and nitrogen atom

216. *Biscationic dyes*

217. *Azacyanines*

2171. Monoazacyanines

2172. Diazacyanines

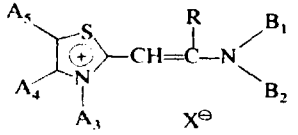
2173. Triazacyanines

22. **Neutrocyanines**
    221. *Zeromethine*
    222. *Dimethine*
    223. *Tetramethine*
    224. *Hexamethine*
    225. *Azaneutrocyanines*

3. TRINUCLEAR CYANINES
    31. **Linear cyanine**
        311. *Cyanine-cyanine*
        312. *Cyanine-neutrocyanine*
        313. *Cyanine-oxonol*
        314. *Rhodacyanine*
            3141. Cationic dyes
            3142. Non-ionic dyes
        315. *Azacyanines*
    32. **Branched cyanines**
        321. *Trimethine cyanines substituted in α-position: neocyanines*
        322. *Trimethine cyanines substituted in β-position*

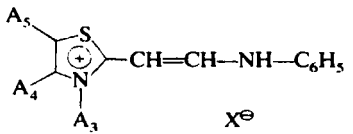
4. TETRANUCLEAR CYANINES
    41. **Two cyanines**
    42. **Two neutrocyanines linked by the thiazole ring**
    43. **Two neutrocyanines linked by the ketomethylene nucleus**
    44. **One cyanine and one neutrocyanine**

TABLE 1111. AMINOVINYL COMPOUNDS



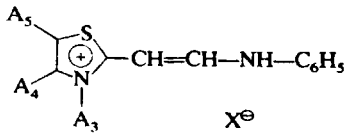
A_3	A_4	A_5	B_1	B_2	R	X	m.p. (°C)	Ref.
Me	Ph	Ph	Me	–C(Ph)=C(Ph)SMe	Me	I	183	45
Et	Ph	H	H	COPh	H	OTs	218	114
Et	$-C_6H_4$	(σ)–CH_2–CH_2–	H	COPh	H	OTs	176	114
$(CH_2)_2$–OH	Me	H	H	H	H	Br	—	343

TABLE 1112A. ANILINOVINYL COMPOUNDS



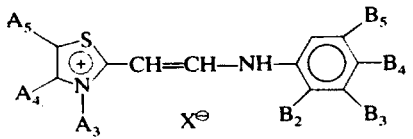
A_3	A_4	A_5	X	Method	m.p. (°C)	λ (nm)	Ref.
Me	H	H	OTs	C	—	—	*112*
Me	H	Br	OTs	—	—	—	*112*
Me	Me	H	I	A	248	—	*135*, 344, 345
Me	Me	H	2,4-di-OH-benzoate	—	201	—	*346*
Me	Me	H	α-Naphthenate	—	117	—	*347*
Me	Me	H	4-NH_2-3-OH-benzoate	—	200	—	*347, 348*
Me	Me	H	α-naphthyl acetate	—	117	—	*349*
Me	Me	Me	I	A	218	—	*139*
Me	Me	COO^-	—	A	206	412	*222*
Me	Ph	OPh	OTs	C	191	—	*111, 350, 351*
Me	Ph	*p*-Ph-C_6H_4O	I	—	266	—	*111, 350, 351*
Me	Ph	*p*-Me-C_6H_4S	I	—	243	—	*111, 350, 351*
Me	8-Anilinomethylindeno-1,2		OTs	C	195	—	*352*
Me	*p*-Xylyl	Ph	I	C	247	—	*111*
Me	*p*-Xylyl	*p*-Me-C_6H_4	I	—	230	—	*111*
Me	*p*-$MeOC_6H_4$	Ph	OTs	—	246	—	*111*
Me	*p*-$MeOC_6H_4$	OPh	OTs	C	202	—	*111, 350, 351*
Me	*p*-$MeOC_6H_4$	*p*-*t*-Octyl-C_6H_4O	OTs	C	236	—	*111*
Et	H	Ph	OTs	C	142	—	*353, 354*
Et	H	α-Naphthyl	OTs	—	204	—	*354*
Et	H	α-Naphthyl	OTs	—	139	—	*354*
Et	H	2-Benzofuryl	OTs	—	150	—	*354*
Et	H	2-Thienyl	OTs	—	185	—	*354*
Et	Me	H	*i*-Nicotinate	—	157	—	355
Et	Me	4-Thiazolyl	I	C	244	—	*356*

TABLE 1112A (*Continued*)



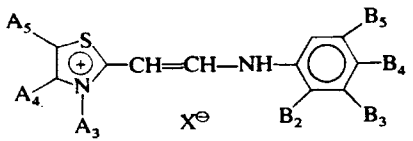
A_3	A_4	A_5	X	Method	m.p. (°C)	λ (nm)	Ref.
Et	Ph	H	OTs	C	176	—	*354, 357*
Et	$-C_6H_4(o)-CH_2-CH_2-$		OTs	—	218	—	*114*
Et	Ph	Ph	OTs	C	233	—	*111*
Et	Ph	OPh	I	C	196	—	*111, 350, 351*
Et	Ph	*p*-*t*-Octyl-C_6H_4O	I	—	176	—	*111, 350, 351*
Et	Ph	*p*-MeC_6H_4S	I	—	225	—	*111, 350, 351*
Et	$-CH_2-(o)-C_6H_4-$		OTs	C	236	—	*352*
Et	*p*-Xylyl	Ph	I	C	226	—	*111*
Et	*p*-Xylyl	*p*-MeC_6H_4	I	—	168	—	*111*
Et	*p*-BrC_6H_4	*p*-BrC_6H_4	I	C	193	—	*111, 350, 351*
Et	*p*-ClC_6H_4	*p*-ClC_6H_4	I	—	247	—	*111, 350, 351*
Et	*p*-$MeOC_6H_4$	Ph	OTs	C	250	—	*111*
Et	*p*-$MeOC_6H_4$	Ph	I	—	233	—	*111*
Et	*p*-$MeOC_6H_4$	OPh	I	C	196	—	*111, 350, 351*
Et	3,4-di$MeOC_6H_3$	Ph	OTs	C	161	—	*111*
Et	*p*-Phenetyloxy	*p*-Phenetyloxy	I	C	185	—	*111, 350, 351*
Et	Veratryl	*p*-$EtOC_6H_4O$	I	C	185	—	*111*
Et	β-Naphthyl	H	OTs	—	197	—	354
Et	β-Naphthyl	*p*-MeC_6H_4S	I	C	234	—	*111*
Et	2-Pyrrolyl	H	I	C	—	—	*358*
Et	2-Furyl	H	OTs	—	176	—	354, 359
Et	2-Furyl	H	I	—	—	—	359
n-Bu	Me	H	I	A	180	—	*135*
i-Bu	Me	Me	I	A	221	—	*139*
n-Heptyl	Me	H	*i*-Nicotinate	—	138	—	*360*

TABLE 1112B



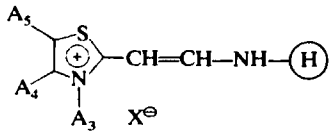
A_3	A_4	A_5	B_2	B_3	B_4	B_5	X	Method	m.p. (°C)	λ (nm)	Ref.
Me	H	COOEt	H	H	OMe	H	I	B	—	—	361
Me	H	COOEt	OMe	H	H	H	I	B	—	—	361
Me	Me	H	H	OH	COOH	H	*p*-Aminosalicylate	—	280	—	*348*
Me	Me	H	OMe	H	H	H	I	A	95	—	*362*
Me	Me	Me	H	H	Me	H	I	A	263	—	*139*
Me	Me	Me	H	H	Et	H	I	A	228	—	*139*
Me	Me	Me	H	H	N-diEt	H	I	A	212	—	*139*
Me	*i*-Bu	Me	H	H	Me	H	I	A	235	—	*139*
Me	*i*-Bu	Me	H	H	COOEt	H	I	A	238	—	*139*
Me	*i*-Bu	Me	H	H	OMe	H	I	A	216	—	*139*
Me	*i*-Bu	Me	H	H	OEt	H	I	A	220	—	*139*
Me	*i*-Bu	Me	H	Me	H	H	I	A	233	—	*139*
Me	*i*-Bu	Me	Me	H	H	H	I	A	236	—	*139*
Me	Benzyl	Me	H	H	Me	H	I	A	259	—	*363*
Me	Benzyl	Me	H	H	COOEt	H	I	A	153	—	*363*
Me	Benzyl	Me	H	H	Cl	H	I	A	255	—	*363*
Me	Benzyl	Me	H	H	OMe	H	I	A	257	—	*363*
Me	Ph	Me	H	H	Me	H	I	A	245	—	*363*
Me	Ph	Me	H	H	COOEt	H	I	A	243	—	*363*
Me	Ph	Me	H	H	Cl	H	I	A	224	—	*363*
Me	Ph	Me	H	H	N-diEt	H	I	A	235	—	*363*
Me	Ph	Me	H	H	OH	H	I	A	247	—	*363*
Me	Ph	Me	H	H	OMe	H	I	A	247	—	*363*

TABLE 1112B (*Continued*)



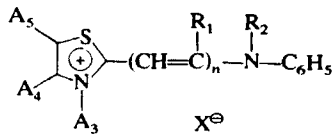
A_3	A_4	A_5	B_2	B_3	B_4	B_5	X	Method	m.p. (°C)	λ (nm)	Ref.
Me	Ph	Me	H	H	OEt	H	I	A	239	—	*363*
Me	Ph	Me	Me	H	Me	H	I	A	204	—	*363*
Et	Me	H	H	H	Me	H	*i*-Nicotinate	A	183	—	360
Et	Me	H	H	H	Br	H	I	A	120	—	*362*
Et	Me	H	H	H	Cl	H	*i*-Nicotinate	—	185	—	*144* e, 360
Et	Me	H	H	H	N-diEt	H	I	D	—	451	*364*
Et	Me	H	H	H	OMe	H	I	A	105	—	*362*
Et	Me	H	H	H	OMe	H	*i*-Nicotinate	—	163	—	360
Et	Me	H	H	H	OEt	H	I	A	122	—	*362*
Et	Me	H	Me	H	H	Me	I	A	145	—	*362*
n-Pr	Me	H	Me	H	H	Me	I	—	190	—	*135*
Allyl	Me	H	Me	H	H	H	*i*-Nicotinate	—	110	—	360

TABLE 1112C.



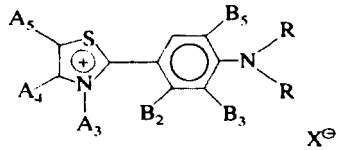
H	A_3	A_4	A_5	X	Method	m.p. (°C)	Ref.
α-naphtyl	Me	*i*-Bu	Me	I	A	214	*139*
α-naphtyl	Me	Benzyl	Me	I	A	243	*363*
β-naphtyl	Me	Me	Me	I	A	225	*139*
β-naphtyl	Me	*i*-Bu	Me	I	A	229	*139*
β-naphtyl	Me	Ph	Me	I	A	247	*363*
2-(5-Br-pyridyl)	Me	Me	Me	I	A	249	*139*
2-(5-Br-pyridyl)	Me	*i*-Bu	Me	I	A	225	*139*
2-(5-Br-pyridyl)	Me	Benzyl	Me	I	A	229	*363*
2-(5-Br-pyridyl)	Et	Me	H	I	A	256	*362*
2-(5-Br-pyridyl)	Et	Me	H	*i*-Nicotinate	—	154	360
2-(5-Cl-pyridyl)	Et	Me	H	I	A	140	*362*
2-(5-Cl-pyridyl)	Et	Me	H	*i*-Nicotinate	—	142	360
2-(5-I-pyridyl)	Me	*i*-Bu	Me	I	A	242	*139*
2-(5-I-pyridyl)	Me	Benzyl	Me	I	A	253	*363*
2-(5-I-pyridyl)	Me	Ph	Me	I	A	220	*363*
2-(5-I-pyridyl)	Et	Me	H	I	A	274	*362*
2-(5-I-pyridyl)	*n*-Bu	Me	H	I	A	178	*365*
2-(3,5-diBr-pyridyl)	Me	Benzyl	Me	I	A	230	*363*
2-(3,5-diBr-pyridyl)	Me	Ph	Me	I	A	232	*363*

TABLE 1112D.



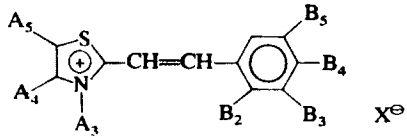
n	R_1	R_2	A_3	A_4	A_5	X	Method	m.p. (°C)	Ref.
1	H	COMe	Me	Me	H	I	E	—	*348* e
1	H	COMe	Et	H	Ph	OTs	E	130	*366*
1	H	COMe	Et	Ph	H	OTs	E	138	*367*
1	H	COMe	Et	2-Furyl	H	I	E	160	*359*
1	Me	H	Et	*p*-$MeOC_6H_4$	Ph	I	—	233	*111*
2	H	H	Me	H	H	I	—	—	368
2	H	H	Et	H	H	I	—	—	369. *669*
2	H	COOEt	Me	H	H	I	—	—	*368*

TABLE 1113. AMINOPHENYL COMPOUNDS



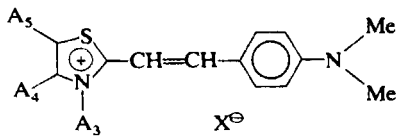
A_3	A_4	A_5	R	B_2	B_3	B_5	X	m.p. (°C)	Ref.
Me	H	H	Me	H	H	H	I	220	*142* e
Me	H	H	Me	H	H	H	CO_3	—	198 e
Me	Me	H	Me	H	H	H	I	165 212	*142* e, 370
Me	Me	H	Me	H	H	H	OTs, SO_4	—	198
Me	Me	H	Me	H	Me	Me	Br	—	198
Me	Me	H	Et	H	H	H	Br	—	198
Me	Me	Me	Me	H	H	H	Cl, Br, I, OTs	—	*136* e, 137 e, 138 e, 198 e
Me	Me	Me	Me	Br	H	OMe	Oleate	—	198
Me	Me	Me	Et	H	H	H	Butyrate	—	198
Me	Me	Me	*n*-Pr	H	Me	H	I	—	198
Me	Me	Et	Me	H	H	H	I	154	*142* e
Me	Me	Pr	Me	H	H	H	I	134	*142* e
Me	Me	*i*-Pr	Me	H	H	H	I	135	*142* e
Me	Me	*n*-Bu	Me	H	H	H	I	119	*370*
Me	Me	*n*-Bu	Me	H	H	H	Formate	—	198
Me	Me	*n*-Octyl	Me	H	H	H	I	102	*142* e
Me	Et	Me	Me	H	H	H	I	203	*142* e, *370*
Me	Et	Pr	Me	H	H	H	I	149	*142* e
Me	Pr	H	Me	H	H	H	I	198	*142* e
Me	*n*-Pr	Et	Me	H	H	H	I	125	*142* e
Me	*n*-Amyl	H	Me	H	H	H	I	134	*370*
Me	$-(CH_2)_4-$		Me	H	H	H	I	223	*142* e
Me	$-(CH_2)_4-$		Me	H	H	H	OTs	—	198 e
Me	$-(CH_2)_5-$		Me	H	H	H	I	190	*142* e, 198
Me	$-(CH_2)_6-$		Me	H	H	H	I	—	198 e
Me	Ph	H	Me	H	H	H	I	—	371
Me	Ph	Me	Me	H	H	H	I	159	*142* e
Et	H	Et	*i*-Bu	Cl	H	Cl	Valerate	—	198 e
Et	$-(CH_2)_4-$		Me	H	H	H	SO_4	—	198 e
n-Pr	Et	Et	Me	H	H	H	Cl, Salicylate	—	198 e
i-Bu	Me	Me	Me	H	H	H	I	—	198 e
i-Bu	Me	Me	Et	H	H	H	Cl	—	198 e

TABLE 1121A. STYRYL DYES



A_3	A_4	A_5	B_2	B_3	B_4	B_5	X	m.p. (°C)	λ (nm)	Ref.
Me	H	H	H	NMe_2	H	H	I	218	—	*372*
Me	H	COOEt	OMe	H	H	H	I	—	—	*361*
Me	H	Ph	H	H	H	H	I	90	—	*373* e
Me	Me	H	H	H	OH	H	OH	—	—	374
Me	Me	H	H	H	OH	H	I	—	—	343 e
Me	Me	H	H	H	OMe	H	I	—	—	*361*
Me	Me	H	H	NH_2	OMe	H	4-NH_2-5-OH-benzoate	283	—	*347* e
Me	Me	H	OMe	H	H	H	I	—	—	*361*
Me	Me	Me	H	H	NO_2	H	I	222	—	*139*
Me	Me	Me	H	H	OMe	H	I	236	—	*139*
Me	Me	Me	H	OH	H	H	I	227	—	*139*
Me	Me	Me	H	OMe	OH	H	I	229	—	*139*
Me	*i*-Bu	Me	H	H	NO_2	H	I	246	—	*139*
Me	*i*-Bu	Me	H	NO_2	H	H	I	198	—	*139*
Me	*i*-Bu	Me	H	OMe	OH	H	I	215	—	*139*
Me	*i*-Bu	Me	H	–O–CH_2–O–		H	I	213	—	*139*
Me	Benzyl	Me	H	H	NO_2	H	I	211	—	*363*
Me	Benzyl	Me	H	H	OH	H	I	213	—	*363*
Me	Benzyl	Me	H	OMe	OH	H	I	237	—	*363*
Me	Benzyl	Me	H	–O–CH_2–O–		H	I	209	—	*363*
Me	Ph	Me	H	H	NO_2	H	I	227	—	*363*
Me	Ph	Me	H	H	OH	H	I	254	—	*363*
Me	Ph	Me	H	NO_2	H	H	I	222	—	*363*
Me	Ph	Me	H	OMe	OH	H	I	214	—	*363*
Me	Ph	Ph	H	Cl	H	Cl	I	—	—	375
Me	Ph	Ph	OH	H	OH	H	I	—	—	375
Me	Ph	Ph	H	Cl	OH	Cl	Cl	—	—	376
Et	H	H	H	I	OH	I	$EtSO_4$	—	—	376
Et	H	H	OH	I	H	I	$EtSO_4$	—	—	376
Et	H	Styryl	H	H	H	H	I	234	525	*357*
Et	H	Ph	H	H	H	H	I	228	—	*113*
Et	Me	H	H	H	OH	H	I	257	400	*76*
Et	Me	H	H	H	OMe	H	I	255	—	377
Et	Me	H	OH	H	H	H	I	215	394	*76*
Et	Me	H	OH	H	OH	H	I	201	—	*113*
Et	Ph	H	H	H	H	H	I	222	406	*76*, 145
Et	Ph	H	OH	H	H	H	I	—	—	145
Et	Ph	H	H	H	OH	H	I	—	—	145
Et	Ph	Ph	H	Br	OH	Br	I	—	—	375, 378
Et	Ph	Ph	H	Cl	OH	Cl	Cl	—	—	376
Et	Ph	Ph	H	I	OH	I	$EtSO_4$	—	—	376
Et	Ph	Ph	OH	Br	H	Br	$EtSO_4$	—	—	376

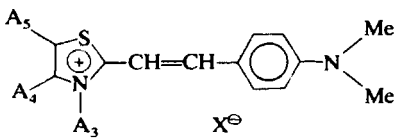
TABLE 1121B.



A_3	A_4	A_5	X	m.p. (°C)	λ (nm)	Ref.
Me	H	CH_2OH	OTs	212	489	*379*
Me	H	Br	I	238	510	*112*
Me	Me	H	Cl	—	—	380
Me	Me	H	Erythrosine	—	—	*381*
Me	Me	Me	I	—	—	*139*
Me	Me	COO^-	—	194	490	*222*
Me	*i*-Bu	Me	I	216	—	*139*
Me	Benzyl	Me	I	218	—	*363*
Me	CH_2OH	H	OTs	297	485	*379*
Me	Ph	H	I	205	490	80, 143, 382, 383
Me	Ph	Me	I	216	—	*363*
Me	Ph	Ph	I	44	498	*83*
Me	Ph	*p*-ClC_6H_4	I	55	520	*83*
Me	Ph	*p*-$NO_2C_6H_4$	I	148	570	*83*
Me	*p*-MeC_6H_4	H	I	187	490	*382*
Me	*p*-MeC_6H_4	H	I	239	—	384
Me	*p*-PhC_6H_4	H	I	167	490	*382*
Me	*p*-PhC_6H_4	H	I	253	—	*141* e
Me	*m*-BrC_6H_4	H	I	225	495	*382*
Me	*p*-BrC_6H_4	H	I	191	490	80, 82, *382*
Me	*p*-BrC_6H_4	H	I	223	—	*384*
Me	*p*-ClC_6H_4	H	I	232	490	80, 82, *382*

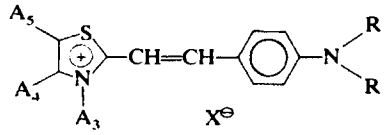
Me	p-ClC_6H_4	H	I	217	—	*384*
Me	p-ClC_6H_4	Ph	I	81	506	*83*
Me	p-IC_6H_4	H	I	229	—	143, *384*
Me	o-$NO_2C_6H_4$	H	I	224	490	*382*
Me	p-$MeOC_6H_4$	H	I	195	480	143, *382*
Me	p-$EtOC_6H_4$	H	I	225	490	*382*
Me	2,3-di$MeOC_6H_3$	p-$NO_2C_6H_4$	I	60	505	*83*
Me	α-Furyl	H	I	—	—	385
Me	α-Thienyl	H	I	—	—	385
Me	NH_2	H	I	262	520	*386*
Et	H	H	I	—	490	*387*
Et	H	H	I	142	483	*16*
Et	H	CH_2OEt	ClO_4	167	492	*379*
Et	H	Styryl	I	234	525	*357*
Et	H	Ph	I	255	495	*357*
Et	H	p-$MeOC_6H_4$	I	—	505	*388*
Et	H	p-(p-$MeOC_6H_4$)C_6H_4	Cl	—	516	*388*
Et	H	p-$PhOC_6H_4$	I	—	508	*388*
Et	H	2-Benzothiazolyl	ClO_4	264	—	*389*
Et	H	2-Benzothiazolyl	I	253	—	*389*
Et	Me	H	Br	242	—	377
Et	Me	H	I	241	470	*76*
Et	Me	H	I	—	480	*72, 667*
Et	Me	H	OTs	—	—	390
Et	Me	4-Thiazolyl	I	243	510	*356*
Et	Me	4-(2-Me-thiazolyl)	I	235	510	*356*
Et	i-Bu	Me	I	230	—	*391*
Et	Tetradecyl	Me	I	114	—	*391*
Et	Hexadecyl	Me	I	115	—	*391*
Et	p-MeOCOBenzyl	Me	I	94	—	*391*
Et	CH_2COMe	H	ClO_4	193	496	*379*
Et	Styryl	H	ClO_4	228	493	*357*
Et	Ph	H	I	255	495	*357*

TABLE 1121B (*Continued*)



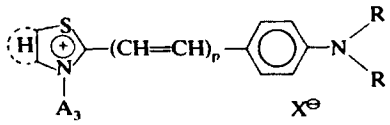
A_3	A_4	A_5	X	m.p. (°C)	λ (nm)	Ref.
Et	Ph	H	I	195	490	*16*
Et	*p*-PhC_6H_5	H	I	233	—	*141* e
Et	*p*-(*p*-$MeOC_6H_4$)C_6H_4	H	Cl	—	490	*388*
Et	*p*-$PhOC_6H_4$	H	I	238	490	*141* e, *388*
Et	*p*-$SO_3C_6H_4$	H	—	—	—	*392*
Et	β-Naphthyl	*p*-MeC_6H_4S	ClO_4	—	—	*351*
Et	2-Benzothiazolyl	H	ClO_4	234	511	*389*
Et	OEt	H	ClO_4	168	491	*379*
p-HOOCBenzyl	Me	H	—	—	—	*393*
Ph	Me	H	I	—	—	*394*
Ph	Me	H	ClO_4	240	500	*16*
p-PhC_6H_4	Me	H	ClO_4	237	504	*16*
2-Pyridyl	Me	Me	ClO_4	—	—	116
2-Thiazolyl	Me	Me	ClO_4	—	—	116
2-Benzothiazolyl	H	H	I	—	—	395
2-Benzothiazolyl	Me	Me	ClO_4	—	—	116

TABLE 1121C.



A_3	A_4	A_5	R	X	m.p. (°C)	λ (nm)	Ref.
Me	H	Me	Et	I	227	—	*396*
Me	Me	H	Et	I	157	—	*397*
Me	Me	Me	Et	I	217	—	*396*
Me	Ph	H	Et	I	211	490	*83, 397*
Me	Ph	H	$(CH_2)_4$	Br	236	—	*141* e
Me	Ph	H	$(CH_2)_4$	I	234	—	*141* e
Me	Ph	Me	Et	I	201	—	*398*
Me	Ph	Ph	Et	I	218	—	*398*
Me	Ph	*p*-ClC_6H_4	Et	I	149	525	*83*
Me	Ph	*p*-$NO_2C_6H_4$	Et	I	196	570	*83*
Me	*p*-MeC_6H_4	H	Et	I	184	—	*398*
Me	*p*-PhC_6H_4	H	Et	I	208	—	*141* e
Me	*p*-PhC_6H_4	H	$(CH_2)_4$	I	262	—	*141* e
Me	*p*-(*p*-$MeOC_6H_4$)C_6H_4	H	$(CH_2)_4$	I	279	—	*141* e
Me	*p*-BrC_6H_4	H	Et	I	198	—	*398*
Me	*p*-BrC_6H_4	H	$(CH_2)_4$	I	211	—	*141* e
Me	*p*-ClC_6H_4	H	Et	I	160	—	*398*
Me	*p*-ClC_6H_4	H	$(CH_2)_4$	I	219	—	*141* e
Me	*p*-ClC_6H_4	Ph	Et	I	159	519	*83*
Me	*p*-FC_6H_4	H	$(CH_2)_4$	I	238	—	*141* e
Me	*p*-IC_6H_4	H	Et	I	211	—	*398*
Me	2,4-diMeO-C_6H_3	*p*-$NO_2C_6H_5$	Et	I	120	515	*83*
Et	Ph	H	$(CH_2)_4$	I	228	—	*141* e
Et	*p*-Ph-C_6H_4	H	$(CH_2)_4$	I	264	—	*141* e
Et	*p*-BrC_6H_4	H	$(CH_2)_4$	I	223	—	*141* e
Et	*p*-ClC_6H_4	H	$(CH_2)_4$	I	217	—	*141* e
C_2H_4OH	Me	H	C_2H_4OH	Cl	231	482	668
C_2H_4OH	Me	H	C_2H_4OH	Br	227	482	668
C_2H_4OH	Ph	H	C_2H_4OH	Cl	217	492	668
C_2H_4OH	Ph	H	C_2H_4OH	Br	187	492	668

TABLE 1121D.



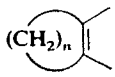
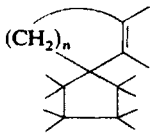
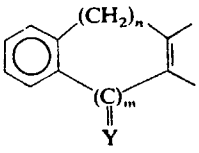
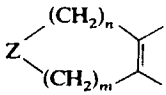
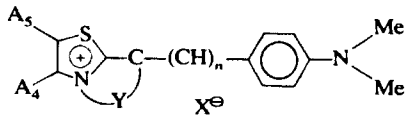
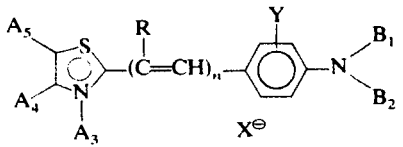
H		p	A_3	R	m.p. (°C)	λ (nm)	Ref.
	*n*						
	3	1	Et	Me	267	470	*399*
	4	1	Et	Me	246	480	*16, 72*
	4	1	Et	Me	—	490	87
	4	1	Et	Et	—	490	*400*
	4 (4-*i*-Pr, 7-Me)	1	Me	Me	228	490	*401*
	5	1	Et	Me	238	476	*402*
	*n*						
	2	1	Et	Me	145	490	*403*
	3	1	Me	Me	232	470	*404*
	*n* *m* *Y*						
	2 0 —	1	Me	Me	215	496	405
	0 1 H, H	1	Et	Me	249	523	*352*
	0 1 $=CHC_6H_4N$ Et_2(p)	1	Et	Me	—	534	*352*
	*n* *m* *Z*						
	1 2 O	1	Et	Me	233	495	87, *406*
	3 0 O	1	Et	Me	315	494	*407*
	1 2 S	1	Et	Me	247	490	87, *408*
	0 3 S	1	Et	Me	256	506	87, *409*
	0 3 S	2	Et	Me	236	548	87, *409*

TABLE 1121E.



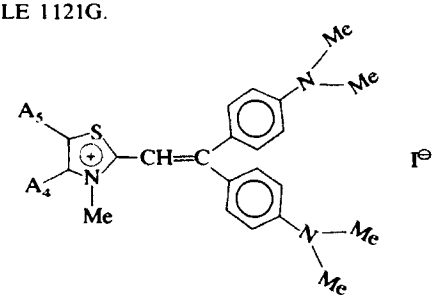
Y	*n*	A_4	A_5	X	m.p. (°C)	λ (nm)	Ref.
$-(CH_2)_3-$	1	Ph	H	I	281	498	410
$-(CH_2)_3-$	1	H	Ph	I	—	—	410
$-(CH_2)_2-O-$	1	Me	H	ClO_4	218	492	411
$-(CH_2)_2-S-$	1	Me	H	ClO_4	232	502	411
$-CH_2-C_6H_4(o)CH_2-$	1	Me	H	ClO_4	216	468	412
$-CH_2C_6H_4(o)-$	1	Me	H	ClO_4	156	446	412
$-C_6H_4(o)(CH_2)_2-$	1	Me	H	ClO_4	—	444	413, 414
$-C_6H_4(o)-$	1	Me	H	ClO_4	221	585	*415*
$-C_6H_4(o)-$	3	Me	H	ClO_4	233	670	*415*
$-C_6H_4(o)-O-$	1	Me	H	ClO_4	266	550	*121*, 413, 414
$-C_6H_4(o)-Se-$	1	Me	H	ClO_4	—	516	413, 414
$-C_{10}H_6(1,2)-O-$	1	H	H	ClO_4	240	550	*121*, 413, 414

TABLE 1121F.



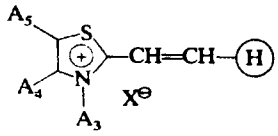
n	R	A_3	A_4	A_5	B_1	B_2	Y	X	m.p. (°C)	λ (nm)	Ref.
1	H	Me	H	H	$(CH_2)_3OCOOEt$	$(CH_2)_4SO_3^-$	H	—	—	—	*674*
1	H	Me	Me	H	H	COMe	H	I	285	—	*416*
1	H	Me	Me	Me	H	COMe	H	I	—	—	*139*
1	H	Me	*i*-Bu	Me	H	COMe	H	I	255	—	*139*
1	H	Me	Ph	Me	H	COMe	H	I	255	—	*363*
1	H	Et	*p*-KO_3S–C_6H_4	H	Me	CH_2CHOH-CH_2SO_3Na	H	OTs	—	—	*674*
1	H	$(CH_2)_3SO_3^-$	H	H	Me	$(CH_2)_2CHMe$-SO_3H	3-OMe-6-NHCOPh	—	—	—	*674*
1	H	$(CH_2)_3SO_3^-$	Ph	H	Me	(3-SO_3K-4-OMe)-C_6H_3	H	—	—	—	*674*
1	H	$(CH_2)_3SO_3$	*p*-KO_3S–C_6H_4	H	$(CH_2)_3SO_3Na$	$CH_2CHMeSO_3H$	2-NH-COPh	—	—	—	*674*
1	H	$CHMe(CH_2)_2$-SO_3H	Me	Me	$(CH_2)_3SO_3Na$	$(CH_2)_3SO_3Na$	H	—	—	—	674
1	COMe	Ph	Me	Me	Me	Me	H	Br	247	430	*120*
1	COMe	Ph	Ph	H	Me	Me	H	Br	219	435	*120*
1	COOEt	Ph	Ph	H	Me	Me	H	Br	193	422	*120*
1	CN	Ph	Ph	H	Me	Me	H	Br	192	516	*120*
4	H	Me	Me	H	Me	Me	H	I	243	533	*416*
4	H	Et	Ph	H	Et	Et	H	ClO_4	—	702	417

TABLE 1121G.



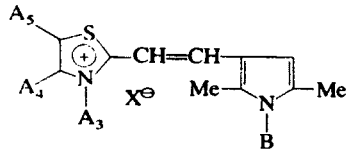
A_4	A_5	m.p. (°C)	λ (nm)	Ref.
Me	H	261	475	123
Me	COOEt	214	526	123
Ph	H	170	492	123

Table 1122A. DIMETHINECYANINES



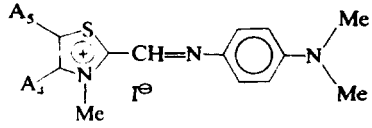
H	A_3	A_4	A_5	X	m.p.	λ(nm)	Ref.
α-naphthyl	Me	Me	Me	I	199	—	*139*
α-(4-NEt_2-naphthyl)	Me	Me	H	I	202	—	383
1-Tropylium	Me	H	H	ClO_4	257	481	418
1-Tropylium	Me	Me	H	I	266	481	418
1-(3-Me-tropylium)	Me	H	H	ClO_4	264	502	418
1-(3-Me-tropylium)	Me	Me	H	ClO_4	291	500	418
1-(4,6,8-triMe-tropylium)	Me	H	H	ClO_4	270	499	418
1-(4,6,8-triMe-tropylium)	Me	Me	H	I	268	499	418
1-(4,6,8-triMe-tropylium)	Me	Me	H	ClO_4	296	499	418
1-(3,8-diMe-5-*i*-Pr-tropylium)	Me	H	H	ClO_4	254	525	418
2-cyclopentadienylidene triphenylphosphorane	Et	H	H	ClO_4	—	460	419
α-Furyl	Me	Me	Me	I	202	—	*139*
α-Furyl	Me	Benzyl	Me	I	206	—	*363*
4-Quinolyl	Me	Me	H	I	226	—	*57*
5-(2-NMe_2-4-Me-thiazole)	Et	H	H	I	—	—	420
5-(2-MePh-amino-4-Me-thiazole)	Et	H	H	I	—	—	420
5-(2-MePh-amino-4-Ph-thiazole)	Et	H	H	I	—	—	420
5-(2-SMe-4-Me-thiazole)	Et	H	H	I	—	—	420

TABLE 1122B.

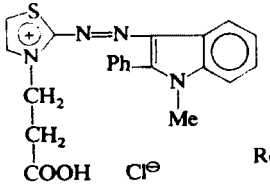


A_3	A_4	A_5	B	X	m.p.(°C)	λ(nm)	Ref.
Me	Ph	H	Me	I	228	—	*421* e, 422
Me	Ph	H	Et	I	208		*421* e, 422
Me	Ph	H	*n*-Bu	I	182	—	*421* e, 422
Me	Ph	H	*n*-Amyl	I	108	—	*421* e, 422
Me	Ph	H	Ph	I	223	—	*421* e, 422
Me	Ph	H	*p*-ClC_6H_4	I	—	—	422
Me	$-C_6H_4(o)-(CH_2)_2-$		Ph	I	226	456	*405*
Me	*p*-PhC_6H_4	H	Me	I	222	—	*421* e
Me	*p*-PhC_6H_4	H	Et	I	192	—	*421* e
Me	*p*-PhC_6H_4	H	Ph	I	216	—	*421* e, 422
Me	*p*-PhC_6H_4	H	*p*-ClC_6H_4	I	227	—	*421* e
Me	*p*-BrC_6H_4	H	Me	Br	216	—	*421* e
Me	*p*-BrC_6H_4	H	*n*-Bu	I	181	—	*421* e
Me	*p*-BrC_6H_4	H	*n*-Amyl	I	176	—	*421* e
Me	*p*-BrC_6H_4	H	Ph	I	222	—	*421* e, 422
Me	*p*-ClC_6H_4	H	Me	I	229	—	*421* e
Me	*p*-ClC_6H_4	H	*n*-Bu	I	169	—	*421* e
Me	*p*-ClC_6H_4	H	*n*-Amyl	I	181	—	*421* e
Me	*p*-$MeOC_6H_4$	H	*n*-Bu	I	148	—	*421* e
Me	*p*-$MeOC_6H_4$	H	Ph	I	—	—	422
Me	β-Naphthyl	H	Me	I	221	—	*421* e
Me	β-Naphthyl	H	Ph	I	—	—	422
Et	Me	H	1-Ph-2,5-diMe-pyrrolyl (3)	I	—	434	*667*
Et	$-(CH_2)_3-$		Et	I	273	440	87, *399*
Et	$-(CH_2)_2-O-CH_2-$		Ph	I	>300	440	87, *406*
Et	$-(CH_2)_3-S-$		Ph	I	229	444	87, *409*

TABLE 1123. AZASTYRYL COMPOUNDS



A_4	A_5	m.p. (°C)	λ(nm)	Ref.
Ph	H	209	530	80, 82, 83
		235	530	382
Ph	Ph	113	550	83
Ph	p-ClC_6H_4	85	545	83
Ph	p-$NO_2C_6H_4$	151	552	83
p-MeC_6H_4	H	238	535	382
p-PhC_6H_4	H	195	540	382
p-BrC_6H_4	H	234	530	383
		193	540	80
m-BrC_6H_4	H	215	530	382
p-ClC_6H_4	H	225	540	382
		190	530	80, 82
p-ClC_6H_4	Ph	>310	545	83
p-$MeOC_6H_4$	H	215	530	382
p-$EtOC_6H_4$	H	200	530	382
m-$NO_2C_6H_4$	H	224	530	382
2,4-di$MeOC_6H_3$	p-$NO_2C_6H_4$	101	526	83



Ref. *670*

TABLE 121. KETOMETHYLENE COMPOUNDS

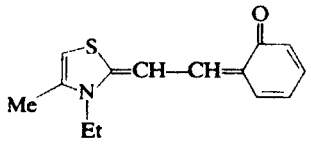
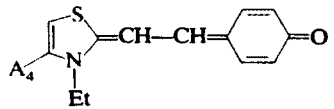
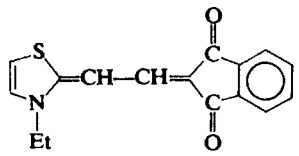
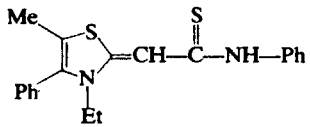
	A_4	m.p. (°C)	Ref.
		173	*76*
	Me	178	*76*
	Ph	150	*76*
		—	423
		146	*424*

TABLE 122. ANILINOVINYL BASE

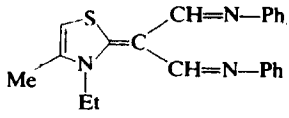
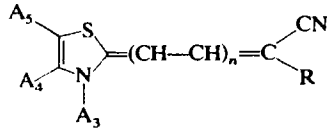
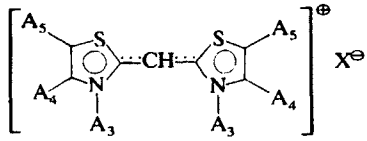
	m.p. (°C)	λ(nm)	Ref.
	111	347	*13*

TABLE 123. SEMICYANINES



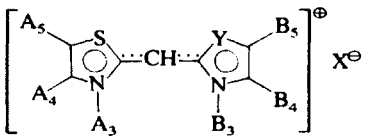
n	R	A_3	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
1	CS-NMePh	Me	H	H	119	—	*425, 426*
1	CS-pyrrolidinyl	Me	H	H	153	—	*425, 426*
1	P-$Ph_2(ClO_4)$	Et	H	H	180	388	419
3	CN	Et	Ph	Ph	208	658	*427*

TABLE 2111. SYMMETRICAL MONOMETHINE CYANINES



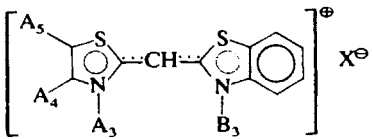
A_3	A_4	A_5	X	Method	m.p. (°C)	λ(nm)	Ref.
Me	Me	H	I	B,C	>320	—	1(p. 72), *428*
Me	Me	H	I_2	B	233	—	*428*
Me	Ph	H	I	—	—	420	429
Me	Ph	Ph	I	—	—	440	429
Et	H	H	I	A	240	438	430, 431, *432*
Et	Me	H	I	A	298–308	409	109, *432*, *433*, 666
Et	Ph	H	I	A	260	—	*432*
Et	Ph	Ph	I	A	265	439	109, *433*, 667
n-Heptyl	Me	H	*i*-Nicotinate	—	132	—	360
Ph	Ph	H	Br	D	—	—	434
p-$MeOC_6H_4$	Ph	H	Br	D	—	—	434
p-$EtOC_6H_4$	Ph	H	Br	D	—	—	434
o-$MeOC_6H_4$	Ph	H	Br	D	—	—	434

TABLE 2112A. UNSYMMETRICAL MONOMETHINE CYANINES



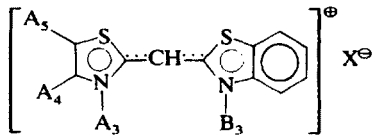
Y	A_3	A_4	A_5	B_3	B_4	B_5	X	Method	m.p. (°C)	λ(nm)	Ref.
O	Et	Ph	Ph	Et	Ph	Ph	I	F	—	420	1(p. 69), 435
O	Bu	Ph	Ph	Et	Ph	Ph	ClO_4	F	—	—	1(p. 69), 435
S	Me	Me	H	$(CH_2)_3$–SO_3^-	Me	H	—	—	—	—	343 e
S	Me	Ph	H	Ph	Me	H	I	G	220	440	*436*
S	Me	Ph	H	p-MeC_6H_4	Me	H	I	G	215	440	*436*
S	Me	Ph	H	p-BrC_6H_4	Me	H	I	G	220	440	*436*
S	Me	Ph	H	o-MeC_6H_4	Me	H	I	G	243	440	*436*
S	Et	Me	H	Ph	Ph	H	I	D	222	—	*437, 438*
S	Et	Ph	Ph	Et	=O	=CHNHPh	$EtSO_4$	—	232	—	440, 441, 439
S	Et	Ph	Ph	Allyl	=O	=CHNHPh	$EtSO_4$	—	—	661	439, 440, 441
S	Et	Ph	Ph	Bu	Ph	Ph	ClO_4	F	—	438	1(p. 69), *435*
S	Ph	Ph	H	p-$NH_2SO_2C_6H_4$	Ph	H	Br	F	>300	—	*442*
S	p-MeC_6H_4	Ph	H	p-BrC_6H_4	Ph	H	Br	F	—	—	*442*
S	p-MeC_6H_4	Ph	H	p-ClC_6H_4	Ph	H	Br	F	—	—	*442*
S	p-MeC_6H_4	Ph	H	p-$NH_2SO_2C_6H_4$	Ph	H	Br	F	—	—	*442*

TABLE 2112B



A_3	A_4	A_5	B_3	X	Method	m.p. (°C)	λ(nm)	Ref.
Me	H	CH_2OH	Et	I	—	256	414	*379*
Me	H	Br	Et	I	F	>320	423	*112*
Me	H	NH_2	Et	I	F	254	457	*112*
Me	Me	H	Me	Br	F	—	—	1(p. 69), *60*
Me	Me	H	Et	I	FG	276	—	*416, 443, 444*
Me	Me	COO^-	Et	—	F	210	420	*222*
Me	Ph	H	Me	I	F	—	418	1(p. 72), *43, 80, 82*
Et	H	H	Et	I	—	279	412	*388*
Et	H	Styryl	Et	I	F	257	634	*357*
Et	H	COMe	Et	OTs	F	235	434	*112*
Et	H	COOMe	Et	OTs	F	233	430	*112*
Et	H	COOEt	Et	I	F	202	428	*112*
Et	H	Ph	Et	I	F	277	437	*354, 357, 388*
Et	H	*p*-PhC_6H_4	Et	I	—	244	444	*388*
Et	H	*p*-(*p*-MeC_6H_4)C_6H_4	Et	I	—	268	447	*388*
Et	H	*p*-$MeOC_6H_4$	Et	I	—	257	440	*388*
Et	H	α-Naphthyl	Et	I	—	274	426	*354, 445*
Et	H	β-Naphthyl	Et	I	—	—	445	*354*
Et	H	α-Furyl	Et	I	—	267	445	*354*
Et	H	α-Benzo(*b*)furyl	Et	I	—	267	454	*354*
Et	H	β-Benzo(*b*)thienyl	Et	I	—	264	434	*354*
Et	H	2-Benzothiazolyl	Et	I	F	277	457	*389*

TABLE 2112B (*Continued*)

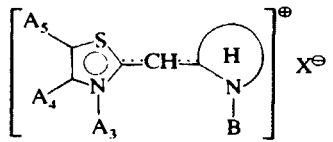


A_3	A_4	A_5	B_3	X	Method	m.p. (°C)	λ(nm)	Ref.
Et	H	NHCOMe	Et	I	G	—	430	*446*
Et	H	NHCOMe	$(CH_2)_2COO^a$	I	G	—	430	*446*, 447
Et	H	OEt	Et	I	—	222	425	*388*
Et	Me	4-Thiazolyl	Et	I	F	276	436	*356*
Et	Me	4-(2-Me-Thiazolyl)	Et	I	F	285	437	*356*
Et	Styryl	H	Et	I	F	251	424	*357*
Et	Ph	H	Et	I	F	238	419	114, *354*, *357*
Et	p-$MeOC_6H_4$	Ph	Me	I	F	304	425	1(p. 69), *111*
Et	α-Naphthyl	H	Et	ClO_4	—	228	419	*354*
Et	β-Naphthyl	H	Et	I	—	—	419	*354*
Et	2-Pyrrolyl	H	Et	I	F	262	417	*358*
Et	α-Furyl	H	Et	I	—	248	419	*354*
Et	α-Benzo(*b*)furyl	H	Et	I	—	251	418	*354*
Et	α-Thienyl	H	Et	I	—	251	417	*354*
Et	β-Benzo(*b*)thienyl	H	Et	I	—	243	417	*354*
Et	2-Benzothiazolyl	H	Et	ClO_4	F	256	420	*389*
$(CH_2)_2SH$	Ph	H	Ph	Br	—	—	—	*63*
Ph	H	Ph	Et	ClO_4	F	—	—	*325*
Ph	Me	H	Me	I	G	264	—	*60*
Ph	Ph	H	Me	I	D	—	—	*437*
Ph	Ph	H	Et	Br	D	—	—	1(p. 304), *437*

Ph	Ph	H	Et	I	D	271	—	*437, 438*
Ph	Ph	H	Et[a]	Br	—	298	—	*438*
Ph	Ph	H	Et[a]	I	D	—	—	*437*
Ph	Ph	CH_2COO	Et	Br	—	—	—	*438*
Ph	Ph	COOMe	Et	Br	D	—	—	*437*
Ph	OH	*o*-$MeOC_6H_4$-N=N-	Et	Br	—	—	—	*448*
Ph	OH	2-(6-EtObenzo thiazolyl-N=N-	Et	Br	—	—	583	*448*
2-Thiazolyl	Me	Me	Et	I	G	—	—	*117*
2-Benzothia-zolyl	H	H	Et	I	—	—	—	395
6-(2Me-benzo-thiazolyl)	Me	H	Me	Cl	F	210	—	*118*
6-(2Me-benzo-thiazolyl	Me	H	Me	ClO_4	F	240	—	*118*

[a] 5-Cl-benzothiazole.

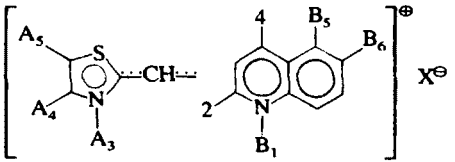
TABLE 2112C



H	A_3	A_4	A_5	B	X	Method	m.p. (°C)	λ(nm)	Ref.
3,3-diMe-indolenyl	Me	Me	H	Me	I	F–G	244	414	*449*
3,3-diMe-indolenyl	Me	Ph	H	Me	I	F–G	244	417	*449*
3,3-diMe-indolenyl	Ph	Ph	H	Me	I	D	204	—	*437, 438*
3,3-diMe-indolenyl	Ph	OH	*p*-MeC_6H_4-N=N-	Et	Br	—	—	—	*448*
2-Pyridinyl	Et	H	H	Et	I	—	442	—	*450*
2-Pyridinyl	Et	Me	H	Me	I	F	—	—	1(p. 66), *451, 452 453, 454*
2-Pyridinyl	Et	Me	H	Et	I	F	447	—	1(p. 53), *450, 452* 454
2-Pyridinyl	Et	Ph	H	Et	I	F	447	—	*450*
1-Isoquinolyl	Et	Me	H	Me	I	F	—	—	*455*
3-Benzo(f)quinolyl	Et	H	H	Et	I	F	268	483	1(p. 48), *450, 456, 457*
3-Benzo(f)quinolyl	Et	Me	H	Et	I	—	—	—	1(p. 48), *450, 456, 457*
3-Benzo(f)quinolyl	Et	Ph	H	Et	I	—	—	—	1(p.48), *450, 456, 457*
2-(5-MeS-4,4-diMe-imidazolyl)	Me	Ph	H	Me	ClO_4	F	246	—	*458*
2-(3,3-diMe-pyrrolo-(2,3-*b*)pyridyl	Me	Me	H	Et	I	G	203	—	459
2-(1-Me-benzimi-dazolyl)	Ph	Me	H	Me	I	G	240	235	*436*

2-Benzoxazolyl	Et	Me	H	Et	I	—	—	—	1(p. 69), 460
2-Benzoxazolyl	Ph	Me	H	Me	I	G	213	410	*436*
2-Benzoxazolyl	p-MeC_6H_4	Me	H	Me	I	G	239	410	*436*
2-Benzoxazolyl	p-BrC_6H_4	Me	H	Me	I	G	170	410	*436*
2-Benzoxazolyl	o-$MeOC_6H_4$	Me	H	Me	I	G	247	410	*436, 438*
2-(5,6-diMe-benzoxazolyl)	Ph	OH	p-ClC_6H_4–N=N–	Et	I	—	—	—	*448*
2-Thiazolyl	Ph	Ph	H	Me	ClO_4	—	204	—	*437, 438*
2-(4-Oxothiazolinyl)	Me	Me	H	Ph	Br	—	—	—	*461, 462*
2-(4-Oxothiazolinyl)	Ph	Ph	Me	Ph	I	—	—	—	*461, 462*
2-(4-Oxo-5-α-MeS-propylidene thiazolinyl)	Me	Ph	Me	Ph	I	—	255	—	*461, 462*
2-β-Naphthothiazolyl	Ph	Ph	H	Et	Br	D	240	—	*437, 438*
2-Benzoselenazolyl	Me	Me	H	Et	I	F	273	—	*416*
2-Benzoselenazolyl	Ph	Ph	H	Et	Br		>310	—	*438*
2-Benzoselenazolyl	Ph	Ph	H	Et	I	D	—	—	*437*
2-(5-Me-benzo-selenazolyl)	Et	H	NHCOMe	Et	I	G	—	436	*446*, 447
2-(5-MeO-benzo-selenazolyl)	Et	H	NHCOMe	Et	I	G	—	441	*446*, 447
2-(5,6-diMe-benzoselenazolyl)	Et	H	NHCOMe	$(CH_2)_2$ COOH	—	G	—	441	*446*, 447
2-(5,6-diMe-benzoselenazolyl)	Ph	OH	p-$HO_3SC_6H_4$–N=N–	Et	Br	—	—	—	*448*
9-(3-Et-2Me-imidazo (4,5-f)quinolyl)	Me	Me	H	Et	I	G	—	506	*463, 464*

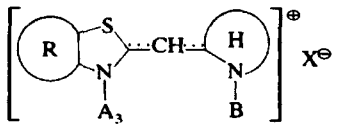
TABLE 2112D



2 or 4	A_3	A_4	A_5	B_1	B_5	B_6	X	Method	m.p. (°C)	λ(nm)	Ref.
2	Me	H	H	Et	H	H	I	F	—	—	*456*
2	Me	H	COMe	Et	H	H	I	F	282	489	*112*
2	Me	Me	H	Me	H	Me	OTs	F	—	—	1(p. 63), *60*, 295
2	Me	H	Et	Et	H	H	I	F-G	—	472	*443*, *444*, *450*, *468*
2	Me	Me	COO^-	Et	H	Me	—	F	206	482	*222*
2	Me	COOEt	Me	Et	H	OMe	I	—	—	—	303
2	Me	Ph	H	Me	H	H	I	F	—	475	80, 83, *456*
2	Me	Ph	Me	Et	H	H	I	F	—	—	*456*
2	Me	Ph	Ph	Me	=O	H	I	—	—	484	467
2	Me	Ph	*p*-MeC_6H_3-S	Et	H	H	I	F	227	485	1(p; 65) *111*, *351*
2	Me	α-Furyl	COOEt	Et	H	H	Br	F	—	—	*468*
2	Me	NH_2	H	Et	H	H	I	F	270	454	1(p. 48), *386*
2	Et	H	H	Et	H	H	I	F	267	465	1(p. 48), *111*, *387*, *457*, 469
2	Et	Me	H	Me	H	H	OTs	—	—	—	*465*
2	Et	Me	H	Et	H	H	I	F	—	472	1(p. 48), *111*, *456*, *457*
2	Et	Ph	H	Et	H	H	I	F	—	—	1(p. 48), *111*, *453*, *456*, *457*
2	Et	Ph	Me	Et	H	H	I	—	—	—	*453*
2	Et	Ph	Ph	Me	H	H	I	F	271	490	*111*
2	Et	Ph	OPh	Me	H	H	I	F	258	480	1(p. 65), *42*, *111*

2	Et	*p*-$MeOC_6H_4$	Ph	Me	H	H	I	F	267	490	1(p. 65), *42*, *111*
2	Et	3,4-di$MeOC_6H_3$	Ph	Me	H	H	I	F	227	485	1(p. 65), *42*, *111*
2	Et	2-Pyrrolyl	H	Et	H	H	I	F	227	479	*358*
2	Et	α-Furyl	H	Et	H	H	OTs	F	—	—	*468*
2	Et	α-Furyl	H	Et	H	OMe	I	F	—	—	*468*
2	Et	α-Thienyl	H	Et	H	H	I	F	—	—	110, *470*
2	Et	α-Benzo(*b*)-thienyl	H	Et	H	H	I	F	—	—	*468*, *471*
2	Et	α-Benzo(*b*)-thienyl	H	Et	H	Me	I	F	—	—	*468*, *471*
2	Et	α-Benzo(*b*)-thienyl	H	Et	H	OMe	I	F	—	—	*468*, *471*
2	Et	COOEt	H	Et	H	H	I	—	—	—	62
2	CH(Me)Ph	Me	H	Me	H	H	Cl	F	166	480	*472* v
2	Ph	Me	H	Me	H	H	I	F	230	—	*62*, *394*, *473*
2	Ph	Ph	H	Et	H	H	Br	D	272	—	*437*, *438*
2	Ph	OH	H	Me	H	H	Br	—	—	—	*448*
2	*p*-MeC_6H_4	Me	H	Me	H	H	I	G	201	480	*436*
2	*p*-BrC_6H_4	Me	H	Me	H	H	I	G	292	480	*436*
2	*o*-MeC_6H_4	Me	H	Me	H	H	I	G	249	480	*436*
2	*o*-$MeOC_6H_4$	Me	H	Me	H	H	I	G	249	480	*436*
4	Me	Ph	H	Me	H	H	I	—	240	—	1(p. 39), *42*
4	Et	H	H	Et	H	H	I	H	—	505	*387*
4	Et	H	NHCOMe	Et	H	H	I	G	—	523	*446*
4	Et	H	NHCOMe	Et	H	Me	I	—	—	—	447
4	Et	Ph	H	Et	H	H	I	F	—	—	*474*
4	CH(Me)Ph	Me	H	Et	H	H	I	F	200	511	*472* v
4	Ph	Me	H	Me	H	H	I	G	258	520	*436*
4	Ph	Ph	H	Me	H	H	I	D	301	—	*437*, *438*
4	*p*-MeC_6H_4	Me	H	Me	H	H	I	G	195	520	*436*
4	*p*-BrC_6H_4	Me	H	Me	H	H	I	G	275	520	*436*
4	*o*-MeC_6H_4	Me	H	Me	H	H	I	G	188	520	*436*
4	*o*-$MeOC_6H_4$	Me	H	Me	H	H	I	G	188	520	*436*

TABLE 2112E



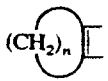
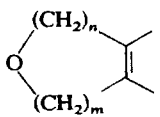
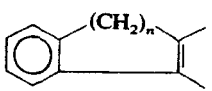
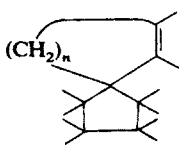
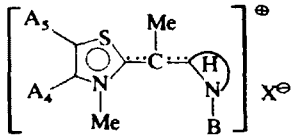
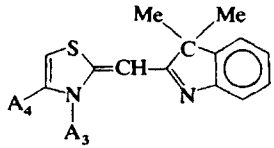
R		H	A_3	B	X	Method	m.p. (°C)	λ (nm)	Ref.
	n								
	3	2-Quinolyl	Et	Et	I	F	284	490	*399*
	4	4-(6-Me-quinolyl)	Me	Et	ClO_4	F	—	515	*400*
	4	2-(7-Me-quinolyl)	Me	Et	I	F	—	500	*400*
	4	2-Benzothiazolyl	$(CH_2)_2SH$	Et	Br	—	—	—	*63*
	4 (4-i-Pr, 7Me)	2-Quinolyl	Me	Et	I	F	240	484	*401*
	5	2-Quinolyl	Et	Et	I	E	263	476	*402*
	n *m*								
	1 2	2-Quinolyl	Me	Et	I	F	280	—	*406*
	1 2	2-Quinolyl	Et	Et	I	F	273	—	*406*
	3 0	2-Quinolyl	Me	Et	I	F	265	500	*407*
	n								
	1	2-Benzothiazolyl	Me	Me	ClO_4	F	238	523	*352*
	2	2-Quinolyl	Me	Et	I	F	246	490	*405*
	2	2-Benzothiazolyl	Et	Et	I	—	248	435	114
	*n*								
	2	2-Quinolyl	Et	Et	I	F	268	468	*404*
	3	2-Quinolyl	Et	Et	I	F	—	476	*404*

TABLE 2113. MONOMETHINE CYANINES WITH SUBSTITUENT ON THE CHAIN



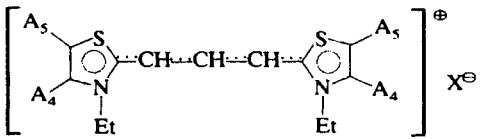
H	A_4	A_5	B	X	λ(nm)	Ref.
2-Quinolyl	H	H	Et	OTs	518	26
2-(4-Me-thiazolyl)	H	H	Me	OTs	448	26
2-Benzothiazolyl	H	H	Me	OTs	450	26
2-Benzothiazolyl	$-CH_2)_4-$		Me	ClO_4	—	400

TABLE 2114. CYANINE BASES



A_3	A_4	m.p. (°C)	λ(nm)	Ref.
Me	H	—	—	1(p. 361), *475*
Me	Me	237	405	*449*
Me	Ph	182	405	*449*
Et	H	—	—	*475*

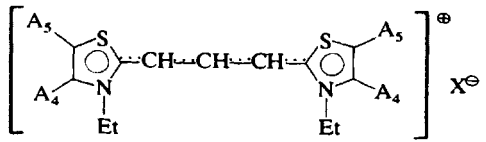
TABLE 2121A. SYMMETRICAL UNSUBSTITUTED TRIMETHINE CYANINES



A_4	A_5	X	Method	m.p. (°C)	λ(nm)	Ref.
H	H	I	—	—	541	476
			F	223	542	1(p. 129), *16*
			A	—	543	*110*
			—	—	545	113
			—	—	548	79
			—	—	553	477
			A	—	555	*387*
			A	—	580	478
H	H	ClO_4	—	—	—	479
H	Me	I	A	—	553	*110*, 477
H	CH_2OH	ClO_4	A	191	555	*379*
H	Styryl	I	A	199	634	*357*
H	COOEt	I	A	134	583	*112*
H	Ph	ClO_4	A	—	592	17, *110*
H	Ph	I	A	—	592	17, 114, 354, *388*, 480, 477
H	*p*-PhC_6H_4	I	A	178	608	*481*
					612	480
H	*p*-(*p*-$NO_2C_6H_4$)C_6H_4	I	—	—	645	480
H	*p*-(*p*-$MeOC_6H_4$)C_6H_4	Cl	A	198	612	*388*
H	*p*-$Me_2NC_6H_4$	I	—	—	623	17
H	*p*-$Me_2NC_6H_4$(ClH)	ClO_4	—	—	608	17

H	*p*-$MeCONHC_6H_4$	I	—	265	608	17
H	*p*-$NO_2C_6H_4$	I	—	230	650	480
H	*p*-HOC_6H_4	ClO_4	—	266	600	17
					620	17
H	*p*-$MeOC_6H_4$	I	A	190	612	1(p. 101), 17, *388*, *445*
H	*p*-$PhOC_6H_4$	Cl	A	250	606	*388*
H	α-Naphthyl	I	A	180	578	1(p. 101), 17, *388*, *445*
H	4-MeO-α-Naphthyl	I	A	135	580	*445*
H	β-Naphthyl	OTs	A	249	610	1(p. 101), 354, *445*, *481*
H	5-Acenaphthyl	I	A	205	606	*481*
H	α-Furyl	ClO_4	—	203	609	354
H	α-Thienyl	I	—	184	610	354
H	α-Benzo(*b*)furyl	I	—	244	623	113, 354
H	β-Benzo(*b*)thienyl	I	—	200	594	354
H	2-Benzothiazolyl	ClO_4	A	267	630	*389*
H	MeCONH	ClO_4	D	—	576	*112*
Me	H	I	—	—	548	79
			A	—	552	*13*
			A	271	556	16, 75 u, 109 i, 110, 387, *433*, *466*, *482*, 483, *484*, *485*, 667
Me	H	*i*-nicotinate	—	193	—	360
Me	Me	I	A	—	563	*110*, 477
Me	$CF_4(CF_2)_2$	ClO_4	A	256	—	*487*
Me	COMe	I	D	240	598	*112*
Me	4-Thiazolyl	ClO_4	D	228	597	*356*
Me	4-(2-Me-thiazolyl)	ClO_4	D	202	600	*356*
Me	NO_2	I	—	—	640	480
i-Bu	Me	I	A	162	—	*391*

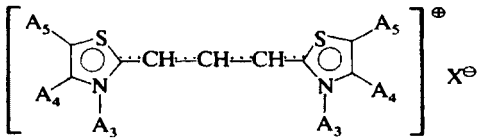
TABLE 2121A (*Continued*)



A_4	A_5	X	Method	m.p. (°C)	λ(nm)	Ref.
Tetradecyl	Me	I	—	119	—	*391*
Hexadecyl	Me	I	—	129	—	*391*
(p-$MeOCOC_6H_4$)CH_2	Me	I	—	214	—	*391*
Phthalimidomethylene	H	I	—	241	545	1(p. 101), *488*
Styryl	H	I	A	239	572	*357*
CH_2OH	H	ClO_4	A	183	553	*379*
COOEt	H	I	D	173	542	*112*
Ph	H	I	A	240	559	*16*, *110*, 114, 354, 477, *484*, *486*
Ph	Ph	I	A, F	247	588	1(p. 104), *110*, *111*, 477, 483, *489*, 667
p-Xylyl	Ph	ClO_4	F	225	592	1(p. 104), *111*
p-PhC_6H_4	H	I	A	222	560	1(p. 104), *481*, *490*
p-PhC_6H_4	p-PHC_6H_4	I	A	155	602	*481*
p-(p-$MeOC_6H_4$)C_6H_4	H	Cl	A	262	565	*388*
p-$MeOC_6H_4$	H	I	A	240	560	*388*
p-$MeOC_6H_4$	Ph	I	F	181	590	1(p. 104), *111*
3,4-diMe-OC_6H_3	Ph	I		179	590	1(p. 104), *111*
p-$PhOC_6H_4$	H	Cl	A	198	560	*388*
p-$CF_3SO_2C_6H_4$	H	I	A	239	—	*491*
o-$NO_2C_6H_4$	H	I	—	—	—	492
m-$NO_2C_6H_4$	H	I	—	—	—	492

α-Naphthyl	H	I	A	190	560	1(p. 101), 354, *481*, *490*
p-MeO-α-Naphthyl	H	Br	A	144	568	*388*
β-Naphthyl	H	I	A	215	560	1(p. 101), 354, 481, 490
β-Naphthyl	*p*-MeC_6H_4–S	I	F	194	585	1(p. 104), *111*, *351*
5-Acenaphthyl	H	ClO_4	A	201	560	*481*, *490*
2-Pyrrolyl	H	I	A	199	555	*358*
α-Furyl	H	I	A	234	563	354, *468*, *493*
α-Thienyl	H	I	—	—	559	354, 494
α-Benzo(*b*)furyl	H	$EtSO_4$	—	220	562	354
2-Benzothiazolyl	H	I	A	215	565	*389*
2-Benzothiazolyl	H	ClO_4	—	264	—	*389*
NH_2	H	I	A	235	526	1(p. 101), *386*

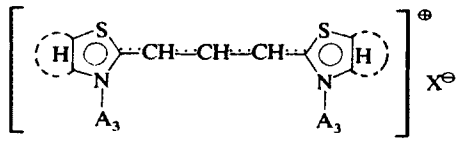
TABLE 2121B



A_3	A_4	A_5	X	Method	m.p. (°C)	λ(nm)	Ref.
Me	H	H	I	E, F	227	550	*495*
Me	H	Styryl	I	A	199	446	*357*
Me	H	Ph	I	—	—	592	17
Me	H	*p*-$Me_2NC_6H_4$	ClO_4	—	213	623	17
Me	H	*p*-$Me_2NC_6H_4$,ClH	I	—	—	603	17
Me	H	*p*-$NO_2C_6H_4$	I	—	—	650	17
Me	H	*p*-HO-C_6H_4	—	—	—	620	17
Me	H	*p*-$MeOC_6H_4$	I	—	—	612	17
Me	H	Br	ClO_4	F	183	566	*112*
Me	H	NH_2	OTs	F	—	530–580	*112*
Me	Me	H	Acetate	A	173	560	*496*
Me	Me	H	*p*-NH_2salicylate	—	246	—	347, 348
Me	Me	H	ClO_4	A	234	—	*496*
Me	Me	H	1,3-diCN-1,3-diCOOEt-propene	—	170	558	497
Me	Me	H	I	A, C	247	550–556	1(p. 101, 110, 129), 17, 387, 482, 484, *485*, *486*, *496*, *498*, *499*
Me	Me	H	I	E, F	268	—	*495*
Me	Me	H	3-Indoleacetate	—	218	—	347, 349
Me	Me	H	Resorcylate	—	243	—	346, 347, 349
Me	Me	H	1,2,3,4-tetra-CN-butadieme	—	251	558	500
Me	Me	COOH	—	F	219	554–574	*222*
Me	Me	COOEt	I	A	—	—	*501*

Me	Me	NO_2	I	—	—	638	17
Me	Ph	H	I	A, F	187	560	1(p. 100), *43*, *484*, *486*, *502*
Me	Ph	H	I	—	—	585	383, 429
Me	Ph	Ph	I	—	177	591	503
Me	Ph	p-MeC_6H_4S–	I	F	224	585	1(p. 104), *111*, 351
Me	p-PhC_6H_4	p-Ph–C_6H_4	SO_4Me	A	229	602	*481*
Me	p-BrC_6H_4	H	I	A	240	—	1(p. 101), *502*
Me	p-$NO_2C_6H_4$	H	I	—	191	—	1(p. 101), *502*
Me	p-$MeOC_6H_4$	H	I	—	183	—	1(p. 101), *502*
Me	p-$MeOC_6H_4$	OPh	ClO_4	F	240	580	1(p. 105), *111*, *351*
Me	p-$EtOC_6H_4$	H	I	A	172	—	1(p. 101), 502
Me	β-Naphthyl	β-Naphthyl	SO_4Me	A	—	586	*481*
Me	2-Pyrrolyl	H	I	A	—	—	*358*
Me	α-Furyl	H	I	—	—	—	385
Me	α-Furyl	COOEt	I	A	—	—	*468*, *493*
Me	α-Thienyl	H	I	—	—	—	385
Me	NH_2	H	I	A	221	516	1(p. 101), *358*
Pr	2-Pyrrolyl	H	I	A	—	—	*358*
Allyl	Me	H	Br	E, F	222	—	1(p. 120), *135*
Ph	Me	H	I	A	—	559	*394*, 473
				A	221	561	*16*
Ph	Me	H	ClO_4	—	232	566	504
Ph	Ph	H	I	—	—	570	120
Ph	Ph	H	I	—	—	570	120
Ph	p-PhC_6H_4	H	Cl	A	233	570	*490*
p-PhC_6H_4	Me	H	ClO_4	A	172	564	*16*
p-ClC_6H_4	Me	H	Cl	A	—	560	*394*, 473
p-$CH_3OC_6H_4$	Me	H	ClO_4	—	238	565	504
p-$Me_2NC_6H_4$	Me	H	ClO_4	—	247	568	504
α-Naphthyl	Me	H	ClO_4	—	258	569	504
α-Pyridyl	Me	Me	ClO_4	—	—	—	116
2-Thiazolyl	Me	Me	ClO_4	—	—	—	116
2-Benzothiazolyl	Me	Me	ClO_4	—	—	—	116

TABLE 2121C



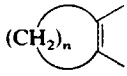
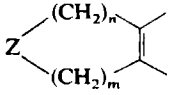
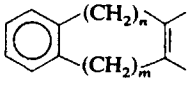
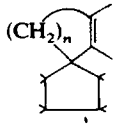
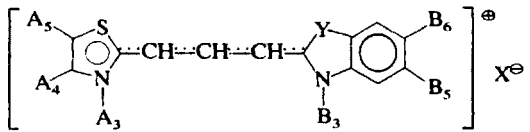
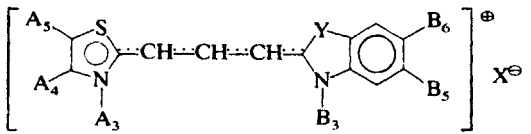
H				A_3	X	Method	m.p. (°C)	λ(nm)	Ref.
	n								
	3			Et	I	A	258	580	*399*
	4			Et	I	A	—	568	*478*
						A	216	570	*16, 87*
	4 (4-*i*-Pr7-Me)			Me	ClO_4	A	238	572	*401*
	5			Et	I	C	208	566	*402*
	5			Et	SO_4Et	A	—	564	*478*
	z	*n*	*m*						
	0	1	2	Me	I	A	>300	—	*406*
	0	1	2	Et	I	C	—	570	*87*
	0	3	0	Et	I	—	170	580	*407*
	NMe_2	3	1	Me	3I	—	230	575	505
	S	0	3	Et	ClO_4	F	215	575	87, *409*
	S	1	2	Me	I	A	192	566	*408*
	S	1	2	Et	I	—	—	570	*87*
		n	*m*						
	0	1	Et	I	F	—	637	*352*	
	0	2	Et	I	—	247	635	114	
	1	0	Me	ClO_4	A	>300	560	32, *352*	
	2	0	Me	I	A	244	586	*405*	
	2	0	Et	I	A	244	586	*405*	
	2	0	Et	I	—	213	594	114	
	n								
	2		Et	I	C	178	580	*403*	
	3		Me	I	A	193	570	*404*	

TABLE 2122A. UMSYMMETRICAL UNSUBSTITUTED TRIMETHINE CYANINES



Y	A_3	A_4	A_5	B_3	B_5	B_6	X	Method	m.p. (°C)	λ(nm)	Ref.
MeCMe	Me	H	*p*-[5-(2,3-diMe-thiazolium]C_6H_4	Me	H	H	$2ClO_4$	—	205	562	506
MeCMe	Me	H	*p*-[4-(2,3-diMe-thiazolium]C_6H_4	Me	H	H	$2ClO_4$	—	220	538	506
MeCMe	Me	NH_2	H	Me	H	H	I	F	244	528	1(p. 136), 386
MeCMe	Et	Me	H	Me	H	H	I	—	—	516	79
MeCMe	Et	Ph	H	$(CH_2)_2COO^-$	H	H	—	—	—	—	507
MeCMe	Ph	H	H	Me	H	H	ClO_4	—	—	—	338
MeCMe	Ph	Me	H	Me	H	H	ClO_4	—	—	534	121, 339
MeCMe	*p*-[3-(2,4-diMe-thiazolium)]C_6H_4	Me	H	Me	H	H	$2ClO_4$	—	181	540	506
MeCMe	2-Thiazolyl	Me	Me	Me	H	H	ClO_4	—	—	—	116
MeCMe	2-Benzothiazolyl	Me		Me	H	H	ClO_4	—	—	—	116
NEt	Me	H	H	$C_3H_6SO_3$	CF_3	CN	—	E	—	471	*508*
NEt	Me	H	H	$C_3H_6SO_3$	CF_3	Br	—	E	—	471	*509*
NEt	Me	H	H	$C_3H_6SO_3$	CF_3	Cl	—	E	—	471	*509*
NEt	Et	H	H	$C_3H_6SO_3$	CF_3	H	—	E	—		*508*
NEt	Et	H	H	$C_3H_6SO_3$	CF_3	Br	—	E	—	474	*508, 509*
NEt	Et	H	H	$C_3H_6SO_3$	CF_3	Cl	—	E	—	473	*508, 509*
O	Me	Me	H	Et	OCH_2COOH	H	OTs	—	—	—	510
O	Me	Ph	H	Me	H	H	I	—	—	520	429
O	Me	Ph	Ph	Me	H	H	I	—	—	525	429
O	Me	NH_2	H	Me	H	H	I	F	240	500	1(p. 129), 386

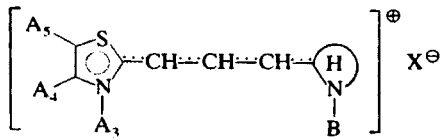
TABLE 2122A (*Continued*)



Y	A_3	A_4	A_5	B_3	B_5	B_6	X	Method	m.p. (°C)	λ(nm)	Ref.
O	Et	H	H	Et	Ph	H	I	—	—	—	511
O	Et	Me	H	Et	OH	H	I	F	253	—	*512*
O	Et	Me	H	Et	H	H	I	—	—	508	79
O	Et	Me	H	Et	OCOMe	H	I	F	217	—	*512*
O	Et	NH_2	H	Et	H	H	I	F	246	504	*386*
O	Lauryl	Me	H	Benzyl	H	H	Br	—	—	—	438
O	Benzyl	Me	H	Me	H	Cl	I	E	262	—	368
O	*p*-HOCO-benzyl	Me	H	*p*-HOCO-benzyl	H	H	Br	—	—	—	368
O	$(CH_2)_3SO_2NH_2$	Me	H	Et	H	H	—	F	—	517	*513*
O	$CH_2CONHSO_2Me$	Me	H	Benzyl	H	H	I	F	—	514	*513*
O	$CH_2COOCH_2SO_3$	Me	H	Et	H	H	—	F	—	518	*514*
S	Me	H	CH_2OH	Et	OMe	ClO_4	—		176	567	*379*
S	Me	Me	H	Et	H	H	I	F	255	560	1(p. 129), 70, *135*
S	Me	Me	H	Et	H	Me	I	—	—	560	70
S	Me	CH_2OH	H	Et	OMe	H	ClO_4	—	167	560	*379*
S	Me	Ph	H	Me	H	H	I	—	540 560	—	80, 85, 429
S	Me	Ph	Ph	Me	H	H	I	—	—	580	429
S	Me	*p*-BrPh	H	Me	H	H	I	F	215	554	*515*
S	Et	Me	H	Et	H	H	I	—	—	550	79
S	Et	Me	H	Ph	H	H	—	—	246	538	504
S	Et	Ph	*p*-$MeSC_6H_4$	Et	H	H	I	F	195	560	1(p. 131), *111*
S	Et	α-Naphthyl	H	Et	H	H	ClO_4	—	—	562	504

S	Et	β-Naphthyl	*p*-$MeSC_6H_4$	Et	H	H	ClO_4	F	205	565	1(p. 131), *111*
S	Et	Tropyl	H	Et	H	H	ClO_4	F	221	555	*516*
S	Et	Tropyl	H	Et	Me	H	ClO_4	F	218	560	*516*
S	Et	Tropyl	H	Et	OMe	H	ClO_4	F	225	564	*516*
S	Et	α-Furyl	H	Et	H	H	I	F	—	—	*468*
S	Et	α-Benzo(*b*)furyl	H	Et	H	H	I	F	—	—	*468, 471*
S	*n*-Bu	Me	H	Et	H	H	I	F	188	—	1(p. 129), *135*
S	*i*-amyl	Me	H	Et	H	H	I	F	207	—	1(p. 129), *135*
S	Ph	Me	H	Et	H	H	I	—	—	566	121
S	α-Naphthyl	Me	H	Et	H	H	ClO_4	—	230	558	504
S	2-Benzothiazole	H	H	Et	H	H	I	—	—	—	395
S	6-(2-Me-Benzo-thiazole)	Me	H	Et	H	H	I	F	190	—	*118*
Se	Et	Tropyl	H	Et	H	H	ClO_4	F	208	558	55
Se	Et	Tropyl	H	Et	OMe	H	ClO_4	F	206	567	*516*
Se	Et	α-Benzo(*b*)furyl	H	Et	H	H	I	F	—	—	*516*
Se	Et	Me	H	Et	H	H	I	F	—	554	79

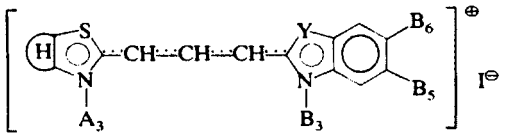
TABLE 2122B



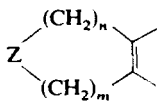
H	A_3	A_4	A_5	B	X	Method	m.p. (°C)	λ(nm)	Ref.
2-Pyrrolidinyl	Et	Me	Ph	Et	ClO_4	G	—	—	*517*
2-Pyrrolidinyl	Et	Ph	Ph	Et	ClO_4	G	186	—	*517*
2-(3-Me-pyrrolidinyl)	Me	2-thienyl	H	Me	ClO_4	E	158	—	*518*
2-(1-Et-pyridyl)	Et	Me	H	Et	I	—	—	557	55
3-(1-Isoindolenyl)	Me	Ph	Ph	Ph	ClO_4	—	—	450	519
2-Quinolyl	Me	Me	H	Et	I	F	280	580	1(p. 128), 70, *485*, 520
2-Quinolyl	Me	Ph	H	Me	I	—	—	600	80, 82
2-Quinolyl	Me	*p*-BrC_6H_4	H	Me	I	F	218	590	*515*
2-Quinolyl	Et	Me	H	Et	I	—	—	583	79
	Et	Me	H	Et	ClO_4	K	263	—	*521*
2-Quinolyl	Et	α-Benzo(*b*)furyl	H	Et	I	F	—	—	*468*, *469*
2-Quinolyl	Allyl	Me	H	Et	I	F	220	—	1(p. 128), *135*
2-Quinolyl	Ph	Me	H	Et	I	—	—	589	121
4-Quinolyl	Me	Me	H	Et	I	—	—	635	70
4-Quinolyl	Me	Me	COO^-	Et	—	F	196	610–648	*222*
4-Quinolyl	Me	Ph	H	Me	I	—	—	640	429
4-Quinolyl	Et	Me	H	Et	I	—	—	645	79
4-(2-Me-quinolyl)	Me	Ph	Ph	Me	I	—	—	699	429
4-(6-MeS-quinolyl)	Me	Me	Me	Me	I	F	—	690	*522*, *523*
4-(6-MeS-quinolyl)	Me	Me	COOEt	Me	I	—	—	695	*522*, *523*
4-(6-MeS-quinolyl)	Me	Me	Ph	Me	I	—	—	705	*522*, *523*
4-(6-MeS-quinolyl)	Me	Ph	Ph	Me	I	F	—	700	*522*, *523*
4-(6-MeS-quinolyl)	Me	Ph	Ph	Allyl	I	F	—	705	*522*, *523*
4-(6-MeS-quinolyl)	Me	Ph	Ph	$(CH_2)_3SO_3^-$	—	F	—	700	*522*, *523*

4-(6-MeS-quinolyl)	Et	Ph	H	Me	I	F	—	695	*522, 523*
9-(10-Et-acridyl)	Me	H	Me	Et	I	—	248	—	524
2-(4,4-di-Me-oxazolinyl)	Et	H	H	Me	ClO_4	F	—	419	*525*
2-(4,4-di-Me-oxazolinyl)	Et	Ph	Ph	Me	ClO_4	F	—	490	*525, 526*
2-Oxazolyl	Et	H	H	Me	ClO_4	F	—	417	*525*
2-(4,4,6-triMe-4,5-didydro-1,3-oxazinyl)	Et	H	H	Me	ClO_4	F	—	423	*525*
2-(6-Ph-1,3-oxazinyl)	Me	Ph	Ph	Me	ClO_4	F	—	496	*525*
2-(6-Ph-1,3-oxazinyl)	Et	H	H	Me	ClO_4	F	—	424	*525*
3-(1,2-Benzisoxzolyl)	Me	Me	H	Et	I	E	255	507	*527*
3-(1,2-benzisoxzolyl)	Benzyl	H	H	$(CH_2)_3SO_3$	—	E	302	515	*527*
2-Tetrahydrobenzoxazolyl	Et	Me	H	Et	I	F	244	518	1(p. 129), *528*
2-(5,6-Tetramethylene benzoxazolyl)	Benzyl	H	H	Et	I	—	206	525	529
2-(6,7-Tetramethylene benzoxzolyl)	Benzyl	Me	H	Me	I	—	197	522	529
2-Thiazolinyl	Et	Me	H	Et	I	—	—	493	79
2-(4-Me-thiazolyl)	Me	Me	COO^-	Et	—	F	183	564	*222*
2-(4-Me-thiazolyl)	Allyl	Me	H	Me	Br	F	219	—	*135*
2-(4-Ph-thiazolyl)	Me	Ph	Ph	Me	I	—	—	575	224
α-Naphthothiazole	Me	Ph	H	Me	I	—	—	568	224
α-Naphthothiazole	Me	Ph	Ph	Me	I	—	—	590	224
α-Naphthothiazole	Et	Benzo(*b*)furyl	H	Et	I	F	—	—	*468*
β-Naphthothiazole	Me	H	CH_2OH	Et	ClO_4	—	241	571	*379*
β-Naphthothiazole	Me	Me	H	Et	I	—	—	570	70
β-Naphthothiazole	Me	CH_2OH	H	Et	ClO_4	—	236	568	*379*
β-Naphthothiazole	Me	Ph	H	Me	I	—	—	568	429
β-Naphthothiazole	Me	Ph	Ph	Me	I	—	—	590	429
β-Naphthothiazole	Et	Me	H	Et	I	—	—	569	111
β-Naphthothiazole	Et	Tropyl	H	Et	ClO_4	F	235	574	*516*
β-Naphthothiazole	Et	α-Furyl	H	Et	I	F	—	—	*468*
β-Naphthothiazole	Et	α-Benzo(*b*)furyl	H	Et	I	F	—	—	*471*
β-Naphthoselenazole	Et	α-Furyl	H	Et	I	F	—	—	*468*
4-[(5,6-*b*)(3′-Et-2′-Me-thiazolo)quinolyl]	Et	Ph	Ph	Et	I	—	—	655	*464*

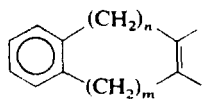
TABLE 2122C



H			Y	A_3	B_3	B_5	B_6	Method	m.p. (°C)	λ(nm)	Ref.
	n										
	3		MeCMe	Me	Me	H	H	G	236	524	*399*
	3		O	Me	Me	H	H	F	272	516	*399*
	3		O	Me	Me	Me	Me	F	283	530	*399*
	3		O	Me	Me	Ph	H	F	259	520	*399*
	3		O	Me	Me	Cl	H	F	280	516	*399*
$(CH_2)_n$	3		O	Et	Et	H	H	F	249	516	*399*
	4		O	Et	Et	H	H	—	—	512	87
	4		S	Et	Me	H	H	F	—	555	*399*
	4		O	Et	Et	H	H	F	235	517	*401*
	(4-*i*-Pr, 7-Me)										
	5		O	Et	Et	H	H	F	236	516	*402*
	n										
$(CH_2)_n$	2		O	Me	Et	H	H	F	190	526	*403*
	3		O	Et	Et	H	H	F	266	516	*404*
z	*n*	*m*									
0	1	2	MeCMe	Et	Et	H	H	G	165	526	*406*
0	1	2	O	Me	Me	H	H	F	274	—	*406*

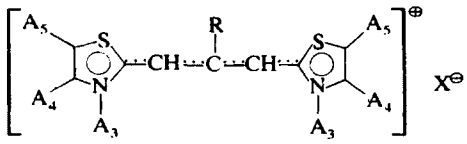


0	1	2	O	Et	Et	H	H	F	275	516	87, *406*
0	1	2	O	Et	Et	Me	Me	F	263	526	*406*
0	1	2	O	Et	Et	Ph	H	F	274	524	*406*
0	1	2	O	Et	Et	Cl	H	F	292	516	*406*
0	1	2	O	Benzyl	Benzyl	H	H	F	277	518	*406*
0	3	0	O	Et	Et	H	H	F	232	528	*407*
0	3	0	O	Et	Et	Cl	H	F			*407*
S	0	3	O	Et	Et	H	H	F	246	530	87, *409*
S	1	2	O	Me	Me	H	H	F	240	516	408
S	1	2	O	Et	Et	H	H	—	—	520	87
S	1	2	O	Et	Et	H	H	F	196	518	408



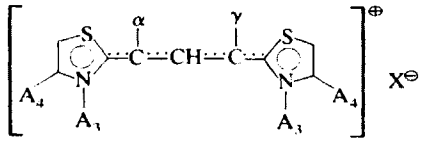
n	*m*									
0	1	O	Et	Et	H	H	F	212	558	*352*
2	0	MeCMe	Et	Et	H	H	G	195	546	*405*
2	0	O	Et	Et	H	H	F	224	530	*405*

TABLE 2123A. SYMMETRICAL SUBSTITUTED TRIMETHINE CYANINES



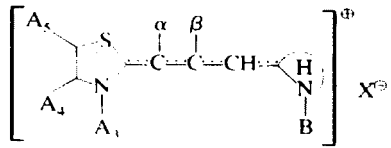
R	A_3	A_4	A_5	X	Method	m.p. (°C)	λ(nm)	Ref.
Me	Me	Ph	H	I	B	—	—	1(p. 167), *484*, *486*, 530
Me	Et	H	H	I	B	174	553	*445*
Me	Et	H	Me	I	B	—	526	*110*
Me	Et	H	Ph	I	B	—	566	*110*
Me	Et	H	*p*-$MeOC_6H_4$	I	—	245	600	*388*
Me	Et	H	3,4-di$MeOC_6H_3$	I	—	—	578	531
Me	Et	H	β-Naphthyl	I	B	218	585	*481*
Me	Et	H	α-Benzofuryl	ClO_4	—	226	—	*354*
Me	Et	Me	H	I	B	—	526	*110*
Me	Et	Me	Me	I	B	—	536	*110*
Me	Et	Ph	H	I	B	—	530	*110*
Me	Et	Ph	Ph	OTs	B	240	—	*532*
Me	Et	Ph	Ph	I	B	253	560	*388*, *481*, *489*
Me	Et	Ph	Ph	ClO_4	B	—	562	*110*
Me	Et	*p*-$MeOC_6H_4$	Ph	I	—	249	561	111
Me	Et	5-Acenaphthyl	H	ClO_4	B	200	533	*490*
Me	Et	α-Furyl	H	I	—	188	—	*354*, 468
Me	Et	α-Thienyl	H	I	B	—	—	*470*, 494
Me	Et	α-Benzofuryl	H	ClO_4	—	218	—	*354*
Me	Ph	Me	H	I	B	—	548	*394*, 473
Et	Me	Ph	H	I	B	—	—	1(p. 167), *484*, *486*, 530
Et	Et	H	Me	I	B	—	530	*110*
Et	Et	H	Ph	I	B	—	570	*110*
Et	Et	H	*p*-$MeOC_6H_4$	ClO_4	—	221	600	*388*
Et	Et	H	3-ME, 4-$MeOC_6H_3$	I	B	—	583	*533*
Et	Et	H	3,4-di$MeOC_6H_3$	I	B	—	578	531, *533*
							583	531
Et	Et	H	α-Naphthyl	I	B	156	558	*445*
Et	Et	H	β-Naphthyl	I	B	231	585	*481*
Et	Et	H	5-Acenaphthyl	I	B	185	565	*481*
Et	Et	Me	H	I	B	—	530	1(p. 167), *110*, *484* *486*
Et	Et	Me	4-Thiazolyl	I	B	240	570	*356*
Et	Et	Ph	H	I	B	—	534	*110*
Et	Et	Ph	Ph	I	B	—	564	*110*
					B	261	567	*489*
Et	Et	*p*-PhC_6H_4	*p*-PhC_6H_4	OTs	B	233	580	*481*
Et	Et	α-Furyl	H	I	B	—	—	*354*
Et	Et	α-Furyl	H	ClO_4	—	182	—	*354*
Et	Et	α-Thienyl	H	I	B	—	—	*470*

TABLE 2123B



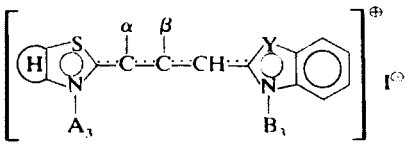
α	γ	A_3	A_4	X	Method	m.p. (°C)	λ(nm)	Ref.
CN	CN	Ph	Ph	Br	—	275	503	*120*
CN	CN	*p*-MeC_6H_4	Ph	Br	—	300	503	*120*
COMe	H	Me	Me	I	L	210	470	*71*
COMe	COMe	Me	Me	I	L	227	470	*71*
COPh	H	Me	Me	I	L	199	480	*71*
COPh	COPh	Me	Me	I	L	280	445-465	*71*

TABLE 2124A. UNSYMMETRICAL SUBSTITUTED TRIMETHINE CYANINES



H	α	β	A_3	A_4	A_5	B	X	Method	m.p. (°C)	λ(nm)	Ref.
3,3-di Me Indolenyl	CN	H	Ph	Ph	H	Me	Br	—	261	529	*120*
3,3-di Me Indolenyl	COMe	H	Ph	Me	Me	Me	I	—	256	442	*120*
3,3-di Me Indolenyl	COMe	H	Ph	Ph	H	Me	Br	—	277	446	*120*
3,3-di Me Indolenyl	COOEt	H	Ph	Ph	H	Me	I	—	210	490	*120*
2-quinolyl	PhNHCH=	H	Et	Me	H	Et	$2ClO_4$	—	264	—	521, *534*
2-quinolyl	COMe	H	Me	Me	H	Et	I	L	245	500	*70, 71*
4-quinolyl	PhNHCH=	H	Et	Me	H	Et	$2ClO_4$				521, *534*
4-quinolyl	COMe	H	Me	Me	H	Et	I	L	190	550	*70, 71*
2-thiazolinyl	PhNHCH=	H	Et	Me	H	Et	I				*354*
2-benzothiazolyl	H	SEt	Me	H	H	Me	I	I	—	—	*535*
2-benzothiazolyl	COMe	H	Me	Me	Me	Et	I	L	251	465–470	*70-71*
2-benzothiazolyl	COMe	H	Ph	Me	H	Et	I	—	205	458	*120*
2-benzothiazolyl	COMe	H	Ph	Ph	H	Et	I	—	249	460	*120*
2-benzothiazolyl	COOEt	H	Ph	Ph	H	Et	I	—	Oil	520	*120*
2-(5-Me benzothiazolyl)	H	Me	Et	1-Azulenyl	H	Et	ClO_4	H	210	544	*516*
2-(5-Me benzothiazolyl)	H	Et	Et	1-Azulenyl	H	Et	ClO_4	H	209	552	*516*
2-(6-Me Benzothiazolyl)	COMe	H	Me	Me	H	Et	I	L	253	470–490	*70*
2-(5,6diMe benzothiazolyl)	H	Me	Et	COOEt	Me	Et	ClO_4	—	—	555	536
2-(5,6diMe benzothiazolyl)	H	Et	Et	COOEt	Me	Et	ClO_4	—	—	560	536
2-[6(5',6'diMeOC_6H_3) benzothiazolyl]	H	Et	Et	H	5,6-di$MeOC_6H_3$	Et	I	—	—	—	531
β-naphthothiazolyl	H	Ph	Et	Ph	Ph	Et	ClO_4	—	—	590	536
β-naphthothiazolyl	COMe	H	Me	Me	H	Et	I	L	257	490–500	*70–71*

TABLE 2124B



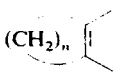
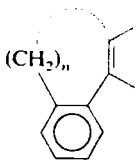
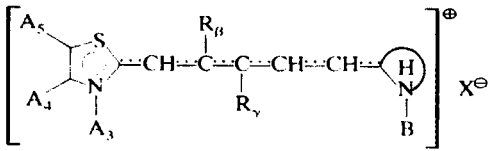
H	n	Y	α	β	A_3	B_3	Method	m.p. (°C)	λ(nm)	Ref.
	4	MeCMe	Me	H	Me	Me	G	—	515	*400*
	3	S	H	Me	Et	Et	H	275	540	*399*
	4	S	H	Me	Me	Et	H	238	540	*401*
	(4-*i*-Pr, 7-Me)									
	1	S	H	Me	Et	Et	H	265	540	*537*
	2	S	H	Me	Et	Et	H	250	550	*405*

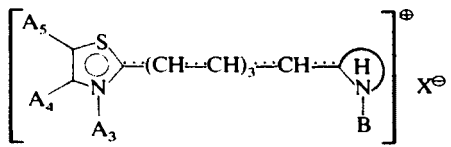
TABLE 213. PENTAMETHINE CYANINES



H	A_3	A_4	A_5	R_β	R_γ	B	X	Method	m.p.(°C)	λ(nm)	Ref.
2-quinolyl	Me	Me	COOEt	H	H	Et	I	B	—	—	1(p. 211), *538*, *539*, 540, 541
2-quinolyl	Me	Ph	H	H	H	Me	I	—	—	700	80, 82
2-quinolyl	Me	*p*-BrC_6H_4	H	H	H	Me	I	B	233	695	80, *515*
4-quinolyl	Me	Me	Me	H	H	Me	I	B	—	—	1(p. 211), *538*, *539*
2-thiazolyl	Me	H	H	H	H	Me	I	A	215	—	1(p. 213), *542*, *543*
2-(4-Me thiazolyl)	Me	Me	H	H	H	Me	I	A	227	—	*495*
								E	241	—	*544*
2-(4-Me thiazolyl)	Et	Me	H	H	H	Et	I	C, D	194	637	*222*, 666, 667
2-(4-Me thiazolyl)	Et	Me	H	H	Br	Et	I	—	—	537	109
2-(4-Me thiazolyl)	Ph	Me	H	H	H	Ph	I	—	—	657	504
2-(4-Me 5-COO thiazolyl)	Me	Me	COO^-	H	H	Me	—	B	199	664	*222*
2-(5-Ph thiazolyl)	Me	Ph	H	H	H	Me	I	—	—	660	*429*
2-(4,5diPh thiazolyl)	Me	Ph	Ph	H	H	Me	I	D	250	—	*545*, 546
2-(4,5diPh thiazolyl)	Et	Ph	Ph	H	H	Et	I	D	196	663	109, *433*, 667
2-(4,5diPh thiazolyl)	Et	Ph	Ph	OMe	H	Et	I	—	—	—	547
2-[4,5-$(CH_2)_3$-N(COOEt)-CH_2-]	Et	$-(CH_2)_3-N(COOEt)-CH_2-$		H	Br	Et	I	—	162	635	505

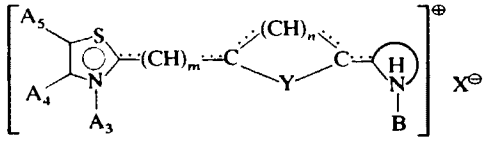
2-(4-α-furyl thiazolyl)	Et	α-Furyl	H	H	Cl	Et	I	A	—	—	*468*
3-benzisoxazolyl	Me	Me	H	H	H	Et	I	B	197	600	*527*
2-benzoxazolyl	Et	$-(CH_2)_3-$		H	H	Et	I	B	216	610	*399*
2-Benzothiazolyl	Me	Ph	H	H	H	Me	I	—	—	640	80, 82
2-Benzothiazolyl	Me	p-BrC_6H_4	H	H	H	Me	I			640	116, 120
								B	224	652	*515*
2-Benzothiazolyl	Me	p-$EtOC_6H_4$	H	H	H	Me	I	—	—	640	116, 120
2-Benzothiazolyl	Et	H	Ph	H	H	Et	ClO_4	—	225	—	548
2(5,6-diMe-benzothiazolyl)	Me	Ph	H	H	Me	Et	I	B	—	665	1(p. 212), 538 539
2-(5,6-diMeO-benzo-thiazolyl)	Me	Me	H	H	H	Et	I	B	—	—	1(p. 212), *538* 539
2-5,6-diMeO-benzo-thiazolyl)	Et	Me	H	H	H	Et	I	B	—	665	*538*
2-(5,6-diEtO-benzo-thiazolyl)	Me	Me	H	H	H	Et	I	—	—	—	1(p. 212), *538* 539
2-(5,6-diEtO-benzo-thiazolyl)	Et	Me	H	H	H	Et	I	B	—	675	*538*
2-Benzoselenazolyl	Et	Me	H	H	H	Et	I	B	—	660	1(p. 212), *538*, 539, *540*, 541
2-(5-MeO-Benzoselenazolyl)	Et	Ph	H	H	H	Et	I	B	—	665	*540*, 541
2-(5-EtO-Benzoselenazolyl)	Me	Me	H	H	H	Et	I	B	—	650	*540*
2-(5-EtO-Benzoselenazolyl)	Et	Me	H	H	Me	Et	I	B	—	655	*540*, 541
α-Naphthothiazolyl	Me	Me	COOEt	H	H	Et	I	B	—	—	*540*, 541
α-Naphthothiazolyl	Et	Me	COOEt	H	H	Et	I	B	—	675	*538*
β-Naphthothiazolyl	Et	$-(CH_2)_2$-O-CH_2-		H	H	Et	I	B	205	675	*406*

TABLE 214. HEPTAMETHINE CYANINES



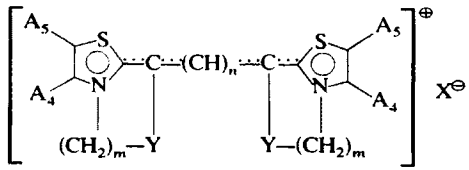
H	A_3	A_4	A_5	B	X	Method	m.p. (°C)	λ(nm)	Ref.
2-Quinolyl	Me	Ph	H	Me	I	—	—	790	80, 82
2-Quinolyl	Me	*p*-BrC_6H_4	H	Me	I	C	161	785	80, 82, 515
2-Thiazolyl	Me	H	H	Me	I	A, B	174	—	1(p. 258), *493*, 498, *542*, 543, 549, 550
2-(4-Me-thiazolyl)	Me	Me	H	Me	I	B	155	—	*365*
						A, B	174	—	1(p. 258), *493*, 498, *542*, 543, 549, 550
2-(4-Ph-thiazolyl)	Et	Ph	Ph	Et	I	—	—	760	26
2-(4-α-Furylthiazolyl)	Et	α-Furyl	H	Et	OTs	B	—	—	*468*
2-(4-α-Benzo(*b*)furylthiazolyl)	Et	α-Benzo(*b*)-furyl	H	Et	OTs	B	—	—	*468*, *471*
2-Benzothiazolyl	Me	Ph	H	Me	I	—	—	740	80, 82
2-Benzothiazolyl	Me	*p*-BrC_6H_4	H	Me	I	C	202	758	515
2-Benzothiazolyl	Me	*p*-$EtOC_6H_4$	H	Me	I	—	—	740	80, 82
2-(5,6-diMe-benzothiazolyl)	Et	Me	H	Et	I	B, C	—	—	1(p. 253), *551–553*
2-(5-Et_2N-benzothiazolyl)	Et	Me	H	Et	ClO_4	B	—	—	1(p. 253), *551–553*
2-Benzoselenazolyl	Et	Me	H	Et	I	—	—	—	1(p. 253), *551–553*
2-(5-MeO-benzoselenazolyl)	Me	Ph	H	Et	—	C	—	—	*553*

TABLE 2151. CHAIN-BRIDGED CYANINES



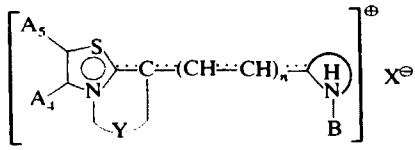
H	Y	m	n	A_3	A_4	A_5	B	X	Method	m.p. (°C)	λ(nm)	Ref.
2-(4-Me-thiazolyl)	$(CH_2)_2$	0	1	Et	Me	H	Et	OTs	A	—	595	1(p. 272), *122*
2-(4-styryl-5-Ph-thiazolyl)	$(CH_2)_2$	0	1	Me	Styryl	Ph	Me	I	A, B, C,	124	612	*503*
2-(4-Ph-thiazolyl)	$(CH_2)_2$	0	1	Et	Ph	H	Et	OTs	A	—	596	1(p. 272), *122*
2-(4-Ph-thiazolyl)	$(CH_2)_2$	0	1	*n*-Pr	Ph	H	*n*-Pr	OTs	A	—	600	1(p. 272), *122*
2-(4-Ph-thiazolyl)	$(CH_2)_2$	0	1	*n*-Bu	Ph	H	*n*-Bu	OTs	B	—	600	1(p. 272), *122*
2-(4,5-diPh-thiazolyl)	$(CH_2)_2$	0	1	Me	Ph	Ph	Me	I	A, B, C,	206	611	*503*
2-(4,5-diPh-thiazolyl)	$(CH_2)_2$	0	1	Et	Ph	Ph	Et	I	A, B, C,	199	623	*503*
2-Benzothiazolyl	CH_2	0	1	Me	Ph	Ph	Me	ClO_4	—	201	556	*554*
2-Benzothiazolyl	$(CH_2)_2$	0	1	Me	Ph	Ph	Me	ClO_4	—	230	596	*554*
2-Benzothiazolyl	O	1	2	Et	H	Ph	Et	I	—	240	—	548

TABLE 2152A. N CHAIN-BRIDGED CYANINES



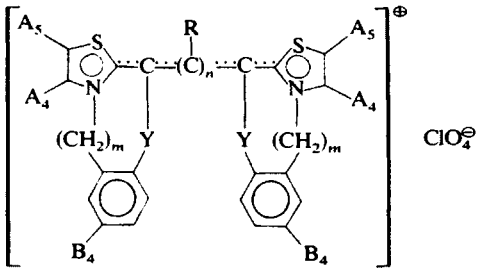
n	Y	m	A_4	A_5	X	m.p. (°C)	λ(nm)	Ref.
1	—	2	Me	H	ClO_4	265	566	*555*
1	—	2	Ph	H	ClO_4	215	573	*555*
1	—	2	Ph	Ph	I	262	608	*555*
1	—	3	Ph	Ph	ClO_4	262	615	*555*
1	—	4	Ph	Ph	ClO_4	232	609	*555*
1	O	2	Me	H	Br	244	630	411
1	O	2	Ph	H	ClO_4	189	638	411
1	S	2	Me	H	ClO_4	249	622	411
1	S	2	Ph	H	Br	249	630	411
3	—	3	Ph	Ph	ClO_4	233	707	*555*
3	O	2	Ph	H	ClO_4	192	730	411
3	S	2	Ph	H	ClO_4	249	722	411

TABLE 2152B



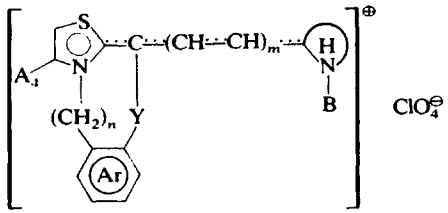
H	n	Y	A_4	A_5	B	X	m.p. (°C)	λ(nm)	Ref.
2-(3,3-diMe-indolenyl)	1	$(CH_2)_2$	Ph	Ph	Me	I	207	540	410
2-(3,3-diMe-indolenyl)	1	$(CH_2)_3$	Ph	Ph	Me	ClO_4	256	548	410
2-(3,3-diMe-indolenyl)	1	(CH_2)–O–	Ph	H	Me	ClO_4	235	554	411
2-(3,3-diMe-indolenyl)	1	(Ch_2)–S–	Ph	H	Me	ClO_4	250	564	411
2-Quinolyl	1	$(CH_2)_2$	Ph	Ph	Et	I	292	606	410
2-Quinolyl	1	$(CH_2)_3$	Ph	Ph	Et	I	301	610	410
2-Quinolyl	1	(CH_2)–O–	Me	H	Et	ClO_4	245	617	411
2-Quinolyl	1	(CH_2)–S–	Me	H	Et	ClO_4	246	610	411
2-(6-Me-quinolyl)	0	$(CH_2)_2$	Ph	Ph	Et	I	261	521	*555*
2-(6-Me-quinolyl)	0	$(CH_2)_3$	Ph	Ph	Et	I	227	572	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_2$	Me	H	Et	I	229	506	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_2$	Ph	Ph	Et	I	242	539	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_3$	Me	H	Et	I	—	542	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_3$	Ph	H	Et	I	154	549	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_3$	Ph	Ph	Et	I	221	578	*555*
2-(6-OMe-quinolyl)	0	$(CH_2)_4$	Ph	Ph	Et	I	—	596	*555*
2-(4-Me-thiazolyl)	1	CH=C(Ph)–	Me	H	Y	ClO_4	194	597	40
2-Benzoxazolyl	1	$(CH_2)_2$	Ph	Ph	Me	I	279	525	410
2-Benzoxazolyl	1	$(CH_2)_3$	Ph	Ph	Me	I	268	535	410
2-Benzothiazolyl	0	$(CH_2)_2$	Ph	Ph	Me	I	289	452	*555*
2-Benzothiazolyl	1	$(CH_2)_2$	Ph	Ph	Et	I	265	563	410
2-Benzothiazolyl	1	$(CH_2)_3$	Ph	Ph	Et	I	280	574	410
2-Benzothiazolyl	1	$(CH_2)_2$–O–	Me	H	Et	ClO_4	237	568	411
2-Benzothiazolyl	1	$(CH_2)_2$–S–	Me	H	Et	ClO_4	228	578	411

TABLE 2152C



n	R	Y	*m*	B_4	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
1	H	—	—	H	Me	H	304	552	*415*
1	H	—	2	H	Me	H	—	580	412
1	H	—	2	H	Ph	H	174	610	412
1	H	CH_2	—	H	Ph	H	229	634	556
1	H	CH_2	1	H	H	H	140	599	412
1	H	CH_2	1	H	Me	H	196	606	412
1	H	CH_2	1	H	Ph	H	146	613	412
1	H	CH_2	1	H	Ph	Me	174	620	412
1	H	CH_2	1	H	Ph	Ph	212	643	412
1	H	CH_2	—	Me	Ph	H	224	637	556
1	H	CH_2	—	OH	Ph	H	257	637	556
1	H	$(CH_2)_2$	—	H	Me	H	—	600	556
1	H	O	—	H	Me	H	234	756	*121*, 413
1	H	S	—	H	Me	H	241	654	121, 413, 414, 557
1	Me	S	—	H	Me	H	132	620	557
1	Et	S	—	H	Me	H	168	620	557
1	H	Se	—	H	Me	H	—	626	413, 414
1	H	$-N(COMe)-CH_2-$	—	H	Me	H	—	586	413, 414
3	H	—	—	H	Me	H	305	668	*415*
3	H	CH_2	—	H	Ph	H	230	733	556
3	H	CH_2	1	H	Me	H	205	680	412
3	H	CH_2	1	H	Ph	H	190	686	412
3	H	O	—	H	Me	H	—	845	412

TABLE 2152D

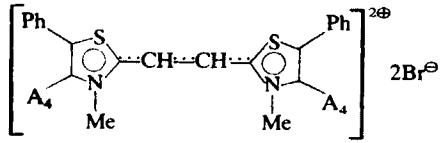


H	Ar	*n*	Y	*m*	A_4	B	m.p.(°C)	λ(nm)	Ref.
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	—	1	Me	Me	252	556	*415*
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	CH_2	1	Ph	Me	205	581	556
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	$(CH_2)_2$	1	Me	Me	—	525	413, 414
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	O	1	Me	Me	265	611	121
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	S	1	Me	Me	197	580	121, 413, 414, 557
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	Se	1	Me	Me	—	576	413, 414
2-(3,3-diMe-indolenyl)	1,2-Benzo	0	$N(AC)CH_2$	1	Me	Me	—	542	200, 201
2-(3,3-diMe-indolenyl)	1,2-Benzo	1	CH_2	1	Me	Me	234	534	412
2-(3,3-diMe-indolenyl)	1,2-Benzo	2	—	1	Me	Me	246	505	412
2-(3,3-diMe-indolenyl)	1,2-Naphtho	0	O	1	H	Me	250	614	121
2-(3,3-diMe-indolenyl)	1,2-Naphtho	0	O	1	Me	Me	—	619	121, 413, 414
2-Quinolyl	1,2-Benzo	0	—	1	Me	Et	298	566	*415*
2-Quinolyl	1,2-Benzo	0	CH_2	1	Ph	Et	209	616	556
2-Quinolyl	1,2-Benzo	0	$(CH_2)_2$	1	Me	Et	—	602	413, 414
2-Quinolyl	1,2-Benzo	0	O	1	Me	Et	—	674	413, 414
2-Quinolyl	1,2-Benzo	0	S	1	Me	Me	205	630	557
2-Quinolyl	1,2-Benzo	0	S	1	Me	Et	—	—	412
2-Quinolyl	1,2-Benzo	0	S	1	Me	Ph	170	645	557
2-Quinolyl	1,2-Benzo	0	$S–CH_2–$	1	Me	Me	214	586	557
2-Quinolyl	1,2-Benzo	0	$S–CH_2—$	1	Me	Ph	193	630	557
2-Quinolyl	1,2-Benzo	0	Se	1	Me	Et	—	614	413, 414
2-Quinolyl	1,2-Benzo	0	Se	2	Me	Et	211	726	413, 414
2-Quinolyl	1,2-Benzo	0	$N(AC)CH_2$	1	Me	Et	—	604	413, 414
2-Quinolyl	1,2-Benzo	0	CH_2	1	Me	Et	243	600	412
2-Quinolyl	1,2-Benzo	0	O	1	H	Et	246	682	121, 413, 414
2-Quinolyl	2,1-Naphtho	0	O	1	Me	Et	—	674	413, 414
2-Quinolyl	2,3-Naphtho	0	S	1	Me	Et	—	—	412
2-(6-OMe-quinolyl)	1,2-Benzo	0	CH_2	0	Ph	Et	297	562	556
2-Thiazolyl	1,2-Benzo	0	$S–CH_2$	1	Me	—	—	582	557
2-(4-Me-thiazolyl)	1,2-Benzo	0	—	1	Me	Ph	205	542	415
2-Benzoxazolyl	1,2-Benzo	0	—	1	Me	Et	>360	515	415
2-Benzoxazolyl	1,2-Benzo	0	O	1	Me	Et	—	644	413, 414
2-Benzoxazolyl	1,2-Benzo	0	Se	1	Me	Et	—	570	413, 414
2-Benzothiazolyl	1,2-Benzo	0	—	0	Me	Et	245	438	415
2-Benzothiazolyl	1,2-Benzo	0	—	1	Me	Et	287	553	415
2-Benzothiazolyl	1,2-Benzo	0	CH_2	0	Ph	Et	218	481	556
2-Benzothiazolyl	1,2-Benzo	0	CH_2	1	Ph	Et	212	596	556
2-Benzothiazolyl	1,2-Benzo	0	$(CH_2)_2$	1	Me	Et	—	560	413, 414
2-Benzothiazolyl	1,2-Benzo	0	O	0	Me	Et	244	502	121
2-Benzothiazolyl	1,2-Benzo	0	O	1	Me	Et	247	644	121, 413, 414

TABLE 2152D (*Continued*)

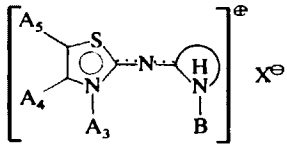
H	Ar	*n*	Y	*m*	A_4	B	m.p. (°C)	λ(nm)	Ref.
2-Benzothiazolyl	1,2-Benzo	0	S	0	Me	Me	200	421	556
2-Benzothiazolyl	1,2-Benzo	0	S	0	Me	Et	—	421	121
2-Benzothiazolyl	1,2-Benzo	0	S	1	Me	Me	85	609	121
2-Benzothiazolyl	1,2-Benzo	0	S	1	Me	Et	—	609	121
2-Benzothiazolyl	1,2-Benzo	0	SCH_2	1	Me	Me	182	549	557
2-Benzothiazolyl	1,2-Benzo	0	Se	1	Me	Et	—	600	413, 414
2-Benzothiazolyl	1,2-Benzo	0	Se	2	Me	Et	192	668	413, 414
2-Benzothiazolyl	1,2-Benzo	0	$N(AC)CH_2$	1	Me	Et	—	565	413, 414
2-Benzothiazolyl	1,2-Benzo	1	CH_2	1	Me	Et	237	556	412
2-Benzothiazolyl	1,2-Benzo	2	—	1	Me	Et	243	565	412
2-Benzothiazolyl	2,1-Naphtho	0	O	1	H	Et	238	648	121
2-Benzothiazolyl	2,1-Naphtho	0	O	1	Me	Et	—	646	413, 414

TABLE 216. BISCATIONIC DYES



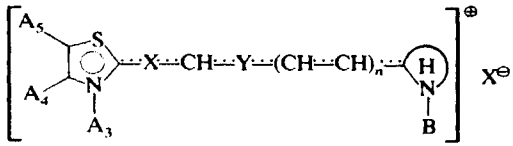
A_4	m.p. (°C)	Ref.
Me	268	*558*
Ph	257	558

TABLE 2171A. MONOAZACYANINES



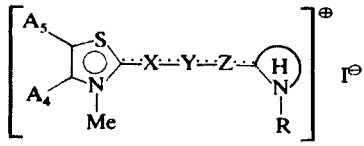
H	A_3	A_4	A_5	B	X	m.p. (°C)	λ(nm)	Ref.
2-Quinolyl	Me	Me	H	Me	I	—	—	*374*(1)
2-Quinolyl	Me	Ph	H	Me	I	247	405	80, 82
2-Quinolyl	Et	H	H	Et	I	239	395	1(p. 385), *559*
2-(4-Me-thiazolyl)	Et	Me	H	Ph	I	190	—	*560*
2-(4-Ph-thiazolyl)	Me	Ph	H	Me	I	187	390	*429*
2-(4,5-diPh-thiazolyl)	Me	Ph	Ph	Me	I	232	400	*429*
2-(4-OH-thiazolyl)	Me	Me	H	Ph	Br	—	—	1(p. 387), *561*
2-(4-OH-thiazolyl)	Me	Ph	Me	Ph	Br	—	—	1(p. 387), *561* *562*
2-Benzothiazolyl	Me	Ph	H	Me	I	168	390	*429*
						246	375	80, 82
2-Benzothiazolyl	Me	Ph	Ph	Me	I	209	410	*429*

TABLE 2171B



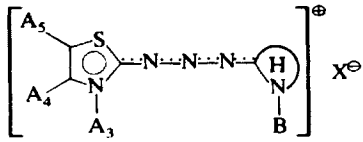
H	X	Y	n	A_3	A_4	A_5	B	m.p. (°C)	λ(nm)	Ref.
2-Pyridyl	N	CH	0	Et	Me	H	Et	161	413	*79*
2-(3,3-diMe-indolenyl)	N	CH	0	Et	Me	H	Me	211	469	*79*
2-Quinolyl	CH	N	0	Et	Me	H	Et	230	460	*79*
2-Quinolyl	N	CH	0	Me	Ph	H	Me	217	520	80, 82
2-Quinolyl	N	CH	0	Et	Me	H	Et	225	500	*79*
2-Quinolyl	N	CH	1	Me	Ph	H	Me	195	590	80, 82
2-Quinolyl	N	CH	1	Me	*p*-BrC_6H_4	H	Me	—	590	80, 82
2-Quinolyl	N	CH	2	Me	Ph	H	Me	210	670	80, 82
2-Quinolyl	N	CH	2	Me	*p*-BrC_6H_4	H	Me	—	670	80, 82
4-Quinolyl	N	CH	0	Me	Ph	H	Me	205	500	*429*
4-Quinolyl	N	CH	0	Et	Me	H	Et	219	534	*79*
4-(2-Me-quinolyl)	N	CH	0	Me	Ph	Ph	Me	215	530	*429*
2-Thiazolinyl	N	CH	0	Et	Me	H	Et	250	427	*79*
2-(4-Me-thiazolyl)	N	CH	0	Et	Me	H	Et	220	449	*79*
2-(4-Ph-thiazolyl)	CH	N	1	Me	Ph	H	Me	230	555	*429*
2-(4-Ph-thiazolyl)	N	CH	0	Me	Ph	H	Me	198	455	*429*
2-(4-Ph-thiazolyl)	N	CH	0	Me	Ph	Ph	Me	215	465	*429*
2-Benzoxazolyl	N	CH	0	Me	Ph	H	Me	225	450	*429*
2-Benzoxazolyl	N	CH	0	Me	Ph	Ph	Me	210	455	*429*
2-Benzoxazolyl	N	CH	0	Et	Me	H	Et	203	439	*79*
2-Benzothiazolyl	CH	N	0	Et	Me	H	Et	257	448	*79*
2-Benzothiazolyl	N	CH	0	Me	Ph	H	Me	240	470	80, 82 *492*
2-Benzothiazolyl	N	CH	0	Me	Ph	Ph	Me	228	485	*429*
2-Benzothiazolyl	N	CH	0	Et	Me	H	Et	252	472	*79*
2-Benzothiazolyl	N	CH	1	Me	Ph	H	Me	160	565	80, 82
2-Benzothiazolyl	N	CH	1	Me	*p*-BrC_6H_4	H	Me	185	570	80, 82
2-Benzothiazolyl	N	CH	1	Me	*p*-$MeOC_6H_4$	H	Me	135	—	80
2-Benzothiazolyl	N	CH	1	Me	*p*-$EtOC_6H_4$	H	Me	175	560	80, 82
2-Benzothiazolyl	N	CH	2	Me	Ph	H	Me	175	655	80, 82
2-Benzothiazolyl	N	CH	2	Me	*p*-$EtOC_6H_4$	H	Me	212	650	80, 82
2-Benzoselenazolyl	N	CH	0	Et	Me	H	Et	263	473	*79*
2-α-Naphthothiazolyl	CH	N	0	Me	Ph	H	Me	205	460	*429*
2-α-Naphthothiazolyl	N	CH	0	Me	Ph	H	Me	248	475	*429*
2-α-Naphthothiazolyl	N	CH	0	Me	Ph	Ph	Me	198	500	*429*
2-β-Naphthothiazolyl	CH	N	0	Me	Ph	H	Me	240	468	*429*
2-β-Naphthothiazolyl	N	CH	0	Me	Ph	H	Me	240	475	*429*
2-β-Napthothiazolyl	N	CH	0	Me	Ph	Ph	Me	200	495	*429*
2-β-Naphthothiazolyl	N	CH	0	Et	Me	H	Et	239	489	*79*

TABLE 2172. DIAZACYANINES



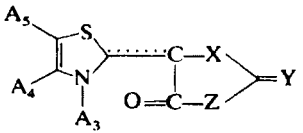
H	R	X	Y	Z	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
2-(4-Ph-thiazolyl)	Me	CH	N	N	Ph	H	235	494	*429*
2-(4-Ph-thiazolyl)	Me	CH	N	N	Ph	Ph	140	495	*429*
2-(4-Ph-thiazolyl)	Me	N	CH	N	Ph	H	200	405	*429*
2-(4-Ph-thiazolyl)	Me	N	CH	N	Ph	Ph	200	408	*429*
2-(4,5-diPh-thiazolyl)	Me	CH	N	N	Ph	H	220	500	*429*
2-(4,5-diPh-thiazolyl)	Me	CH	N	N	Ph	Ph	115	500	*429*
2-(4,5-diPh-thiazolyl)	Me	N	CH	N	Ph	Ph	218	375	*429*
2-(1-Me-benzimidazolyl)	Me	N	N	CH	H	H	—	—	*676*
2-(1-Et-benzimidazolyl)	Et	N	N	CH	H	H	—	—	*676*
2-(1-Et-benzimidazolyl)	Et	N	N	CH	Me	H	—	—	*676*
2-(1-Me-6-Cl-benzimidazolyl)	Me	N	N	CH	H	NO_2	—	—	*676*
2-Benzothiazolyl	Me	CH	N	N	Ph	H	218	463	*429*
2-Benzothiazolyl	Me	CH	N	N	Ph	Ph	210	475	*429*
2-Benzothiazolyl	Me	N	CH	N	Ph	H	250	380	*429*
2-Benzothiazolyl	Me	N	CH	N	Ph	Ph	250	385	*429*
2-Benzothiazolyl	Me	N	N	CH	Ph	H	238	463	*429*
2-Benzothiazolyl	Me	N	N	CH	Ph	Ph	230	510	*429*
2-α-Naphthothiazolyl	Me	N	N	CH	Ph	H	227	505	*429*
2-α-Naphthothiazolyl	Me	N	N	CH	Ph	Ph	170	530	*429*
2-β-Naphthothiazolyl	Me	CH	N	N	Ph	H	205	482	*429*
2-β-Naphthothiazolyl	Me	N	N	CH	Ph	H	240	505	*429*
2-β-Naphthothiazolyl	Me	N	N	CH	Ph	Ph	150	530	*429*

TABLE 2173. TRIAZACYANINES



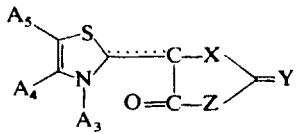
H	A_3	A_4	A_5	B	X	m.p. (°C)	λ(nm)	Ref.
2-Thiazolyl	Et	H	H	Et	BF_4	200	465	*671–673*
2-(4-Me-thiazolyl)	Et	Me	H	Et	BF_4	257	475	*563*
2-(5-Me-thiazolyl)	Et	H	Me	Et	BF_4	238	477	*671*
2-(4,5-diMe-thiazolyl)	Et	Me	Me	Et	BF_4	133	490	*563*
2-(5-Cl-thiazolyl)	Et	H	Cl	Et	BF_4	220	483	*671*
2-(5-Br-thiazolyl)	Et	H	Br	Et	BF_4	230	486	*671*
2-(5-COOEt-thiazolyl)	Et	H	COOEt	Et	BF_4	225	487	*671*
2-(5-NO_2-thiazolyl)	Et	H	NO_2	Et	BF_4	204	502	*671*
2-(5-SO_2Me-thiazolyl)	Et	H	SO_2Me	Et	BF_4	210	477	*671*
2-Benzothiazolyl	Me	H	H	Me	Cl	—	—	*564*
2-Benzothiazolyl	Et	Me	H	Et	BF_4	245	477	*565*
2-Benzothiazolyl	Et	Me	Me	Et	BF_4	231	490	*565*

TABLE 221. O-METHINENEUTROCYANINES



X	Y	Z	A_3	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
CONEt	S	NEt	Me	Me	CH=CHCOOH	—	406	566, 567, 568
CONEt	S	NEt	Me	α-Furyl	H	—	—	359
CONEt	S	NEt	Ph	Ph	Ph	—	—	566
NH	S	NH	Me	α-Furyl	H	—	—	359
NMe	S	NEt	Me	Me	CH=CHCOOH	—	457	567, 568
NMe	S	NPh	Me	Me	CH=CHCOOH	—	455	567, 568
NEt	S	NPh	Et	α-Furyl	H	—	—	359
NPh	S	NMe	Me	$-(CH_2)_3CO-$		>300	—	569
NPh	S	NPh	Et	α-Furyl	H	—	—	569
O	O	NEt	Et	α-Furyl	H	—	—	569
O	S	NEt	Me	Me	H	—	—	444
O	S	NEt	Me	Me	CH=CHCOOH	263	444	567, 568
O	S	NEt	Me	Me	CH=C(CN)CN	—	500	567, 568
O	S	NEt	Me	Me	CH=C(CN)COOH	—	478	567, 568
O	S	NEt	Me	Ph	$CH=CHCOO^{\ominus}$ pyridinium	—	449	567, 568
O	S	NEt	Et	H	NHCOMe	—	425	446
S	N(Et)Ph	N	Me	α-Furyl	H	—	—	359
S	NPh_2	N	Et	α-Furyl	H	281	400	359
S	$C(CN)CS-NC_4H_8$	NEt	Me	Me	CH=CHCOOEt	—	480	567, 568
S	O	*N*-Piperidyl	Me	$-(CH_2)_3CO-$		>335	—	569

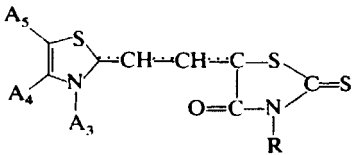
TABLE 221 (*Continued*)



X	Y	Z	A_3	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
S	S	NH	Me	α-Furyl	H	—	—	*359*
S	S	NH	Et	Me	H	—	—	423
S	S	NEt	Me	H	H	—	532	667
S	S	NEt	Me	H	CH_2COONa	—	—	570
S	S	NEt	Me	Me	H	—	—	443
S	S	NEt	Me	Me	$CH{=}CHCONC_4H_8$	—	462	*567, 568*
S	S	NEt	Me	Me	CH=CHCOOH	—	459	566, *567, 568*
S	S	NEt	Me	Me	CH=CHCOOEt	—	460	*567, 568*
S	S	NEt	Me	Me	CH=C(CN)CN	—	510	*567, 568*
S	S	NEt	Me	Me	$CH{=}C(CN)COOH, NEt_3$	—	483	*567, 568*
S	S	NEt	Me	Me	$COCH_3$	—	—	569
S	S	NEt	Me	Ph	CH=CHCOOH	—	462	*567, 568*
S	S	NEt	Me	$-(CH_2)_3CO-$		310	—	569
S	S	NEt	Me	α-Furyl	H	218	424	*359*
S	S	NEt	Et	H	NHCOMe	234	443	*112*
						—	425	*446, 447*
S	S	NEt	Et	Et	H	—	—	423, *571*
S	S	NEt	$(CH_2)_2SO_3Na$	Me	CH=CHCOOEt	—	460	*567, 568*
S	S	NEt	Et	$-CH_2-(o)C_6H_4-$		233	570	352
S	S	NEt	α-Pyridyl	Me	Me	—	—	117
S	S	NEt	α-Thiazolyl	Me	Me	—	—	117
S	S	NEt	α-Benzo-thiazolyl	H	H	—	—	395

S	S	N-*n*-Pr	Et	H	NHCOMe	—	443	*446*, 447
S	S	NCH_2CH_2OH	Me	α-Furyl	H	—	—	*359*
S	S	$N(CH_2)_2COOH$	Et	H	NHCOMe	—	442	*446*, 447
S	S	NCH(Me)COOH	Me	$-(CH_2)_3CO-$		265	—	569
S	S	NCH_2COOH	Me	Me	CH CHCOOEt	—	461	*567*, *568*
S	S	NCH_2COOH	Me	$-(CH_2)_3CO-$		290	331	569
S	S	NCH_2COOH	Et	H	H	—	—	572
S	S	NCH_2COOH	Et	Me	H	—	—	572
S	S	NCH_2COOH	Ph	Me	H	—	—	573
S	S	NPh	Me	$-(CH_2)_3CO-$		380	—	569
S	S	NPh	Et	H	NHCOMe	—	444	*446*, 447
S	S	NPh	Et	α-Furyl	H	—	—	*359*

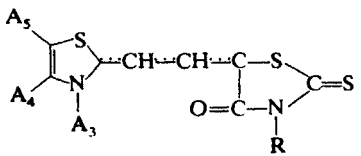
TABLE 222A. DIMETHINE NEUTROCYANINE



A_3	A_4	A_5	R	Method	m.p. (°C)	λ(nm)	Ref.
Me	H	H	Et	A	220	535	*112*
Me	H	Br	Et	A	168	537	*112*
Me	Me	CH=CHCOOH	Et	D	—	562	*567, 568*
Me	Me	COOH	Et	C	258	547	*222*
Me	Ph	H	Ph	—	—	510	80, 82
Me	*p*-Xylyl	Ph	Et	B	111	552	*111*
Me	*p*-$MeOC_6H_4$	Ph	Et	B	216	552	*111*
Me	*p*-$MeOC_6H_4$	OPh	Et	B	186	547	*111*
Me	*p*-$MeOC_6H_4$	*p*-(*t*-C_8H_{17})C_6H_4O	Et	B	161	546	111, 351
Me	NH_2	H	Et	C	270	510	*386*
Et	H	H	H	—	—	—	*423*
Et	H	H	Et	—	—	—	423, 574, 575
Et	H	H	Et	$MeSO_4^-$ salt	165	—	576
Et	H	H	$(CH_2)_2SO_3K$	—	—	—	423
Et	H	H	CH_2COOH	—	—	—	423
Et	H	Styryl	Et	B	205	570	*357*
Et	H	Ph	Et	B	209	556	354, *357*, 575
Et	H	*p*-$NO_2C_6H_4$	Et	—	—	—	575
Et	H	*p*-$MeOC_6H_4$	Et	—	—	—	575
Et	H	α-Naphthyl	Et	—	—	548	354, 575
Et	H	β-Naphthyl	Et	—	221	562	354, 575

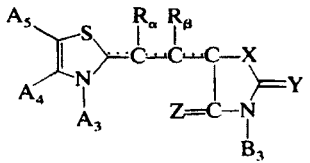
Et	H	α-Furyl	Et	—	198	556	354, 575
Et	H	α-Thienyl	Et	—	192	560	354
Et	H	α-Benzo(*b*)furyl	Et	—	220	562	354, 575
Et	Me	H	Me	—	210	541	*577*
Et	Me	H	Et	—	198	539	*72*
Et	Me	$(CF_2)_2CF_3$	Et	C	136		*487*
Et	Me	4-Thiazolyl	Et	A	210	554	*356*
Et	Me	4-(2-Me-thiazolyl)	Et	A	220	555	*356*
Et	Styryl	H	Et	B	228	544	*357*
Et	Ph	H	Et	B	215	540	114, 354, *357*, 575
Et	Ph	Ph	Et	B	242	550	*111*, 578
Et	Ph	Ph	$(CH_2)_5COOH$	A	106	553	579, *580*
Et	Ph	Ph	$(CH_2)_5COOEt$	A	176	604	*581*
Et	Ph	Ph	$(CH_2)_2COOEt$	—	139	—	579
Et	Ph	Ph	CH_2COOH	—	—	—	579
Et	Ph	Ph	CH_2COOEt	—	—	500	483
Et	Ph	OPh	Et	B	174	544	*111, 351*
Et	Ph	*p*-MeC_6H_4S	Et	B	165	544	*111, 351*
Et	*p*-Xylyl	Ph	Et	B	190	554	*111*
Et	*p*-ClC_6H_4	*p*-ClC_6H_4	Et	B	—	—	*351*
Et	*p*-$MeOC_6H_4$	H	Et	B	225	540	*111*
Et	*p*-$MeOC_6H_4$	Ph	Et	B	197	548	*111*
Et	*p*-$MeOC_6H_4$	OPh	Et	—	150	544	*111*
Et	*p*-$CF_3SO_2C_6H_4$	H	Et	C	222	—	*491*
Et	3,4-di$MeOC_6H_3$	Ph	Et	B	199	554	*111*
Et	α-Naphthyl	H	Et	—	205	540	354
Et	β-Naphthyl	H	Et	—	224	540	354
Et	β-Naphthyl	*p*-MeC_6H_4–S	Et	B	198	544	*111, 351*
Et	α-Azulene	H	Et	—	199	542	*516*
Et	α-Furyl	H	Et	—	200	536	354, 575
Et	α-Benzo(*b*)furyl	H	Et	—	243	536	354
$(CH_2)_2SH$	Ph	H	$(CH_2)_5COOEt$	—	—	—	*63*

TABLE 222A (*Continued*)



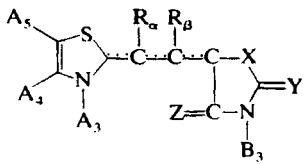
A_3	A_4	A_5	R	Method	m.p. (°C)	λ(nm)	Ref.
$(CH_2)_2SH$	Ph	Ph	Et	—	—	—	*63*
$(CH_2)_2SCOMe$	Ph	Ph	Et	—	—	—	*63*
Ph	H	Ph	Et	—	—	—	*325*
Ph	H	*p*-$MeOC_6H_4$	Et	—	—	—	*325*
Ph	H	β-Naphthyl	Et	—	—	—	*325*
Ph	Me	H	Et	—	—	530	473
α-Pyridyl	H	H	Et	D	—	—	*117*
α-Pyridyl	Me	H	Et	D	—	—	*117*
α-Pyridyl	Me	Me	Et	—	—	—	*117*
2-Thiazolyl	H	H	Et	D	—	—	*117*
2-Thiazolyl	Me	H	Et	D	—	—	*117*
2-Thiazolyl	Me	Me	Et	—	—	—	*117*
2-Benzo-thiazolyl	H	H	Et	—	—	—	395
6-(2-Me-benzo-thiazolyl)	Me	H	Et	C	220	—	*118*

TABLE 222B

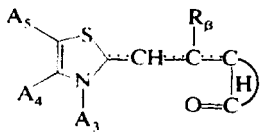


X	Y	Z	A_3	A_4	A_5	R_α	R_β	B_3	Method	m.p. (°C)	λ(nm)	Ref.
NH	S	O	Et	H	H	H	H	H	—	—	—	423
NH	S	O	Et	Me	H	H	H	H	—	—	—	423
NEt	S	O	Et	Ph	Ph	H	H	ET	—	—	—	423
NEt	S	O	Et	Ph	Ph	H	H	COMe	A	—	—	*582*
NCOMe	S	O	Et	Ph	Ph	H	H	Et	A	—	—	*582*
NPh	S	O	Et	Me	H	H	H	—	—	240	—	*521*
NPh	S	O	Et	Me	H	CH=NPh	H	—	—	—	—	*521*
NPh	S	O	Et	Me	H	CH=NPh-ClHsalt	H	—	—	165	—	*521*
O	S	O	Me	Me	COOH	H	H	Et	C	226	547	*222*
O	S	O	Et	Me	H	H	H	H	—	—	—	423
O	S	O	Et	H	H	H	H	Et	—	—	—	423
S	O	O	Et	H	H	H	H	Et	—	—	—	423
S	O	O	Et	Ph	Ph	H	H	Et	—	224	591	583
S	S	O	Me	H	H	H	Me	Et	—	—	—	423
S	S	O	Me	Me	H	H	Me	Me	E	225	—	*584*
S	S	O	Me	Me	CH=CHCOOH	H	Me	Me	D	—	548	*567, 568*
S	S	O	Me	Me	CH=CHCOOH	H	Me	Et	D	—	560	*567, 568*
S	S	O	Me	Me	CH=CHCOOH	H	Me	Allyl	D	—	560	*567, 568*
S	S	O	Me	Me	CH=CHCOOEt	H	Me	Et	D	—	565	*567, 568*
S	S	O	Me	Me	COOH	H	Me	Et	C	214	635	*222*
S	S	O	Me	Ph	H	H	Me	Me	E	232	—	*584*

TABLE 222B (*Continued*)

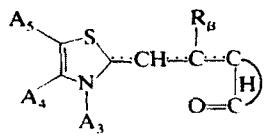


X	Y	Z	A_3	A_4	A_5	R_α	R_β	B_3	Method	m.p. (°C)	λ(nm)	Ref.
S	S	O	Et	H	H	H	Me	Et	—	—	—	575
S	S	O	Et	H	H	H	Me	CH_2COOH	—	—	—	585
S	S	O	Et	H	H	H	$(CH_2)_2OH$	Et	—	—	—	423
S	S	O	Et	H	H	H	$(CH_2)_2COOH$	Et	—	—	—	423
S	S	O	Et	H	H	H	σ-$HOOCC_6H_4$	Et	—	—	—	423
S	S	O	Et	H	H	H	σ-$HOOCC_6H_4$	Allyl	—	—	—	423
S	S	O	Et	H	H	H	OEt	Et	—	—	—	570
S	S	O	Et	Me	H	CH=NPh	H	Et	—	—	—	*521*
S	S	O	Et	Me	H	CH=NPh,	H	Et	—	268	—	*521*
S	S	O	Et	Ph	H	H	Me	Et	E	230	—	586
S	S	O	Et	Ph	Ph	H	σ-$HOOCC_6H_4$	Et	—	—	—	423
S	S	O	α-Pyridyl	H	H	H	Me	Et	D	—	—	*117*
S	S	O	α-Pyridyl	Me	H	H	Me	Et	D	—	—	*117*
S	S	O	α-Pyridyl	Me	H	H	OEt	Et	D	—	—	*117*
S	S	O	2-Thiazolyl	H	H	H	Me	Et	D	—	—	*117*
S	S	O	2-Thiazolyl	Me	H	H	Me	Et	D	—	—	*117*
S	S	O	2-Thiazolyl	Me	Me	H	Me	Et	—	—	—	*117*
S	S	O	2-Thiazolyl	H	H	H	OEt	Et	—	—	—	*117*
S	S	O	2-Thiazolyl	Me	H	H	OEt	Et	—	—	—	*117*
S	S	O	2-Thiazolyl	Me	Me	H	OEt	Et	—	—	—	*117*
S	S	S	Et	H	H	H	H	Et	—	—	—	423



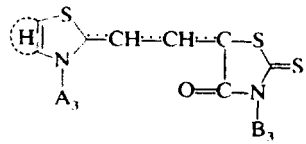
H	A_3	A_4	A_5	R	Method	m.p. (°C)	λ(nm)	Ref.
Chroman-2,4-dione	Me	Ph	H	H	—	149	505	587
7-Hydroxychroman-2,4-dione	Me	Ph	H	H	—	208	452	587
5,6-Benzochroman-2,4-dione	Me	Ph	H	H	—	212	485	587
7,8-Benzochroman-2,4-dione	Me	Ph	H	H	—	92	478	587
3-Dihydro-2-keto-4,5-benzo-thianaphthene)	Et	Ph	Ph	H	C	234	551	588
4-(3-Me-1-Ph-pyrozolone-5)	Me	Me	COOH	Me	C	247	560	*222*
4-(3-Me-1-Ph-pyrozolone-5)	Me	Ph	H	H	—	—	501	80, 82
4-(3-Me-1-Ph-pyrozolone-5)	Et	Ph	H	H	—	—	—	84
4-(3-Me-1-Ph-pyrozolone-5)	Et	p-BrC_6H_4	H	H	—	—	—	84
4-(3-Me-1-Ph-pyrozolone-5)	Et	p-ClC_6H_4	H	H	—	—	—	84
4-(3-Me-1-Ph-pyrozolone-5)	Ph	Me	H	H	—	—	480	473
4-(3-Ph-isoxozolone-5)	Me	Ph	H	H	—	—	—	423
4-(3-Ph-isoxozolone-5)	Et	H	H	H	—	—	496	80, 82
5-(4-Ph-thiazolone-4)	Me	H	H	H	—	—	504	589
5-(4-Ph-thiazolthione-4)	Me	H	H	H	—	—	580	589
4-(2-EtS-thiazolone-5)	Me	Ph	p-MeC_6H_4	H	B	133	544	*111, 351*
4-(2-EtS-thiazolone-5)	Me	p-Xylyl	Ph	H	B	108	548	*111*
4-(2-EtS-thiazolone-5)	Me	p-$MeOC_6H_4$	OPh	H	B	168	543	*111, 351*
4-(2-EtS-thiazolone-5)	Me	p-$MeOC_6H_4$	p-(t-C_8H_{17}) C_6H_4O	H	B	—	—	*351*

TABLE 222C (*Continued*)



H	A_3	A_4	A_5	R	Method	m.p. (°C)	λ(nm)	Ref.
4-(2-EtS-thiazolone-5)	Me	β-Naphthyl	p-MeC_6H_4S	H	B	180	544	*111, 351*
4-(2-EtS-thiazolone-5)	Et	Ph	Ph	H	B	208	547	*111*
4-(2-EtS-thiazolone-5)	Et	Ph	p-MeC_6H_4	H	B	—	—	*351*
4-(2-EtS-thiazolone-5)	Et	p-BrC_6H_4	p-BrC_6H_4-O	H	B	—	—	*351*
4-(2-EtS-thiazolone-5)	Et	p-$MeOC_6H_4$	H	H	B	182	527	*111*
4-(2-EtS-thiazolone-5)	Et	p-$MeOC_6H_4$	Ph	H	B	181	548	*111*
4-(2-EtS-thiazolone-5)	Et	p-$MeOC_6H_4$	OPh	H	B	164	542	*111, 351*
4-(2-EtS-thiazolone-5)	Et	3,4-diMeO-C_6H_3	Ph	H	B	229	550	*111*

TABLE 222D



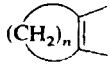
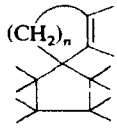
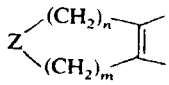
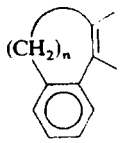
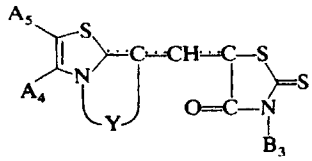
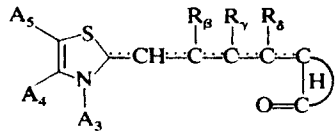
H				A_3	B_3	Method	m.p. (°C)	λ(nm)	Ref.
	n								
	3			Et	Et	C	233	556	*399*
	4			Et	Et	—	222	546	*72*
								495	*87*
	4 (4-*i*-Pr, 7-Me)			Me	Et	C	188	550	*401*
	5			Et	Et	C	192	550	*402*
	n								
	2			Me	Et	C	216	556	*402*
	3			Et	Et	C	238	550	*404*
	n	*m*	*Z*						
	1	2	O	Et	Et	C	234	491	*87, 406*
	3	0	O	Et	Et	C	216	556	*407*
	0	3	S	Et	Et	C	235	549	*409*
								598	87
	1	2	S	Et	Et	C	235	544	*408*
								492	87
	n								
	1			Me	Et	C	248	556	*537*
	2			Me	Et	C	291	554	*405*
	2			Et	Et	—	237	554	114

TABLE 222E



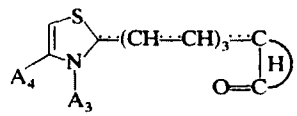
Y	A_4	A_5	B_3	m.p. (°C)	λ(nm)	Ref.
$-(CH_2)_2-$	Ph	Ph	Me	266	572	410
$-(CH_2)_3-$	Me	H	Me	271	558	410
$-(CH_2)_3-$	Me	Me	Me	282	568	410
$-(CH_2)_3-$	Ph	H	Me	269	560	410
$-(CH_2)_3-$	Ph	Ph	Me	262	571	410
$-(CH_2)_4-$	Ph	Ph	Me	235	580	410
$-CH_2-$(1,2-cyclohexenyl)$-CH_2-$	Me	H	Me	215	568	412
$-(CH_2)_2-O-$	Me	H	Et	306	578	411
$-(CH_2)_2-S-$	Me	H	Et	285	572	411
$-(o)C_6H_4-$	Me	H	Et	326	508	*415*
$-(o)C_6H_4-(CH_2)_2-$	Me	H	Et	—	574	413, 414
$-(o)C_6H_4-Se-$	Me	H	Et	237	545	413, 414

TABLE 223. TETRAMETHINE NEUTROCYANINES



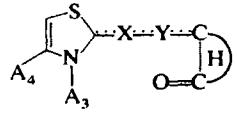
H	R_β	R_δ	R_γ	A_3	A_4	A_5	m.p. (°C)	λ(nm)	Ref.
Chroman-2,4-dione	H	H	H	Me	Ph	H	168	583	587
7-OH-chroman-2,4-dione	H	H	H	Me	Ph	H	190	556	587
5,6-Benzochroman-2,4-dione	H	H	H	Me	Ph	H	>300	550	587
7,8-Benzochroman-2,4-dione	H	H	H	Me	Ph	H	295	554	587
5-(1-Me-3-Ph-pyrazolone)	H	H	H	Et	Ph	H	—	—	84
diEt-thiohydantoine	H	H	H	Me	Me	CH=CHCOOH	—	623	*567*
4-(2-Ph-oxazolone)	H	OEt	H	Et	Ph	Ph	210	—	*590*
N-Et-rhodanine	H	H	H	Me	Me	CH=CHCOOH	—	648	*567*
N-Et-rhodanine	H	H	H	Me	Ph	H	225	—	69
N-Et-rhodanine	H	H	H	Me	p-BrC_6H_4	H	75	—	69
N-Et-rhodanine	H	H	H	Me	p-$MeOC_6H_4$	H	142	—	69
N-Et-rhodanine	H	H	H	Me	p-$EtOC_6H_4$	H	142	—	69
N-Et-rhodanine	Me	H	H	Et	Ph	Ph	213	—	591
N-Et-rhodanine	$-(CH_2)_3-$		H	Me	Me	CH=CHCOOH	—	—	566

TABLE 224. HEXAMETHINE NEUTROCYANINES



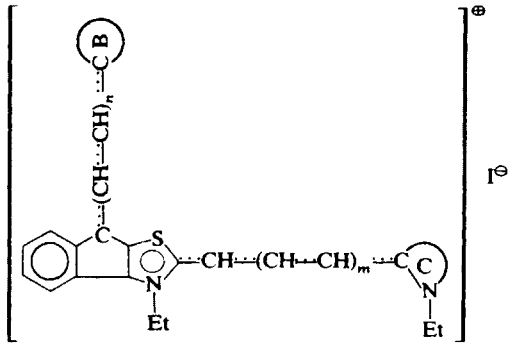
H	A_3	A_4	m.p. (°C)	Ref.
5-(1-Me-3-Ph-pyrazolone)	Et	Ph	—	84
5-N-Et-rhodanine	Me	Ph	145	69
5-N-Et-rhodanine	Me	p-BrC_6H_5	222	69
5-N-Et-rhodanine	Me	p-$MeOC_6H_4$	146	69
5-N-Et-rhodanine	Me	p-$EtOC_6H_4$	178	69

TABLE 225. AZANEUTROCYANINES



H	X	Y	A_3	A_4	Method	m.p. (°C)	λ(nm)	Ref.
4-(3-Me-1-Ph-pyrazolone)	CH	N	Et	Me	B	186	—	*592*
4-(3-Me-1-Ph-pyrazolone)	N	CH	Me	Ph	A	176	490	*80, 82*
4-(3-Ph-isoxozolone)	N	CH	Me	Ph	A	182	490	*80, 82*
5-(N-H-rhodanine)	N	CH	Me	Ph	A	233	470	*80*
5-(N-Et-rhodanine)	N	CH	Me	Ph	A	192	480	*80*
5-(N-Ph-rhodanine)	N	CH	Me	Ph	A	300	485	*80, 82*
5-(N-(*o*)Me-C_6H_4-rhodanine)	N	CH	Me	Ph	A	224	485	*80*
5-(N-(*m*)Me-C_6H_4-rhodanine)	N	CH	Me	Ph	A	221	480	*80*
5-(N-(*p*)Me-C_6H_4-rhodanine)	N	CH	Me	Ph	A	230	480	*80*
5-(N-(*m*)Cl-C_6H_4-rhodanine)	N	CH	Me	Ph	A	300	478	*80*

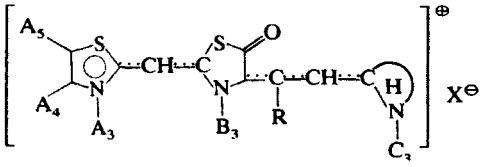
TABLE 311. TRINUCLEAR CYANINES: CYANINE-CYANINE



B	C	m	n	m.p. (°C)	λ(nm)	Ref.
4-(1-Me-quinolyl)	2-Benzothiazolyl	0	0	240	448–625	1(p. 622), *537*
2-(3-Et-benzoxazolyl)	2-Benzoxazolyl	1	1	288	458–460	1(p. 622), *537*
2-(3-Et-benzoxazolyl)	2-Benzothiazolyl	1[a]	1	236	474–650	1(p. 622), *537*
2-(3-Et-thiazolinyl)	2-Thiazolyl	1	1	286	446–625	1(p. 622), *537*
2-(3-Et-benzothiazolyl)	2-Benzothiazolyl	0	0	280	430–524	1(p. 622), *86*, *537*

[a] Mesomethyl.

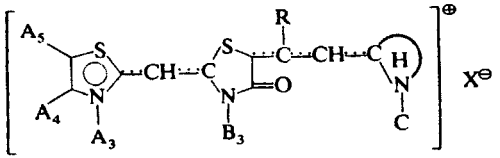
TABLE 312A. CYANINE-NEUTROCYANINE



H	A_3	A_4	A_5	B_3	C_3	R	m.p. (°C)	λ(nm)	Ref.
2-(4,5-diPh-oxazolyl)	Et	p-$MeOC_6H_4$	Ph	Me	Et	H	247	598	1(p.656), *593*
2-(4,5-diPh-thiazolyl)	Et	Ph	Ph	Me	Et	H	243	643	*593*
2-(4-Ph-5-p-MeC_6H_4S-thiazolyl)	Me	Ph	p-MeC_6H_4S	Me	Me	H	205	633	*351, 593*
2-(4-p-Xylyl-5-Ph-thiazolyl)	Me	p-Xylyl	Ph	Me	Me	H	220	642	*593*
2-(4-p-Xylyl-5-Ph-thiazolyl)	Et	p-Xylyl	Ph	Me	Et	H	265	651	*593*
2-(4-β-Naphthyl 5-MeC_6H_4S-thiazolyl)	Me	β-Naphthyl	p-MeC_6H_4S	Me	Me	H	222	635	*593*
2-(4-p-$BrC_6H_4$5-p-BrC_6H_4O-thiazolyl)	Me	p-BrC_6H_4	p-BrC_6H_4O	Me	Et	H	190	629	*351, 593*
2-(4-p-$MeOC_6H_5$-5-Ph-thiazolyl)	Et	p-$MeOC_6H_4$	Ph	Me	Et	H	263	643	*593*
2-Benzoxazolyl	Et	p-$MeOC_6H_4$	Ph	Me	Et	H	278	538	*593*
2-Benzothiazolyl	Me	Ph	OPh	Me	Et	H	—	—	*351*
2-Benzothiazolyl	Et	Ph	Ph	Me	Et	H	246	620	*593*
2-Benzothiazolyl	Et	Ph	Ph	Et	Et	Me	264	631	*594*
2-Benzothiazolyl	Et	Ph	OPh	Me	Et	H	242	619	*593*
2-Benzothiazolyl	Et	p-$MeOC_6H_4$	Ph	Me	Et	H	269	624	*593*
2-(5-Cl-benzothiazolyl)	Et	Ph	Ph	Me	Et	H	249	621	*593*
2-Benzoselenazolyl	Me	Ph	OPh	Me	Et	H	263[a]	622	*351, 593 595*
2-Benzoselenazolyl	Et	Ph	Ph	Me	Et	H	268	624	1(p. 656), *593*
2-Benzoselenazolyl	Et	p-$OMeC_6H_4$	Ph	Me	Et	H	271	624	1(p. 656), *593*
2-β-Naphthothiazolyl	Me	Ph	OPh	Me	Et	H	264[a]	636	1(p. 656), *593*
2-β-Naphthothiazolyl	Et	Ph	Ph	Me	Et	H	263	643	*593*

[a] $X = OTs^{\ominus}$.

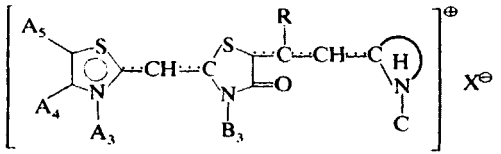
TABLE 312B



H	A_3	A_4	A_5	B_3	C	R	X	m.p. (°C)	λ(nm)	Ref.
4-Pyridinyl	Et	Ph	Ph	Et	Et	H	I	210	—	596
2-(1,1-diMe-indolenyl)	Et	Ph	Ph	Et	Et	H	I	—	—	597, 598
2-Quinolyl	Et	Ph	Ph	Et	Et	H	I	—	—	596
2-(5-Oxoquinolyl)	Et	Ph	Ph	Et	Et	H	I	—	617	*467*
4-Quinolyl	Et	Ph	Ph	Et	Et	H	I	—	—	599
4-Quinolyl	Et	Ph	COOEt	Et	Et	H	I	—	—	599
4-Quinolyl	$(CH_2)_3SO_3$	Ph	Ph	Et	$(CH_2)_3SO_3$	H	—	—	—	600
4-Quinolyl	$(CH_2)_3SO_3$	Ph	Ph	Allyl	H	H	—	—	—	600
4-Quinolyl	$(CH_2)CH(OH)$-CH_2OSO_3	Ph	Ph	Et	Et	H	—	—	—	600
4-Quinolyl	$(CH_2CH_2O)_2$-$(CH_2)_3SO_3$	Ph	Ph	Allyl	Et	H	—	—	—	600
4-Quinolyl	$CH(Me)CH_2SO_3$	Ph	Ph	Et	Et	H	—	—	—	600
4-Quinolyl	$(CH_2CH_2O)_2SO_3$	Ph	Ph	Et	Et	H	—	—	—	600
4-Quinolyl	$(CH_2)_2SO_3$	Ph	Ph	Hexyl	Et	H	—	—	—	600
4-(2-Me-oxo-5-quinolyl)	Me	Ph	Ph	Et	Me	H	I	—	641	*467*
2-(4,5-diPh-oxazolyl)	Et	*p*-$MeOC_6H_4$	Ph	Et	Et	H	I	210	575	*593*
2-(4-Me-thiazolyl)	Et	Ph	Ph	Et	Et	H	I	—	—	596, 675
2-(4,5,6,7-Tetrahydrobenzo-thiazolyl)	Et	Ph	Ph	Et	Et	H	I	—	—	601
2-(4,5-diPh-thiazolyl)	Et	Ph	Ph	Et	Me	Me	I	228	610	*594, 602*
2-(4,5-diPh-thiazolyl)	Et	Ph	Ph	Et	Et	H	I	275	615	*593*
2-(4,5-diPh-thiazolyl)	Et	Ph	Ph	Allyl	Et	H	I	—	—	596
2-(4-Ph-5-*p*-MeC_6H_4S-thiazolyl)	Et	Ph	*p*-MeC_6H_4S	Et	Et	H	I	—	—	1(p. 656), *351*

2-(4-*p*-MeC$_6$H$_4$5-Ph-3-Me-thiazolyl)	Me	*p*-MeC$_6$H$_4$	Ph	Et	Me	H	I	237	—	603
2-(4-*p*-Xylyl-5-Ph-thiazolyl)	Me	*p*-Xylyl	Ph	Et	Me	H	I	240	613	*593*
2-(4-*p*-Xylyl-5-Ph-thiazolyl)	Et	*p*-Xylyl	Ph	Et	Et	H	I	262	614	*593*
2-(4-*β*-Naphthyl-5-*p*-Me-C$_6$H$_4$S-thiazolyl)	Me	*β*-Naphthyl	*p*-Me-C$_6$H$_4$S	Et	Et	H	I	241	613	*351, 593*
2-(4-*p*-MeOC$_6$H$_4$-5-Ph-thiazolyl)	Et	*p*-MeOC$_6$H$_4$	Ph	Et	Et	H	I	282	613	*593*
2-[4-*p*-MeOC$_6$H$_4$5-(*p*-1′,1′,3′,3′-tetramethylbutyl-C$_6$H$_4$-thiazolyl)]	Et	*p*-MeOC$_6$H$_4$	Ph	Et	Me	H	I	228	608	*593*
2-(4,5-diMeO-thiazolyl)	Et	4,5-diMeO-C$_6$H$_3$	H	Et	Et	H	I	227	616	*593*
2-(4-*p*-MeOC$_6$H$_4$5-PhO-thiazolyl)	Me	*p*-MeOC$_6$H$_4$	PhO	Et	Me	H	I	266	605	*593, 351*
2-(4-*p*-MeOC$_6$H$_4$5-PhO-thiazolyl)	Et	*p*-MeO-C$_6$H$_4$	PhO	Et	Me	H	I	—	—	*351, 593*
2-Benzoxazolyl	Et	Ph	Ph	Et	Et	H	I			675
2-Benzoxazolyl	Et	*p*-MeO-C$_6$H$_4$	Ph	Et	Et	H	I	283	552	593, 603
2-(5-Ph-benzoxazolyl)	Et	H	H	Et	Et	H	I	—	—	1(p. 294), 511
2-Benzothiazolyl	Et	Me	COOEt	Et	Et	H	I	—	—	599
2-Benzothiazolyl	Et	Ph	Ph	Me	Et	H	I	—	—	596
2-Benzothiazolyl	Et	Ph	Ph	Et	Me	Me	I	265	594	*594, 602*
2-Benzothiazolyl	Et	Ph	Ph	Et	Me	Et	I	242	598	*594, 602*
2-Benzothiazolyl	Et	Ph	Ph	Et	Me	*n*-Pr	I	—	—	*602*
2-Benzothiazolyl	Et	Ph	Ph	Et	Me	$(CH_2)_2$Ph	I	240	600	*594, 602*
2-Benzothiazolyl	Et	Ph	Ph	Et	Me	CH_2Ph	I	—	—	*602*
2-Benzothiazolyl	Et	Ph	Ph	Me	Et	H	I	—	—	596
2-Benzothiazolyl	Et	Ph	Ph	Et	Et	H	I	264	584	1(p. 651), 593, 599, 604, 605
2-Benzothiazolyl	Et	Ph	Ph	Et	Et	Me	I	—	—	*594, 602*
2-Benzothiazolyl	Et	Ph	Ph	Et	Et	Et	I	—	—	599
2-Benzothiazolyl	Et	Ph	Ph	Et	Et	Ph	I	—	—	599, 606
2-Benzothiazolyl	Et	Ph	Ph	Heptyl	Et	Me	ClO_4	252	596	*594, 602*

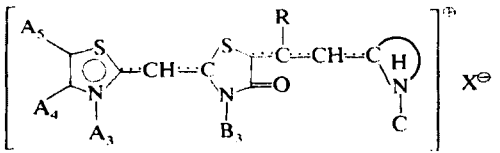
TABLE 312B. (*Continued*)



H	A_3	A_4	A_5	B_3	C	R	X	m.p. (°C)	λ(nm)	Ref.
2-Benzothiazolyl	Et	Ph	Ph	Allyl	Et	CH_2Ph	I	200	605	*594*
2-Benzothiazolyl	Et	Ph	Ph	Allyl	3-*p*-HOOC-C_6H_4-CH_2	H	I	—	590	607
2-Benzothiazolyl	Et	*p*-$MeOC_6H_4$	Ph	Et	Et	H	I	285	583	*593*
2-Benzothiazolyl	*p*-HOOC-$C_6H_4CH_2$	Ph	Ph	Et	Me	Me	Br	215	606	*594, 602*
2-Benzothiazolyl	*p*-HOOC-$C_6H_4CH_2$	Ph	Ph	Allyl	Et	Ph	I	—	611	607
2-Benzothiazolyl	(2-Benzo-thiazolyl)-CH_2	H	H	Et	Et	Et	I	—	—	*608*
2-Benzothiazolyl	(2-Benzo thiazolyl)-CH_2	Ph	Ph	Et	Et	Et	I	—	640	609
2-(5-Cl-benzothiazolyl)	Et	Ph	Ph	Et	$(CH_2)_2COO$-Me	H	I	—	—	596
2-(7-Styryl-benzothiazolyl)	Et	Ph	Ph	Et	Et	H	Cl	204	604	*610*
2-(7-Styryl-benzothiazolyl)	Et	Ph	Ph	Et	Et	Et	Cl	207	615	*610*
2-(7-Styryl-benzothiazolyl)	Et	Ph	Ph	Et	Et	Ph	Cl	196	618	*610*
2-(5,*o*-diMe-benzothiazolyl)	Et	Ph	Ph	Et	*n*-Pr	H	I	—	—	597, 598
2-(5-EtO,6-Me-benzo-thiazolyl)	Et	Ph	Ph	Et	Et	Me	I	—	—	596
2-(5-EtO,6-Me-benzo-thiazolyl)	Et	Ph	Ph	Et	Et	Ph	I	—	—	597, 598
2-(5-EtO,6-Me-benzo-thiazolyl)	$(CH_2)_2COOH$	Ph	Ph	Et	Et	*p*-HOOC C_6H_4	—	—	—	596

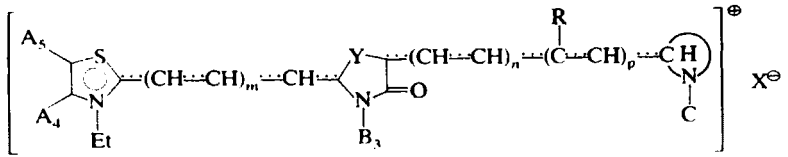
2-(5-EtO,6-Me-benzothiazolyl)	$(CH_2)_2OH$	Ph	Ph	Et	Et	H	I	—	—	596
2-(5-EtO,6-Me-benzothiazolyl)	Et	Ph	Ph	Et	*n*-Pr	H	I	—	—	596, 611
2-Benzoselenazolyl	Et	Ph	Ph	Et	Et	H	I	—	—	599, 604
2-(5-MeO-benzoselenazolyl)	Et	Ph	Ph	Et	Et	Ph	I	—	—	596
2-(5,6-diMe-benzoselenazolyl)	Et	Ph	Ph	Et	Et	Ph	I	—	—	596
2-(5,6-Tetramethylene benzothiazolyl)	Et	H	2-Benzothiazolyl	Et	Et	Ph	I	292	635	*389*
2-(5,6-Tetramethylene benzothiazolyl)	Et	2-Benzothiazolyl	H	Et	Et	Ph	I	246	607	*389*
2-(6,7-Tetramethylene benzothiazolyl)	Et	H	α-Naphthyl	Et	Et	Ph	SO_4Me	—	—	612
2-(6,7-Tetramethylene benzothiazolyl)	Et	Me	4-thiazolyl	Et	Et	H	SO_4Me	>300	615	356
2-(6,7-Tetramethylene benzothiazolyl)	Et		$-C_6H_4(o)(CH_2)_2-$	Et	Et	Ph	SO_4Me	273	612	114
2-(6,7-Tetramethylene benzothiazolyl)	Et	Ph	Ph	Et	Et	Ph	I	262	—	603, 611
2-α-Naphthothiazole	Et	Ph	Ph	Et	Et	H	I	—	—	599, 675
2-β-Naphthothiazole	Et	H	Ph	Et	Et	Ph	SO_4Me	278	619	*354*
2-β-Naphthothiazole	Et	H	2-Naphthyl	Et	Et	Ph	SO_4Me	—	622	*354*
2-β-Naphthothiazole	Et	H	α-Furyl	Et	Et	Ph	SO_4Me	287	622	*354*
2-β-Naphthothiazole	Et	H	α-Benzofuryl	Et	Et	Ph	SO_4Me	288	630	*354*
2-β-Naphthothiazole	Et	H	β-Benzofuryl	Et	Et	Ph	SO_4Me	293	616	*354*
2-β-Naphthothiazole	Et	Ph	Ph	Et	Et	H	I	—	—	596
2-β-Naphthothiazole	Et	Ph	Ph	Et	Et	Et	I	—	—	596
2-β-Naphthothiazole	$(CH_2)_3COO$	Ph	Ph	Et	Et	H	—	—	—	596
2-β-Naphthothiazole	$(CH_2)_3SO_3$	Ph	Ph	Et	Et	Ph	—	—	—	596
2-(Acenaphtho[1,2-*d*]-thiazolyl)	Et	H	Ph	Et	Et	H	OTs	242	655	*353*
2-(Acenaphtho[1,2-*d*]-thiazolyl)	Et	Ph	H	Et	Et	H	SO_4Me	274	645	*353*

TABLE 312B (*Continued*)



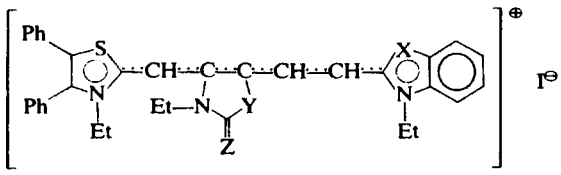
H	A_3	A_4	A_5	B_3	C	R	X	m.p. (°C)	λ(nm)	Ref.
2-(Acenaphtho[1,2-*d*]-thiazolyl)	Et	Ph	Ph	Et	Et	H	OTs	284	651	*353*
5-(7,7-diMe-hexahydro-1,4-diazepine)	Me	Ph	Ph	Et	Et	H	I	175	584	*613*
7-(5,5-diMe-hexahydro-1,5-thiazepine)	Et	Ph	Ph	Et	Et	H	I	210	549	*613*
7-(5-Et5-Me-hexahydro-1,5-thiazepine)	Me	Ph	Ph	Et	Et	Et	I	194	560	*613*
7-(3,5,5-tri Me-hexa-hydro-1,5-thiazepine)	Et	Ph	Ph	Et	Et	H	I	180	551	*613*
2-(3'-Me-1'-Ph-pyrazolo-[4,5-*d*]thiazolyl)	Et	Ph	Ph	Et	Et	H	I	243	—	*264*
2-[Thieno(3,2-*c*)thiazolyl]	Et	Ph	Ph	Et	Et	H	$EtSO_4$	269	607	497, 578
2-[Thieno(3,2-*d*)thiazolyl]	Et	Ph	Ph	Et	Et	H	I	236	—	578
5-(4-Me-tetrazole)	Et	Ph	Ph	Et	Et	H	I	—	—	597, 598 675

TABLE 312C



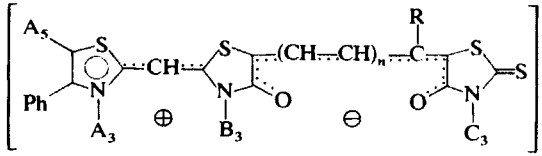
H	*m*	*n*	*p*	Y	A_4	A_5	B_3	C	R	X	m.p. (°C)	λ(nm)	Ref.
4-Quinolyl	1	0	1	S	H	Ph	Et	Et	H	ClO_4	263	650	1(p. 649), *614*
2-(4,5-diPh-thiazolyl)	0	1	1	S	Ph	Ph	Et	Me	OEt	I	—	671	439–441
2-Benzothiazolyl	0	0	1	NEt	Ph	Ph	Et	Et	H	I	—	—	*604*
2-Benzothiazolyl	0	0	0	S	H	Ph	Et	Et	—	I	187	530	1(p. 649), *614*
2-Benzothiazolyl	0	1	1	S	H	H	Et	Et	H	I	—	—	1(p. 651), 615
2-Benzothiazolyl	0	1	1	S	H	Ph	Et	Et	OEt	ClO_4	—	—	439–441
2-Benzothiazolyl	0	1	1	S	Ph	Ph	Et	$(CH_2)_2OH$	OEt	ClO_4	—	653	439–441
2-Benzothiazolyl	0	1	1	S	Ph	Ph	Allyl	$(CH_2)_2OH$	OEt	ClO_4	—	—	439–441
2-Benzothiazolyl	1	0	0	S	H	Ph	Et	Et	OEt	I	228	625	1(p. 649), *614*
2-Benzothiazolyl	1	0	1	S	H	Ph	Et	Et	—	I	239	672	1(p. 649), *614*
2-(5-Me-benzothiazolyl)	0	1	1	S	Ph	Ph	Allyl	$(CH_2)_2OH$	H	ClO_4	—	—	440
2-(5-Cl-benzothiazolyl)	0	1	1	S	Ph	Ph	Et	$(CH_2)_2$-OCOMe	OEt	ClO_4	—	651	439–441
2-(5-MeO-benzothiazolyl)	0	1	1	S	Ph	Ph	Et	Et	OEt	I	—	—	439–441
2-Benzoselenazolyl	0	1	1	S	Ph	Ph	Et	Et	OEt	ClO_4	—	—	439–441
2-(5,6-diMe)-benzoselenazolyl)	0	1	1	S	Ph	Ph	Et	Et	OEt	I	—	—	439–441
2-β-Naphthothiazolyl	0	1	1	S	Ph	Ph	Et	Et	OEt	I	—	—	439–441
2-(6,7-Tetramethylene benzothiazolyl)	0	1	1	S	Ph	Ph	Et	Et	OEt	I	—	660	439–441

TABLE 312D



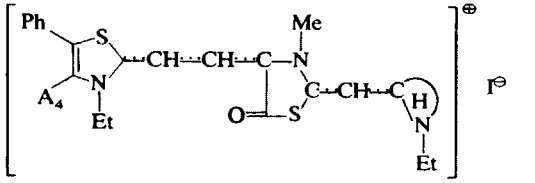
X	Y	Z	m.p. (°C)	λ(nm)	Ref.
O	S	O	185	660	1(p. 656), *605, 616*
S	S	NEt	—	—	1(p. 656), *605*
Se	O	O	—	—	1(p. 656), *605*

TABLE 313. CYANINE-OXONOL



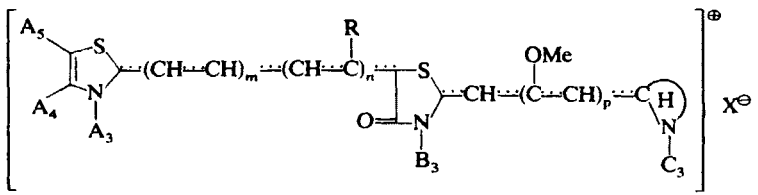
A_3	A_5	B_3	C_3	*n*	R	λ(nm)	Ref.
Me	Me	Ph	Allyl	1	Et	583	*617*
Et	Ph	Et	Et	3	H	—	*618*

TABLE 3141A. CATIONIC RHODACYANINES



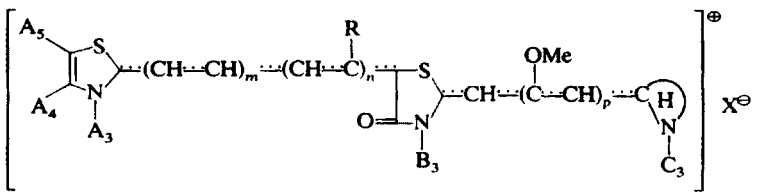
H	A_4	m.p. (°C)	λ(nm)	Ref.
2-(4,5-diPh-Oxazolyl)	*p*-$MeOC_6H_4$	186	616	1(p. 656), *593*
2-Benzothiazolyl	Ph	269	629	1(p. 656), *593*
2-Benzothiazolyl	*p*-$MeOC_6H_4$	272	630	1(p. 656), *593*

TABLE 3141B



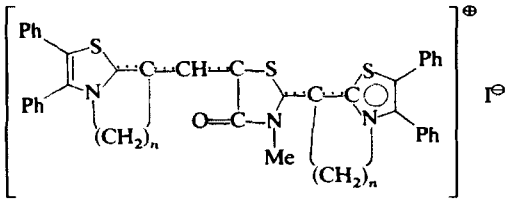
H	m	n	p	A_3	A_4	A_5	B_3	C_3	R	X	m.p. (°C)	λ(nm)	Ref.
2-(4,5-diPh-Oxozolyl)	0	0	0	Me	Me	CH=CH-COOEt	Et	Et	—	I	—	507	567
2-(4,5-diPh-Oxozolyl)	0	0	0	Me	Me	CH=CH-COOEt	CH_2COOH	Et	—	I	—	505	567
2-(4-Me-thiazolidinyl)	0	1	0	Et	Me	H	Et	Et	H	I	—	—	134
2-(4,5-diPh-thiazolyl)	0	0	0	Et	Ph	Ph	Et	Et	—	I	—	—	606
2-(4,5-diPh-thiazolyl)	0	1	0	Me	Me	CH=CH-COOEt	Et	Et	Me	I	—	621	567
2-(1-Me-benzimidazolyl)	0	0	0	Et	Ph	Ph	Et	Me	—	I	—	—	606
2-Benzoxazolyl	0	0	0	Me	Me	CH=CH-COOH	Et	Et	—	$EtSO_4$	—	515	567
2-Benzoxazolyl	0	0	0	Me	Me	CH=CH-COOEt	Et	Et	—	$EtSO_4$	—	508	567
2-Benzoxazolyl	1	0	0	Et	Ph	Ph	Et	Et	OEt	$EtSO_4$	—	669	439-441
2-Benzothiazolyl	0	0	0	Me	Me	CH=CH-COOH	Et	Et	—	$EtSO_4$	—	529	567
2-Benzothiazolyl	0	0	0	Me	Me	CH=CH-COOEt	Et	Et	—	$EtSO_4$	—	520	567
2-Benzothiazolyl	0	0	0	Me	Me	CH=CH-COOEt	Et	Et	—	$EtSO_4$	—	580	567
2-Benzothiazolyl	0	1	0	Et	Me	H	Et	Et	H	I	—	—	620
2-Benzothiazolyl	0	1	0	Et	Ph	Me	Ph	Et	H	I	—	—	1(p. 649), 619
2-Benzothiazolyl	0	1	0	Et	Ph	Ph	Et	Et	H	I	—	—	621

TABLE 3141B (*Continued*)



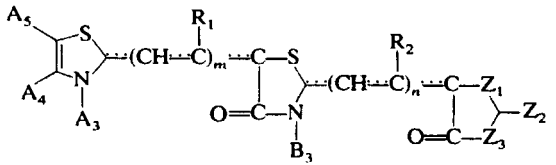
H	*m*	*n*	*p*	A_3	A_4	A_5	B_3	C_3	R	X	m.p. (°C)	λ(nm)	Ref.
2-Benzothiazolyl	0	1	0	Et	Azulenyl	H	Et	Et	H	ClO_4	223	620	*516*
2-Benzothiazolyl	0	1	1	Me	Me	CH=CH-COOEt	Et	Et	Me	$MeSO_4$	—	672	*567*
2-Benzothiazolyl	0	1	1	Me	Ph	Ph	Et	Et	Me	I	—	—	622
2-Benzothiazolyl	0	1	1	Me	Ph	Ph	Et	Et	CH_2Pr	$MeSO_4$	—	—	622
2-Benzothiazolyl	0	1	1	Me	Ph	Ph	Et	Et	Ph	$MeSO_4$	—	—	622
2-Benzothiazolyl	0												
2-(5,6-diMe-benzothiazolyl)	0	1	0	Me	Me	CH CH-COOEt	Et	Et	Me	I	—	626	*567*
2-(5MeO-benzothiazolyl)	0	1	0	Et	Azulenyl	H	Et	Et	H	ClO_4	230	625	*516*
2-Benzoselenazolyl	0	0	0	Et	Ph	Ph	Et	Et	—	Br	—	—	606
2-Benzoselenazolyl	0	1	0	Et	Azulenyl	H	Et	Et	H	I	220	628	*516*
2-Benzoselenazolyl	0	1	0	CH_2-COOEt	Me	H	Et	$(CH_2)_2$ COOH	H	I	—	612	623
2-α-Naphthothiazolyl	0	1	0	Et	H	H	Et	Et	H	I	—	—	*675*
2-α-Naphthothiazolyl	0	1	0	Et	Azulenyl	H	Et	Et	H	ClO_4	234	630	*516*
2-Acenaphtho(1,2-*d*)-thiazolyl	0	1	0	Et	H	Ph	Et	Et	H	OTs	259	640	*353*
2-Benzothieno(2,3-*d*)-thiazolyl	0	1	0	Et	Ph	Ph	Et	Et	H	Br	229	—	578
2-Benzothieno(3,2-*d*)-thiazolyl	0	1	0	Et	Ph	Ph	Et	Et	H	I	249	—	578
2-[4-Me-pyrimidino-(1,2-*a*)benzimidazolyl]	0	1	0	Et	Ph	Ph	$(CH_2)_3N^{\oplus}$-Me_2Et	Et	H	2OTs	218	640	*624*
2-[4-Me-pyrimidino-(1,2-*a*)benzimidazolyl]	0	1	0	Et	Ph	Ph	$(CH_2)_3N^{\oplus}$-Me_2Et	$(CH_2)_3$-$SO_3^{\ominus}$	H	$EtSO_4$	230	649	*624*

TABLE 3141C



n	m.p. (°C)	λ(nm)	Ref.
1	212	655	410
2	226	652	410

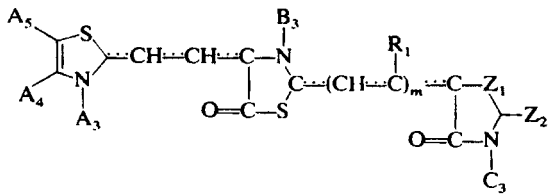
TABLE 3142A. NEUTRO RHODACYANINES



Z_1	Z_2	Z_3	m	n	A_3	A_4	A_5	B_3	R_1	R_2	m.p. (°C)	λ(nm)	Ref.
N	SEt	S	1	0	Me	*p*-MeOC$_6$H$_4$	*p*-(1,1,3,3,-tetraMe-Bu)C$_6$H$_4$O	Et	H	—	201	572	*593*
N	SEt	S	1	0	Et	Ph	Ph	Et	H	—	246	593	*593*
N	SEt	S	1	0	Et	*p*-MeOC$_6$H$_4$	OPh	Et	H	—	276	574	*351, 593*
N	SEt	S	1	1	Et	Ph	Ph	CH_2COOEt	H	OEt	240	630	1(p. 674), *625*
N	SEt	S	1	1	Et	Ph	Ph	CH_2COOEt	H	SEt	—	675	1(p. 674), *625*
O	S	NEt	0	0	Me	Me	CH=CH-COOEt	Et	—	—	—	505	*567*
O	S	NEt	1	0	Me	*p*-MeOC$_6$H$_4$	*p*-(1,1,3,3,-tetraMe-Bu)C$_6$H$_4$O	Et	H	—	—	—	*351*
O	S	NEt	1	0	Et	*p*-MeOC$_6$H$_4$	OPh	Et	H	—	—	—	*351*
S	S	NEt	0	0	Me	Me	CH=CHCOOEt	Et	—	—	—	517	*567*
S	S	NEt	0	1	Me	Me	CH=CHCOOEt	CH_2COOEt	—	Me	—	577	*567*
S	S	NEt	1	0	Me	Me	CH=CHCOOEt	Et	Me	—	—	614	*567*
S	S	NEt	1	0	Me	*p*-Xylyl	Ph	Et	H	—	—	594	1(p. 656), *593*
S	S	NEt	1	0	Me	*p*-MeOC$_6$H$_4$	OPh	Et	H	—	240	584	1(p. 656), *351, 593*
S	S	NEt	1	0	Me	*p*-MeC$_6$H$_4$	*p*-(1,1,3,3,-tetraMe-Bu)C$_6$H$_4$O	Et	H	—	252	585	*351, 593*
S	S	NEt	1	0	Et	Ph	Ph	Et	H	—	298	594	*593, 626*
S	S	NEt	1	0	Et	Ph	OPh	Et	H	—	274	584	*351, 593*
S	S	NEt	1	0	Et	*p*-ClC$_6$H$_4$	*p*-ClC$_6$H$_4$O	Et	H	—	246	584	*351, 593*
S	S	NEt	1	0	Et	*p*-Xylyl	Ph	Et	H	—		596	*593*
S	S	NEt	1	0	Et	*p*-MeOC$_6$H$_4$	Ph	Et	H	—	286	595	*593*
S	S	NEt	1	0	Et	*p*-MeOC$_6$H$_4$	OPh	Et	H	—	278	586	*593*
S	S	NEt	1	0	Et	3,4-diMeO-C$_6$H$_3$	Ph	Et	H	—	243	594	*593*
S	S	NEt	1	0	Et	β-Naphthyl	*p*-MeC$_6$H$_4$S	Et	H	—	247	585	*351, 593*

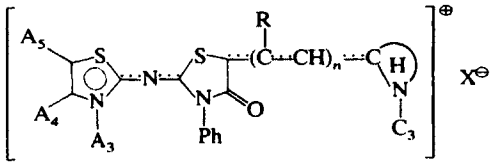
S	S	NEt	1	0	Me	Me	CH=CHCOOEt	Et	Me	Me	—	671	567
S	S	NBu	1	0	Et	H	Ph	Et	H	—	287	—	626
S	S	NBu	1	0	Et	H	2-naphthyl	Et	H	—	283	—	626
S	S	NBu	1	0	Et	H	α-Furyl	Et	H	—	278	—	626
S	S	NBu	1	0	Et	Ph	H	Et	H	—	247	—	626
S	S	NBu	1	0	Et	Ph	H	Et	NHPh	—	240	561	627
S	S	NBu	1	0	Et	Ph	Ph	Bu	H	—	252	—	626
S	S	NBu	1	0	Et	Ph	Ph	$(CH_2)_5COOEt$	H	—	191	601	579
S	S	$NC_5H_{11}(n)$	1	0	Et	Ph	Ph	Bu	H	—	250	605	579
S	S	$NC_5H_{11}(n)$	1	0	Et	Ph	Ph	$C_4H_{11}(n)$	H	—	220	605	579
S	S	$NC_7H_{15}(n)$	1	0	Et	Bh	Ph	Bu	H	—	215	605	579
S	S	$NC_7H_{15}(n)$	1	0	Et	Ph	Ph	$C_7H_{11}(n)$	H	—	185	605	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Me	H	Et	H	—	193	595	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Me	COOEt	Et	H	—	164	587	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	H	Et	H	—	194	589	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	Ph	Et	H	—	150	602	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	Ph	Bu	H	—	177	604	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	Ph	$(CH_2)_5COOEt$	H	—	124	602	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	Ph	$(CH_2)_5COOBu$	H	—	119	603	579
S	S	$N(CH_3)_5COOPr$	1	0	Et	Ph	H	Bu	H	—	170	590	579
S	S	$N(CH_3)_5COOPr$	1	0	Et	Ph	Ph	*n*-Pr	H	—	157	602	579
S	S	$N(CH_2)_5$ COO-*i*-Pr	1	0	Et	Ph	Ph	Bu	H	—	140	602	579
S	S	$N(CH_2)_5COOBu$	1	0	Et	Ph	Ph	Et	H	—	119	603	579
S	S	$N(CH_2)_5COOBu$	1	0	Et	Ph	Ph	Bu	H	—	170	601	579
S	S	$N(CH_2)_5COOBu$	1	0	Et	Ph	Ph	$N(CH_2)_5COOBu$	H	—	167	603	579
S	S	$N(CH_2)_5COOEt$	1	0	Et	Ph	Ph	Bu	H	—	218	602	579
S	S	$N(CH_2)_2COOEt$	1	0	Et	Ph	Ph	Bu	H	—	212	602	579
S	S	$N(CH_2)_2COOBu$	1	0	Et	Ph	Ph	Bu	H	—	200	602	579
S	S	$N(CH_2)_2COO$-(*i*)-Bu	1	0	Et	Ph	Ph	Bu	H	—	224	602	579
S	S	NCH_2COOEt	1	0	Et	H	H	Et	H	—	224	589	579
S	S	NNHCOMe	1	0	Et	Ph	Ph	Pr	H	—	274	—	628

TABLE 3142B



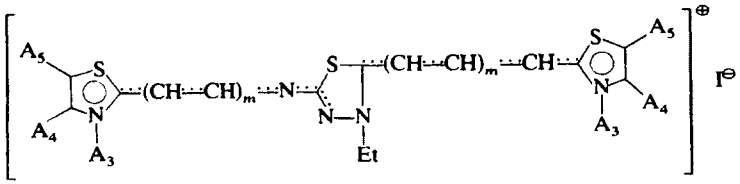
Z_1	Z_2	m	A_3	A_4	A_5	B_3	C_3	R	m.p. (°C)	λ(nm)	Ref.
O	S	0	Me	*p*-$MeOC_6H_4$	*p*-(1,1,3,3,-tetra-MeBu)C_6H_4O	Me	Et	—	248	608	1(p. 656), *351*, *593*
O	S	0	Et	*p*-$MeOC_6H_4$	Ph	Me	Et	—	281	613	*593*
O	S	0	Et	*p*-$MeOC_6H_4$	OPh	Me	Et	—	233	607	*351*, *593*
O	S	0	Me	*p*-Xylyl	Ph	Me	Et	—	277	624	1(p. 656), *593*
S	S	0	Me	*p*-$MeOC_6H_4$	OPh	Me	Et	—	286	613	1(p. 656), *351*, *593*
S	S	0	Me	*p*-$MeOC_6H_4$	*p*-(1,1,3,3,-tetra-MeBu)C_6H_4O–	Me	Et	—	258	613	1(p. 656), *351*, *593*
S	S	0	Me	β-Naphthyl	*p*-MeC_6H_4S-	Me	Et	—	276	613	*593*
S	S	0	Et	Ph	Ph	Me	Et	—	298	622	*593*
S	S	0	Et	Ph	*p*-MeC_6H_4S–	Me	Et	—	224	615	*351*, *593*
S	S	0	Et	*p*-BrC_6H_4	*p*-BrC_6H_4O-	Me	Et	—	236	618	*351*, *593*
S	S	0	Et	*p*-ClC_6H_4	*p*-ClC_6H_4O–	Me	Et	—	275	600	*351*, *593*
S	S	0	Et	*p*-$MeOC_6H_4$	Ph	Me	Et	—	288	623	*593*
S	S	0	Et	*p*-$MeOC_6H_4$	OPh	Me	Et	—	253	617	*351*, *593*
S	S	0	Et	3,4-diMeO C_6H_3	Ph	Me	Et	—	288	622	*593*
S	S	0	Et	β-Naphthyl	*p*-MeC_6H_4S–	Me	Et	—	—	—	*351*
S	S	1	Et	Ph	Ph	Et	Allyl	H	—	682	1(p. 674), *625*
S	S	1	Et	Ph	Ph	Et	Allyl	Me	—	730	1(p. 674, *625*
S	S	1	Et	Ph	Ph	Et	Allyl	OEt	—	710	1(p. 674), *625*
S	S	1	Et	Ph	Ph	Et	CH_2COO Et	SEt	—	752	1(p. 674), *625*
S	NPh_2	0	Et	*p*-$MeOC_6H_4$	OPh	Me	—	—	193	600	*351*, *593*

TABLE 315A. AZA CYANINES



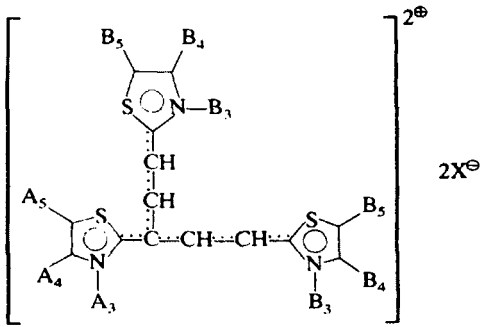
H	*n*	A_3	A_4	A_5	C_3	R	X	λ (n.m.)	Ref.
2-(5,6-diMe-benzoxazolyl)	1	Me	Me	H	Et	H	I	524	*562*
2-Benzothiazolyl	1	Et	Ph	Me	Et	Et	I	—	*562*
2-(5-EtO-benzoselenazolyl)	0	Et	Ph	Me	Me	—	Br	460	*562*

TABLE 315B



m	A_3	A_4	A_5	Ref.
0	Me	*p*-MeC_6H_4	Ph	629, 630
1	Me	H	H	629, 630
1	Et	Ph	Ph	629, 630

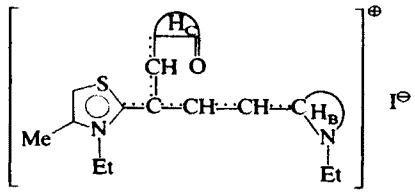
TABLE 321A. α-BRANCHED CYANINES: NEOCYANINES



A_3	A_4	A_5	B_3	B_4	B_5	X	m.p. (°C)	λ(nm)	Ref.
Me	H	H	Me	H	H	I	—	—	374 e
Me	Me	H	Me	Me	H	I	—	—	1(p. 629), *344*, 631
Me	Me	H	Me	Me	H	Nicotinate	148	—	360, 632 a
Me	Me	H	Me	Me	H	Asparate	—	—	633 a
Me	Me	H	Me	Me	H	Glucuronate	—	—	634 a
Me	Me	H	Me	Me	H	Glutamate	—	—	634 a
Me	Me	H	Me	Me	H	EtOCO(CN)C=CH-C(CN)COOEt	170	595	500
Me	Me	H	Me	Me	H	CN-CH=C(CN)CH-(CN)CN	244	600	500
Me		$-(CH_2)_3-$	Me		$-(CH_2)_3-$	I	264	620	*399*
Et	H	H	Et	α-(4-MeO-naphthyl)	H	I	247	605	*388*
Et	H	Styryl	Et	Styryl	H	I	—	668	*357*

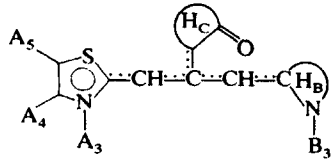
Et	Me	H	Et	Me	H	I	—	587	1(p. 629), *13*
Et	Me	H	Et	CH_2-thiazolinyl	CH_2-thiazolinyl	ClO_4	—	—	*534*
Et	*p*-(*p*-$MeOC_6H_4$)C_6H_4	H	Et	*p*-(*p*-$MeOC_6H_4$)C_6H_4	H	I	190	638	*388*
Et	*p*-$PhOC_6H_4$	H	Et	*p*-$PhOC_6H_4$	H	I	180	600	*388*
Pr	Me	H	Pr	Me	H	I	208	—	*635*
i-Am	Me	H	*i*-Am	Me	H	I	200	—	*635*
n-Heptyl	Me	H	*n*-Heptyl	Me	H	Cl	—	—	146, 636
n-Heptyl	Me	H	*n*-Heptyl	Me	H	Nicotinate	80	—	360

TABLE 321B



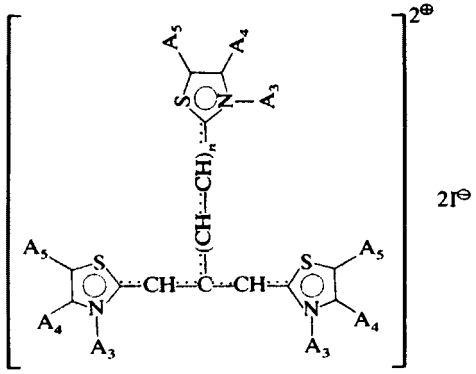
H_B	H_C	m.p. (°C)	λ(nm)	Ref.
2-Thiazolinyl	N-Et-rhodanine	214	536	1(p. 629), *13, 534*
2-Benzothiazolyl	1-Ph-3-Et-thiohydantoine	225	576	1(p. 629), *13, 534*

TABLE 322A. β-BRANCHED HOLOPOLAR CYANINES



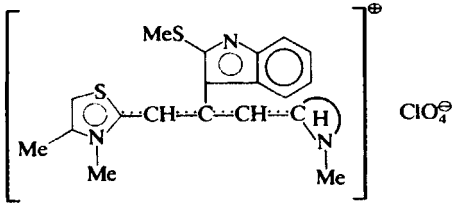
H_B	H_C	A_3	A_4	A_5	B_3	m.p. (°C)	Ref.
2-(4,5-diPh-thiazolyl)	4-(1-Ph-3-Me-2,3′-sulfopropenyl pyrazolonylidene)	Me	Ph	Ph	Me	320	*637–640*
2-Benzothiazolyl	4-(1-Ph-3-Me-2,3′-sulfopropenyl pyrazolonylidene)	Me	Ph	Ph	Me	320	*637–640*
2-Benzothiazolyl	3-(Chroman-2,4-dione)	Et	H	H	Et	—	*641*
2-(6-MeO-benzo	4-(1-Ph-3-Me-2,3′-sulfopropenyl pyrazolonylidene)	Me	Ph	Ph	Me	283	*637–640*
2-(5,6-diMeO-benzo-	4-(1-Ph-3-Me-2,3′-sulfopropenyl pyrazolonylidene)	Me	Ph	Ph	Me	329	*637–640*

TABLE 322B. β-BRANCHED CYANINES



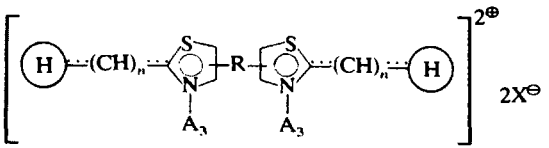
n	A_3	A_4	A_5	m.p. (°C)	Ref.
0	Me	H	H	250	495
0	Me	Me	H	283	495
1	Me	H	H	—	1(p. 677), *485*, 530
1	Me	Me	H	—	1(p. 677), *485*, 530
1	Me	Ph	H	—	1(p. 677), *485*
1	Et	H	H	—	1(p. 677), *485*, 530
1	Et	Me	H	—	1(p. 677), *485*
1	Et	Et	H	—	530
1	Et	$-(CH_2)_4-$		—	1(p. 628), *400*
1	Et	Ph	H	—	1(p. 677), *485*
1	Et	α-Benzofuryl	H	—	*468*
1	Et	α-Thienyl	H	—	*470*, 494

TABLE 322C



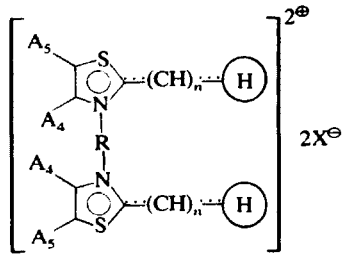
H	m.p. (°C)	λ(nm)	Ref.
2-(4-Ph-thiazolyl)	125	585	*642*
2-Benzothiazolyl	191	620	*642*

TABLE 41A. TETRANUCLEAR CYANINES: TWO CYANINES



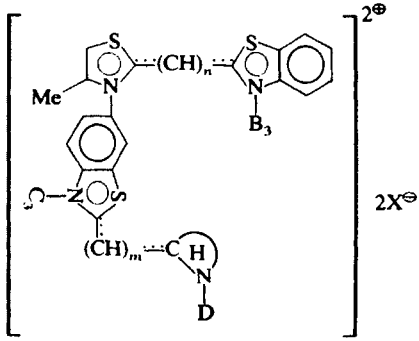
H	n	R	Link	A_3	X	m.p. (°C)	λ(nm)	Ref.
p-$Me_2NC_6H_4$	2	p-C_6H_4	4–4′	Me	I	—	—	*643*
p-$Me_2NC_6H_4$	4	p-C_6H_4	4–4′	Me	I	—	—	*643*
p-$Me_2NC_6H_4N$=	1	p-C_6H_4	4–4′	Me	I	—	—	*643*
1,1,3,-triMe-indolenyl	3	p-C_6H_4	4–4′	Me	ClO_4	281	544	*506*
1,1,3,-triMe-indolenyl	3	p-C_6H_4	5–5′	Me	ClO_4	275	530–602	*506*
2-(6-Me-1-Et-quinolyl)	1	—	4–4′	Et	I	245	497	*644, 645*
2-(3-Et-benzoxazolyl)	3	—	4–4′	Et	I	273	532	*644, 645*
2-(3-Et-benzoxazolyl)	5	—	4–4′	$(CH_2)_2OPh$	I	193	613	*644, 645*
2-(3-Et-benzothiazolyl)	3	—	4–4′	Et	I	235	577	*644, 645*
2-(3-Et-5,6-methylene dioxy-benzothiazolyl)	3(μ-Me)	—	4–4′	Et	I	249	600	*644, 645*
2-(3-Et-5,6-methylene dioxy-benzothiazolyl)	3(μ-Me)	—	4–4′	Et	I	267	573	*644, 645*
2-(3-Et-5-MeO-benzoselenazolyl)	3	—	4–4′	Et	I	230	571	*644, 645*
2-(3-Me-β-naphthothiazolyl)	3	—	4–4′	Et	I	236	590	*644, 645*

TABLE 41B



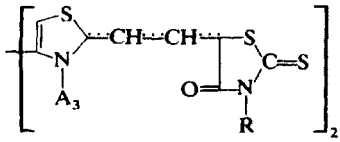
H	n	R	A_4	A_5	X	m.p. (°C)	λ(nm)	Ref.
p-$Me_2NC_6H_4$	2	$(CH_2)_2$	Ph	H	I	281	—	1(p. 677), *646*
2-(1-Et-quinolyl)	1	$(CH_2)_2$	Ph	H	I	292	—	1(p. 677), *646*
2-(1-Bu-quinolyl)	3	$(CH_2)_2$	Ph	H	ClO_4	—	—	1(p. 677), *646*
2-(3-Et-benzoxazolyl)	3	$(CH_2)_2$	Me	H	I	208	—	1(p. 677), *646*
2-(3-Et-benzoxazolyl)	3	$(CH_2)_2$	Ph	H	I	288	—	1(p. 677), *646*
2-(5-Me-3-Et-benzoxazolyl)	3	$(CH_2)_2$	Ph	H	I	261	—	1(p. 677), *646*
2-(5,6-diMe3-Et-benzoxazolyl)	3	$(CH_2)_2$	Me	H	I	—	—	1(p. 678), *460*
2-(5-Ph-3-Et-benzoxazolyl)	3	$(CH_2)_2$	Ph	H	I	314	—	1(p. 677), *646*
2-(3-Et-benzothiazolyl)	3	$(CH_2)_2$	Ph	H	I	298	—	1(p. 677), *646*
2-(3-Et5-Cl-benzothiazolyl)	3	$(CH_2)_2$	Ph	H	I	292	—	1(p. 677), *646*
2-(3-Et-β-naphthothiazolyl)	3	$(CH_2)_2$	Ph	H	I	254	—	1(p. 677), *646*
2-(3-Et-benzoxazolyl)	3	$(CH_2)_3$	Ph	H	I	162	—	1(p. 677), *646*
2-(1,1,3-triMe-indolenyl)	3	p-C_6H_4	H	H	ClO_4	—	—	*339*
2-(1,1,3-triMe-indolenyl)	3	p-C_6H_4	H	Ph	ClO_4	—	—	*339, 647*
2-(1,1,3-triMe-indolenyl)	3	m-C_6H_4	H	Ph	ClO_4	—	—	*339, 647*
2-(1,1,3-triMe-indolenyl)	3	p-C_6H_4	Me	H	ClO_4	230	516–548	*339, 506*
2-(1,1,3-triMe-indolenyl)	3	p-C_6H_4	Ph	H	ClO_4	—	—	*647*
2-(1,1,3-triMe-indolenyl)	3	m-C_6H_4	Ph	H	ClO_4	—	—	*647*
2-(3-Et-2-Me-benzothiazolyl)	3	p-C_6H_4	Me	H	ClO_4	—	—	*339*

TABLE 41C

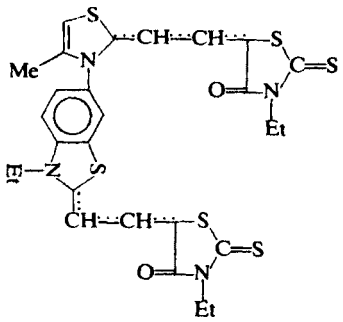


H	m	n	B_3	C_3	D	X	m.p. (°C)	Ref.
2-Quinolyl	3	1	Me	Me	Me	I	300	*118*
2-Benzothiazolyl	1	1	Me	Me	Me	ClO_4	300	*118*
2-Benzothiazolyl	3	1	Me	Me	Et	ClO_4	310	*118*
2-Benzothiazolyl	3	3	Et	Et	Et	ClO_4	240	*118*

TABLE 42 TWO NEUTROCYANINES LINKED BY THE THIAZOLE RING

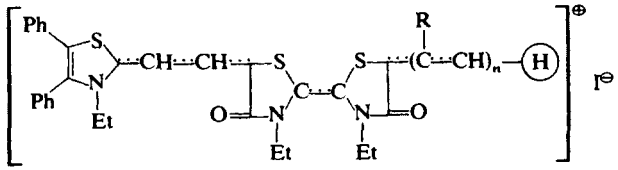


A_3	R	Ref.
Me	Et	1 (p. 626), *648*
Me	Allyl	1(p. 626), *648*
Me	Ph	1(p. 626), *648*
Et	Allyl	1(p. 626), *649*, *650*
Et	Ph	1(p. 626), *649*, *650*



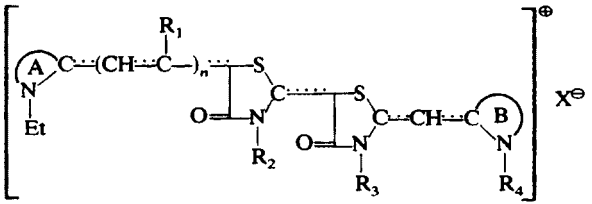
m.p. = 325°C
Ref. 118

TABLE 43A TWO NEUTROCYANINES LINKED BY THE KETOMETHYLENE

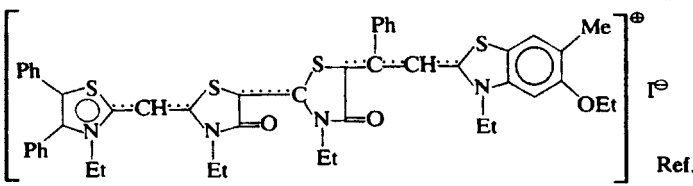


H	*n*	R	Ref.
4-(1-Et-quinolylidene)	1	H	651–654
2-(3-Et-benzothiazolylidene)	2	H	651–654
2-(3-Et-5,6-diMe-benzothiazolylidene)	1	Ph	651–654
2-(3-Et-5-EtO-6-Me-benzothiazolylidene)	1	Ph	651–654
2-(3-Et-5,6-diMe-benzoselenazolylidene)	1	Ph	651–654
5-(5-MeO-benzoselenazolylidene)	1	Ph	651–654

TABLE 43B

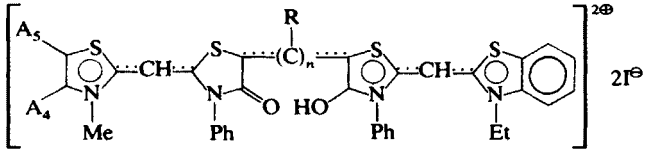


A	B	n	R_1	R_2	R_3	R_4	X	m.p. (°C)	λ(nm)	Ref.
4-Quinolyl	4,5-diPh-thiazolyl	1	H	Et	Et	Et	I	—	708	*665*
4-(3,4-diMeOC_6H_3)-5-Ph-thiazolyl	4-(3,4-diMeOC_6H_3)-5-Ph-thiazolyl	1	H	Et	Et	Et	OTs	192	650	1 (p. 656), 593
4-(*p*-MeO-C_6H_4)-5-Ph-thiazolyl	2-β-Naphthothiazolyl	1	H	Et	Et	Et	OTs	266	620	1(p. 656), *593*
5-MeO-benzothiazolyl	4,5-diPh-thiazolyl	1	Ph	CH_2COOMe	Et	Allyl	I	—	657	*665*
5,6-diMe-benzothiazolyl	4,5-diPh-thiazolyl	1	Ph	Et	Et	Et	I	—	649	*665*
5,6-diMe-benzothiazolyl	4,5-diPh-thiazolyl	1	Ph	CH_2Ph	CH_2Ph	Et	I	—	650	*665*
5-EtO-6-Me-benzothiazolyl	4,5-diPh-thiazolyl	1	Ph	Et	Et	Et	I	—	659	*665*
5,6-diMe-benzo-selenazolyl	4,5-diPh-thiazolyl	1	Ph	Et	Et	Et	I	—	651	*665*
5,6-diMe-benzo-selenazolyl	4,5-diPh-thiazolyl	1	Ph	CH_2Ph	CH_2CH_2OH	C_3H_6-COOH	Br	—	652	*665*
5-MeO-benzoselenazolyl	4,5-diPh-thiazolyl	1	Ph	Et	Et	Et	I	—	650	*665*
Benzothiazolyl	4,5-diPh-thiazolyl	2	H	Et	Et	Et	I	—	690	*665*



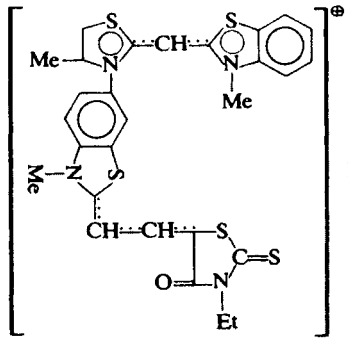
Ref. 655

TABLE 43C

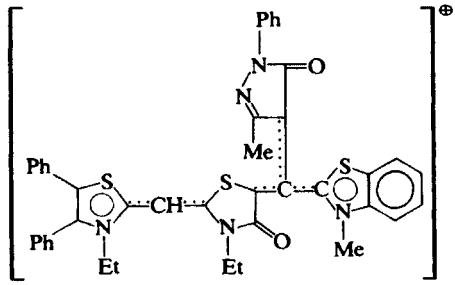


A_4	A_5	n	R	m.p. (°C)	λ(nm)	Ref.
Me	H	1	Pr	279	518–437	1(p. 676), *461*, *462*
Me	H	5	H	237	420–734	1(p. 676), *461*, *462*
Ph	Me	1	Et	225	627	1(p. 676), *461*, *462*

TABLE 44. ONE CYANINE AND ONE NEUTROCYANINE



m.p. = 260°C
Ref. *118*



m.p. = 286°C
$\lambda_{(nm)}$ = 613–645
Ref. 656

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X

Selenazole and Derivatives

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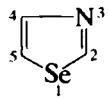
I. INTRODUCTION

1,3-Selenazole is a 5-membered heterocycle of the azole series, containing two heteroatoms. Other members of this group include thiazole and oxazole, whose chemistry is more developed because of their easier access and lower toxicity. The numbering of the heterocyclic system is as follows:



The earliest work on selenazole dates back to 1889, but intensive studies of the compound and its derivatives only really started in 1940. In 1889, the question of the existence under normal conditions of nonsubstituted selenazole was posed as a result of the first studies of the azoles by the group led by Hantzsch.

Hofmann (1), of the Zurich School, was the first to have tried unsuccessfully to prepare the unsubstituted parent compound, selenazole; much later, in 1955, Metzger and Bailly (2) were equally unsuccessful in trying to prepare selenazole from 2-aminoselenazole by reduction of the diazo compound.

This chapter is an attempt to present the important results of studies of the synthesis, reactivity, and physicochemical properties of this series of compounds. The subject was surveyed by Bulka (3) in 1963 and by Klayman and Gunther (4) in 1973. Unlike the oxazoles and thiazoles, there are few convenient preparative routes to the selenazoles. Furthermore, the selenium intermediates are difficult to synthesize and are often extremely toxic: selenoamides tend to decompose rapidly depositing metallic selenium. This inconvenience can be alleviated by choice of suitable reaction conditions. Finally, the use of selenium compounds in preparative reactions is often complicated by the fragility of the cycle and the deposition of metallic selenium.

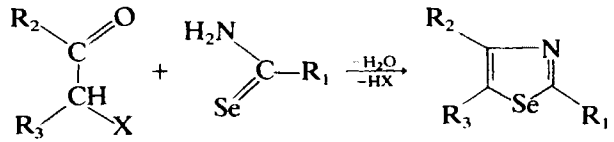
Selenazoles and their derivatives, that is, selenazolines and selenazolidines, are mainly used in cyanine-type dyes and photographic sensitizers as well as in pharmacology and chemotheraphy.

II. GENERAL PREPARATIVE METHODS OF SELENAZOLES

The different functional categories of the selenazoles have been classed in according to the functional priority or to the quantity of prepared compounds.

1. Substituted Alkyl and Arylselenazoles

Hoffmann (1), a student of Hantzsch, used the condensation of selenobenzamide with α-halogenated carbonyl derivatives to prepare a series of 2-phenylselenazoles according to the Scheme 1.



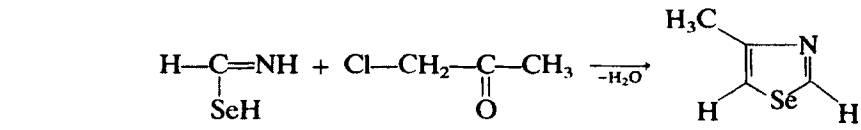
Scheme 1

The alkylselenazoles were prepared much later from selenoacetamide and selenopropionamide (R_1 = Me and Et) (5, 6).

The difficulties posed by the synthesis of 2-alkyl and 2-arylselenazoles substituted in the 4- and 5-positions arise mainly from the preparation of the intermediates, especially the selenoamides.

Thus a second method was envisaged, the reaction of a nitrile, hydrogen selenide, and an α-halogenated ketone in the presence of a condensation catalyst, which can be $POCl_3$ or $POCl_3$ with a Lewis acid such as PCl_3 or anhydrous $ZnCl_2$. The use of fresh $AlCl_3$ leads to the formation of tarry side-products.

The maximum yield of 2-alkylselenazole is 25%. In this way, 4-methylselenazole (7) was obtained starting from hydrogen cyanide, hydrogen selenide and chloroacetone. It is the only known selenazole not substituted in the 2-position. The yield relative to chloroacetone is very low (2.5%) (Scheme 2).



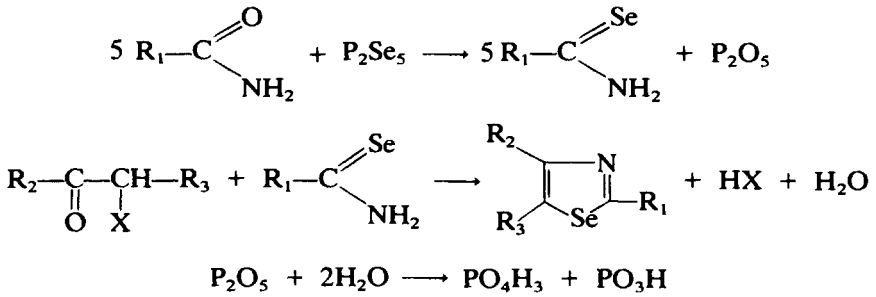
Scheme 2

In thiazole series the application of Tcherniac's method (8), which consists of cyclizing the intermediary iminoketothioether, obtained by reaction of a thiocyanoketone upon a labile hydrogen compound, is suitable and occurs with an average yield of 50%. In selenazole series this cyclization does not happen from selenocyanoketones and by using different acidic media (9).

The O–S exchange method in presence of α-halogenated carbonyl compound is a very good one for thiazole compounds. The thioamide is prepared in situ by the action of amide upon phosphorus pentasulphide with solvent. The α-halogenated aldehyde reacts directly. But the O–Se exchange cannot be performed with α-halogenated carbonyl compounds because of the apparition of phosphoric acid. (Scheme 3). The C–Se bond is very sensitive to acid pH.

Moreover, selenamides are more instable than thioamides; so P_2Se_5 was replaced by Al_2Se_3. In that case the cycle is less broken, but the yield of reaction is not as good.

Lena (9) has used this method to prepare the 2-phenyl-4-methylselenazole and the 2,4-dimethylselenazole. An optimization of the experimental conditions in the O–Se exchange must be necessary.



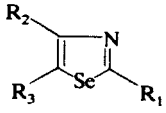
Scheme 3

The physical properties of the principal alkyl- and arylselenazoles synthesized are given in Table X-1 along with the synthetic methods used and bibliographic references.

Alkylselenazoles are oily alkaline liquids possessing a smell similar to that of the corresponding thiazole or pyridine derivatives. The crystalline picrates or 3-methylselenazolium iodides have been used for the purpose of characterization. Alkyl derivatives are partially soluble in water; aryl derivatives are insoluble.

Alkyl and aryl selenazoles are weakly basic, and their quaternary salts are easily hydrolyzed in aqueous solution.

TABLE X-1. ALKYL AND ARYL SELENAZOLES

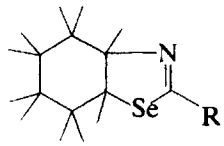


R_1	R_2	R_3	b.p./mm (°C)	m.p. (°C)	m.p. (picrate) (°C)	Ref.
Me	H	H	149/760 32–4/20	—	170	5, 7, 11, 12
H	Me	H	152–3/760	—	197	6
Me	Me	H	163–4/760 56–8/17	—	155	6, 7, 11–13
Me	Me	Me	176/760	—	164	11
Me	Ph	H	—	63–4	—	7, 11–13
Et	Me	H	74–6/20	—	—	5, 11, 12
Ph	Me	H	282–3/737	—	—	1
Ph	Ph	H	—	99	—	1
Ph	Me	COOH	—	206–7	—	1
Ph	Me	COOEt	—	123–4	—	1

It can be noted that the thiazoles are generally more volatile than the corresponding pyridines, while the boiling points of the selenazoles are much higher than others:

	b.p. (°C)		b.p. (°C)		b.p. (°C)
Pyridine	114.8	Thiazole	116.8	Not isolated	—
2-Picoline	129	2-Methyl-thiazole	128	2-Methyl-selenazole	149
3-Picoline	143	4-Methyl-thiazole	130	4-Methyl-selenazole	152.3
2,4-Lutidine	157	2,4-Dimethyl-thiazole	144	2,4-Dimethyl-selenazole	162.4

2-Alkyl or arylhexahydrobenzoselenazoles (Scheme 4) are synthesized by reaction of α-chlorocyclohexylamine with selenocarboxamides (10).

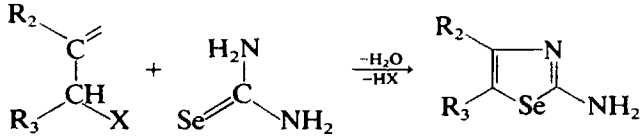


Scheme 4

2. 2-Aminoselenazoles Substituted in the 4- and 5-positions

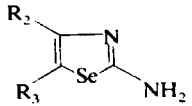
A. *Synthesis from Selenourea*

The replacement of selenoamide by selenourea in the Hantzsch's synthesis (1st method) leads to 2-aminoselenazoles (2, 14, 15). This series of compounds has been well developed, mainly because selenourea is much more easily accessible than the selenoamides, but also because a wide variety of α-halogenated carbonyl compounds are available for the Hantzsch's cyclization reaction (Scheme 5). 2-Aminoselenazole itself was prepared from commercially available chloroacetaldehyde semihydrate



Scheme 5

TABLE X-2. 2-AMINOSELENAZOLES



R_2	R_3	m.p. (°C)	m.p. (picrate) (°C)	m.p. (acetyl derivative) (°C)	m.p. (HCl or HBr derivative) (°C)	Ref.
H	H	121 (121.5)	236 (209)	210	—	1, 2, 14
Me	H	79–80	—	122	—	1
		78–79	225	—	189 (HCl)	16, 18, 19
		99	219	—	223 (HCl)	14
Et	H	63	213	—	—	14
		51–2	220 (dec.)	125–125.5	—	18
Me	Me	108–9	257 (dec.)	155–155.5	HCl 227 (dec.)	18
tBu	H	98.5	212–213	160.5	HBr 196	18
$(CH_2)_4$		125.5–126	240 (dec.)	141	—	18
Ph	H	132–3			—	16, 20
		132	198–200 (dec.)	196.5–197.5	—	1, 2, 18
p-Cl–C_6H_4	H	160–160.5	245–8 (dec.)	263–4	—	18
		160–2	—	269–270	—	20
m-NO_2–C_6H_4	H	194–5	—	306–7	—	20
Ph	Me	141–2	—	206–7	—	20
Ph	Ph	189–190	—	204–5	—	20
Me	COOH	181–2 (~195)	—[a]	200[a]	—	16, 1
Me	COOEt	180–1	—[a]	216–8[a]	—	20
Ph	COOMe	253	—	—	—	17, 21, 22
Ph	CH_2COOH	253	—	—	—	21
Ph	COOEt	250 (dec.)	—	—	—	21
Ph	$(CH_3)_2COOH$	250 (dec.)	—	—	—	21
p-Me–C_6H_4	CH_2COOH	246 (dec.)	—	—	—	21
p-Me-C_6H_4	COOMe	246 (dec.)	—	—	—	21
NH_2	H	—	220–5	—	250 (HCl)	15

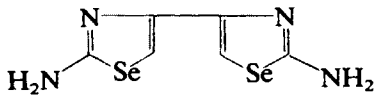
[a] These results seem very surprising because of the little difference between the melting point of the compound with COOH and COOEt.

(14, 2) and from α,β-dichlorodiethylether (1). Selenourea is obtainable by action of hydrogen selenide on an aqueous solution of cyanamide at 50 to 60°C (14) in the form of colorless crystals, which after recrystallization melt at 217°C. The yield of selenium reaches 80%. The cyanamide solution is obtained by the action of carbon dioxide upon calcium cyanamide at 0°C followed by neutralization and precipitation of the residual calcium with oxalic acid.

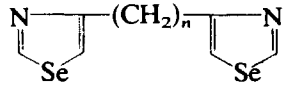
4-Methyl-2-aminoselenazole and 4-ethyl-2-aminoselenazole were prepared similarly from 2-chloropropanal and 2-chlorobutanal, respectively (14). With α-haloketones, 2-aminoselenazoles, substituted in the 4- and 5-positions with alkyl or aryl groups, are obtained (1, 2, 16). α-Haloketoacids or their esters with selenourea give 2-amino-5-carboxy selenazoles or their corresponding esters (1, 16, 17).

The most important 2-aminoselenazoles, along with their physical properties are shown in Table X-2.

With α-halogenated carbonyl derivatives such as α,α'-dibromobiacetyl, $Br{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}Br$, and selenourea, 2,2'-diamino-4,4'-biselenazole (**1**) can be obtained (Scheme 6) (18). 4,4-Biselenazole derivatives ($n = 0$) (**2**) (95) (Scheme 6), as well as the corresponding α,ω bis (selenazol-4-yl) alkanes ($n = 3, 4$) may be synthesized with dibromo diacetyl or other α,α'-dibromo)1,2-diketones .



1



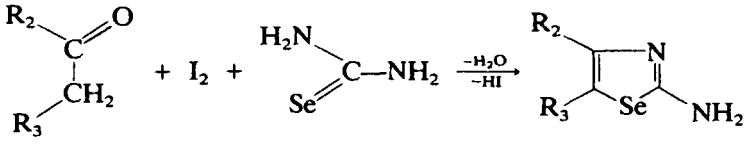
2

Scheme 6

The dibromohydrate is first produced, and treatment with ammonia gives the free base, which after recrystallization in nitrobenzene gives brown crystals (m.p. 215°C). The picrate decomposes around 254°C.

2,4-Diaminoselenazole was obtained by the action of selenourea on chloracetonitrile (15). Its salts are fairly unstable and decompose to give metallic selenium. All attempts to obtain the free base or 2,4-dihydroxyselenazole from 2,4-diaminoselenazole hydrochloride were unsuccessful and led to decomposition of the heterocycle.

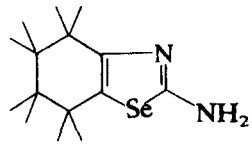
As in the case of the thiazoles, a variation on the Hantzsch's method has been used. This consists of using a nonhalogenated carbonyl derivative directly in the presence of iodine in the reaction with selenourea (Scheme 7) (20). However, in this case the reaction with selenourea is slower than with thiourea, and normally an excess of carbonyl compound is used.



Scheme 7

For 2-amino-4-(*m*-nitrophenyl) selenazole, the yield is particularly high. This has been explained by the oxidizing effect of the nitro group, which liberates iodine from the hydrogen iodide eliminated in the condensation reaction.

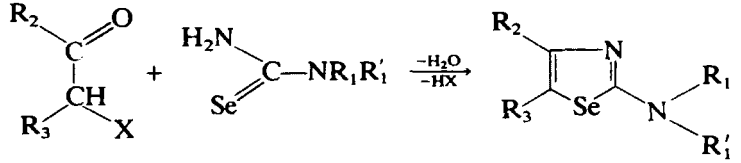
Derivatives analogous to benzoselenazole but possessing an alicyclic ring, such as 2-amino-4,5,6,7-tetrahydrobenzoselenazole (Scheme 8) are obtained from α-chlorocyclohexanone and selenourea (18, 20).



Scheme 8

B. *Synthesis from N-substituted Selenoureas*

N-substituted selenoureas give the same condensation reaction (Scheme 9, Table X-3).

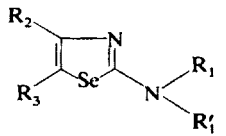


Scheme 9

Mono (H_2N–C(=Se)–NHR_1) or disubstituted (H_2N–C(=Se)–NR_1R_1') selenoureas can be used. The group R_1, R_1' can be hydrogen, alkyl, aryl, acyl, or benzoyl.

The selenoureas needed for condensation can usually be prepared by addition of hydrogen selenide to a solution of the corresponding cyanamides or carbodiimides. They can be less dangerously and quite

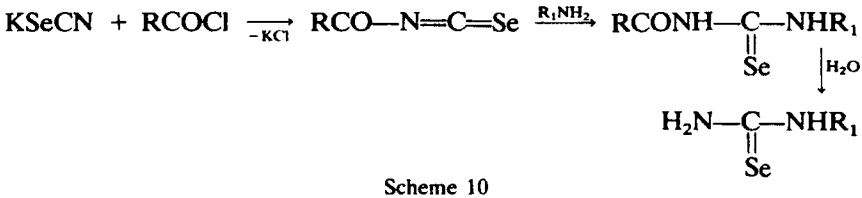
TABLE X-3a. 2-(ALKYLAMINO) AND 2-(ARYLAMINO)-SELENAZOLES



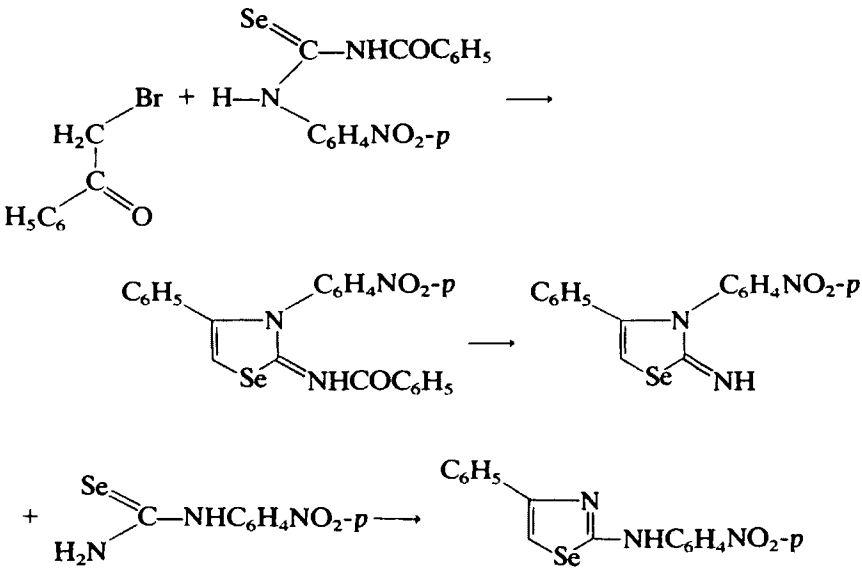
R_1	R_1'	R_2	R_3	b.p./mn (°C)	m.p. (°C)	m.p. (picrate) (°C)	m.p. (acetyl derivative) (°C)	m.p. (HCl or HBr derivative) (°C)	Ref.
Me	H	Me	H	126–7/3	69	213–4 (dec.)	—	—	26
Me	Me	Me	H	—	—	176–8 (dec.)	—	121–4 (HCl)	27
Et	Et	Me	H	125–7/20	—	166–7	—	—	26, 27
Ph	H	H	H	—	145	—	105	—	28
Ph	H	H	Me	—	132	—	120	—	28
Ph	H	Me	H	—	103	204–6 (dec.)	91	154 (HCl)	27, 28
Ph	H	Me	Me	—	81	—	121	129 (HCl	28
Ph	H	Me	CO_2Et	—	144	—	172	185 (HCl)	28
Ph	H	Et	H	—	78	—	98	143 (HCl)	28
Ph	H	Ph	H	—	132	—	134	191 (HBr)	28, 29
Ph	H	Ph	Ph	—	162	—	187	196 (HCl)	28, 29
Ph	H	p-MeC_6H_4	H	—	128	—	160	198 (dec.) (HCl)	28
Ph	H	p-$MeOC_6H_4$	H	—	149	—	93	243 (dec.) (HCl)	
Ph	H	p-ClC_6H_4	H	—	175	—	148	238 (dec.) (HBr)	28
Ph	H	p-$NO_2C_6H_4$	H	—	231	—	132	251 (HBr)	28
p-MeC_6H_4	H	H	H	—	127	207	—	—	28
p-MeC_6H_4	H	Me	H	—	105	—	102	—	28
p-MeC_6H_4	H	Et	H	—	106	—	106	105 (HCl)	28
p-MeC_6H_4	H	Ph	H	—	138	—	147	199 (HBr)	28
p-MeC_6H_4	H	p-MeC_6H_4	H	—	141	—	167	218 (dec.) (HCl)	28
o-MeC_6H_4	H	H	H	—	123	—	80	—	28
o-MeC_6H_4	H	Me	H	—	127 (dec.)	—	89	176 (dec.) (HCl)	28

o-MeC_6H_4	H	Et	H	—	118	206 (dec.)	—	—	28
o-MeC_6H_4	H	Ph	H	—	135	—	130	202 (HBr)	28
o-MeC_6H_4	H	*p*-MeC_6H_4	H	—	143	—	128	188 (dec.) (HCl)	28
p-$MeOC_6H_4$	H	H	H	—	125	180	—	—	28
p-$MeOC_6H_4$	H	Me	H	—	118	—	135	203 (dec.) (HCl)	28
p-$MeOC_6H_4$	H	Et	H	—	144	—	122	109 (HCl)	28
p-$MeOC_6H_4$	H	Ph	H	—	188	—	176	201 (HCl)	28
p-$MeOC_6H_4$	H	*p*-MeC_6H_4	H	—	180	—	160	214 (HCl)	28
p-$MeOC_6H_4$	H	*p*-ClC_6H_4	H	—	219	—	158	248 (dec.) (HBr)	28
o-$MeOC_6H_4$	H	H	H	—	80	195 (dec.)	—	—	28
o-$MeOC_6H_4$	H	Me	H	—	99 (dec.)	—	101	208 (dec.) (HBr)	28
o-$MeOC_6H_5$	H	Et	H	—	54	—	104	—	28
o-$MeOC_6H_4$	H	Ph	H	—	74	—	147	208 (HBr)	28
o-$MeOC_6H_4$	H	p-MeC_6H_4	H	—	159	—	151	202 (HCl)	28
p-ClC_6H_4	H	*p*-ClC_6H_4	H	—	175	—	178	236–7 (dec.) (HBr)	28

smoothly synthesized (101, 25) according to Douglass (24) via the isoselenocyanates by the alkaline hydrolysis of the corresponding acyl-substituted selenoureas (Scheme 10). But in this way one cannot obtain selenourea itself, because the 1-benzoyl-2 selenourea is completely destroyed by the alcaline or acidic hydrolysis. In this case one may first condense the 1-benzoyl-2-selenourea with the α-haloketone followed by hydrolysis of the resulting derivative of 2-benzamidoselenazole to the 2-aminoselenazole (4). This method cannot be successful for 1-acyl-substituted 3-alkyl(aryl)-2-selenoureas, because derivatives of Δ4-selenazolines are formed instead of selenazoles. The ring closure occurs due to the reduced nucleophile character of the acylated amino group with the other nitrogen atom of the selenourea, by giving 2-acylimino-3-alkyl(aryl)-Δ4-selenazolines. For instance the reaction of 1-benzoyl-3-*p*-nitrophenyl-2-selenourea with phenacyl bromide forms the 2-benzoylimino-3-*p*-nitrophenyl-4-phenyl-Δ4-selenazoline (Scheme 11). It



Scheme 10

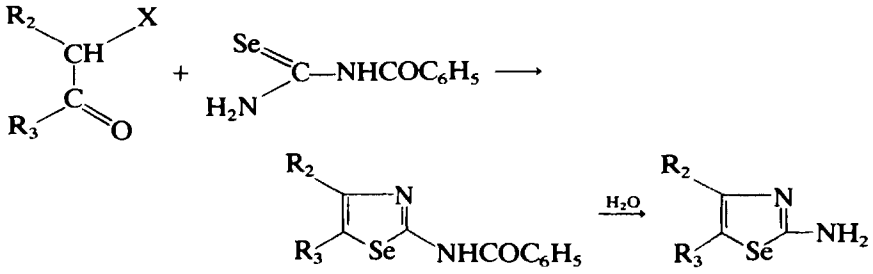


Scheme 11

gives on acidic hydrolysis the 2-imino-3-*p*-nitrophenyl-4-phenyl-Δ4-selenazoline (102). This is not identical with the 2-*p*-nitranilino-4-phenylselenazole (103) obtained from the 1-*p*-nitrophenyl-2-selenourea and phenacyl bromide.

a. HYDROLYSIS OF 2-BENZAMIDOSELENAZOLES (23)

The hydrolysis of 2-benzamidoselenazoles in aqueous phosphoric or sulfuric acid gives 2-aminoselenazoles identical to those prepared from selenourea (Scheme 12).

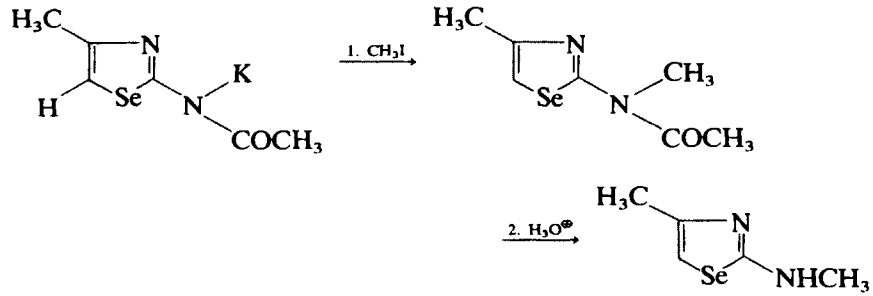


Scheme 12

The advantage of this method is that it avoids the use of hydrogen selenide, necessary for the preparation of selenourea from cyanamide (14). Benzoylselenourea is synthesized by the method of Douglass (24) by the action of potassium selenocyanate on benzoyl chloride in acetone solution.

b. CONDENSATION OF α-HALOKETONES

The condensation of α-haloketones with monosubstituted alkyl or aryl-selenoureas (25) leads to 2-alkylamino- (26, 27) or 2-arylaminoselanazoles (28) while disubstituted selenoureas give 2-(dialkylamino) selenazoles (26, 27) (Table X-3a).

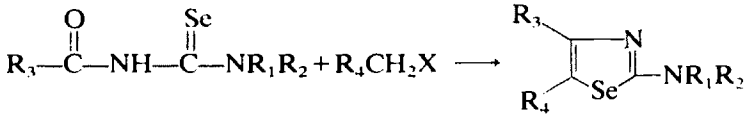


Scheme 13

2-(Methylamino)-4-methylselenazole was obtained by methylation of the potassium salt of 2-acetamido-4-methylselenazole with methyl iodide, followed by hydrolysis (Scheme 13) (26).

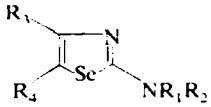
C. *Synthesis from N-acyl Selenoureas* (104)

The general method is described in Scheme 14. The compounds so prepared are listed in Table X-3b.



Scheme 14

TABLE X-3b. 2-(ALKYLAMINO) OR 2-(ARYLAMINO)SELENAZOLES (104)



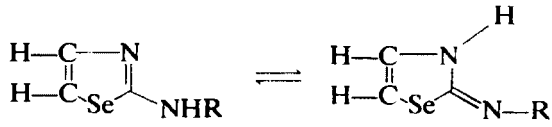
R_1	R_2	R_3	R_4 or Ar	m.p. (°C)	Yield (%)	Ultraviolet λ_{max} (nm) (log ε)		
C_6H_5	CH_3	C_6H_5	C_6H_5CO	138–40 (ethanol)	82	231 s (4.44)	258 s (4.32)	381 (4.08)
C_6H_5	CH_3	C_6H_5	p-BrC_6H_4CO	147–148 (ethanol)	86	237 (4.29)	271 (4.24)	387 (4.11)
C_6H_5	CH_3	C_6H_5	p-ClC_6H_4CO	139–141 (ethanol)	91	237 (4.29)	256 (4.26)	385 (4.08)

D. *General Properties*

2-Aminoselenazoles are crystalline compounds, and with the exception of the nonsubstituted derivative (1) they are stable and practically odorless. They are more basic than 2-aryl- or 2-alkylselenazoles. The hydrochlorides are not easily hydrolyzed in aqueous solution. Some of the N-substituted compounds are oily liquids.

2-Amino- and 2-(methylamino)-4-methylselenazoles can be considered

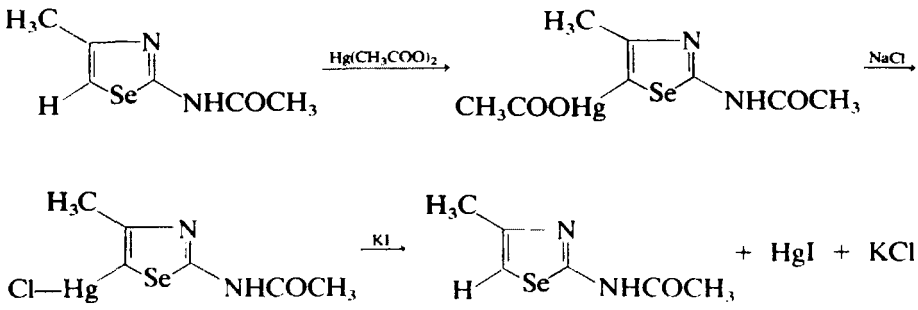
to be in prototropic equilibrium with the 2-iminoselenazolines, as indicated by a comparison of their ultraviolet spectra with that of 2-(diethylamino)-4-methylselenazole (26). In the 2-position there is a substituent with a labile hydrogen (Scheme 15); tautomerism is possible, and this leads to a reduction of the aromatic character of the system. This particularly affects the stability of selenazole and encourages ring opening. These theoretical considerations are in very good agreement with experimental observations (19, 26).



Scheme 15

The 5-position of 2-diethylamino-4-methylselenazole is very reactive. Thus it can undergo coupling with phenyldiazonium chloride or even nitration under mild conditions.

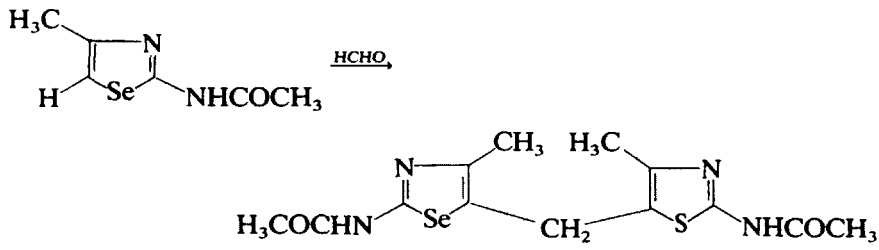
2-Acetamido-4-methylselenazole can react with mercuric acetate to yield 5-mercuriacetate derivatives that can be converted to the chloro derivatives by the action of sodium chloride. Treatment with potassium iodide leads to reduction regenerating the initial compound with loss of mercury (Scheme 16) (4).



Scheme 16

The action of formaldehyde on 2-acetamido-4-methylselenazole can lead to dimerization in the 5-position (Scheme 17) (4).

2-Amino-4-aryl-5-acetic acid selenazoles were used by Knott (21) as intermediates in the preparation of 1',2',4,5-naphthoselenazoles (21, 30, 31).

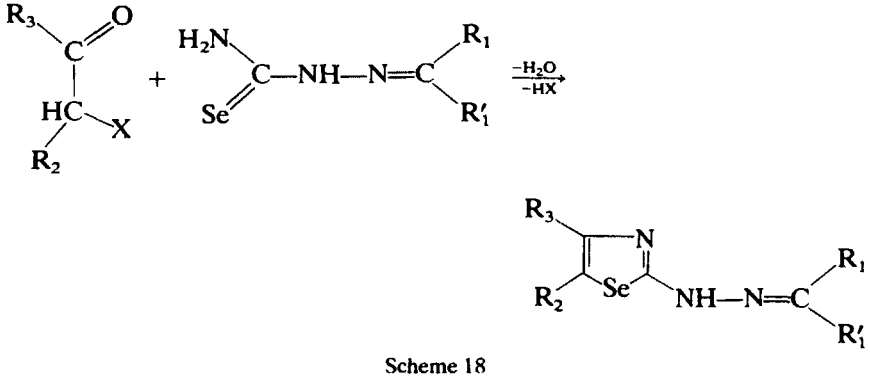


Scheme 17

From the point of view of reactivity, there is little difference between 2-amino-selenazoles and aryl- or alkyl-2-aminoselenazoles, except that the *N*-aryl derivatives are generally less basic and that their salts are more easily hydrolyzed.

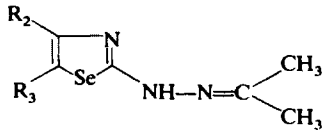
3. 2-Hydrazinoselenazoles and 2-Isopropylidenehydrazino or 2-Benzylidenehydrazinoselenazoles

If in the Hantzsch's synthesis, selenoamide is replaced by a selenosemicarbazide ($H_2N_1–NH_2–C_3Se–NH_4$), condensation can take place upon any of the three nitrogen atoms of the assymmetric molecule. To obtain a hydrazine-type structure, the nitrogen in the 1-position is blocked by forming a hydrazone. Thus selenosemicarbazones were obtained with acetone ($R_1 = R_2 = Me$) and with benzaldehyde ($R_1 = Ph$, $R_2 = H$). Reaction of these selenosemicarbazones with α-halocarbonyls leads to 2-isopropylidenehydrazino or 2-benzylidenehydrazinoselenazoles (32, 33) (Scheme 18), (Tables X-4 and X-5).



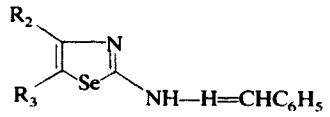
Scheme 18

TABLE X-4. 2-ISOPROPYLIDENE HYDRAZINOSELENAZOLES (32, 33)



R_2	R_3	m.p. (°C)	m.p. (HCl or HBr derivative) (°C)
H	Me	156–7 (dec.)	156–7 (dec.) (HBr)
Me	H	101	171–2 (dec.) (HCl)
Me	Me	138 (dec.)	173–5 (dec.) (HCl)
Ph	H	108–9	187 (dec.) (HCl)
p-MeC_6H_4	H	129	220 (dec.) (HCl)
p-$MeOC_6H_4$	H	125	207 (HCl)
p-ClC_6H_4	H	153	223 (HBr)
p-BrC_6H_4	H	152	216 (dec.) (HCl) 227 (dec.) (HBr)
Ph	Ph	172 (dec.)	—
Me	COOEt	154–5 (dec.)	169–170 (dec.) (HCl)
Ph	COOEt	150	194 (HCl)

TABLE X-5. 2-BENZYLIDENE HYDRAZINOSELENAZOLES (32, 33)



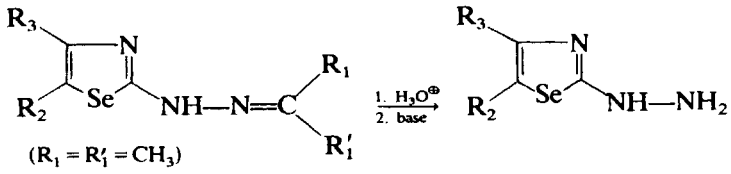
R_2	R_3	m.p. (°C)	m.p. (HCl or HBr derivative) (°C)	m.p. (acetyl derivative) (°C)
Me	H	176	168 (HCl)	—
H	Me	209–210 (dec.)	197 (HBr)	125
Me	Me	192 (dec.)	202 (dec.) (HCl)	112
Me	COOEt	180 (dec.)	204 (dec.) (HCl)	114–5
Ph[a]	H	188 (dec.)	214 (dec.) (HCl)	169–70
Ph	Ph	230 (dec.)	—	150–1
Ph	COOEt	213 (dec.)	—	148
p-MeC_6H_4	H	181	206 (dec.) (HBr)	189
p-$MeOC_6H_4$	H	196 (dec.)	218 (dec.) (HCl)	156
p-ClC_6H_4	H	215	240 (dec.) (HBr)	—
p-BrC_6H_4	H	220 (dec.)	216 (dec.) (HBr)	194

[a] Homolog compound from acetophenone has m.p. = 171°C (33).

Except in the case of the 4,5-diphenyl derivatives, these compounds are obtained as their hydrohalide salts with yields of 70 to 90%: the free heterocyclic base is obtained by treatment with weak alkali.

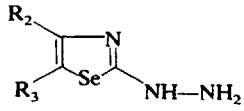
The salts of derivatives possessing phenyl substitutents on the selenazole ring are easily hydrolyzed in aqueous solution.

2-Benzylidenehydrazinoselenazoles are stable to acids and do not decompose with time. The isopropylidene homologs are only stable in the form of the hydrochloride, and they can undergo acid hydrolysis, thus providing a convenient pathway to the free hydrazine (32). Hydrolysis is carried out with hot 2 *N* hydrochloric acid, which, after recooling and filtration, leads to 2-hydrazinoselenazole hydrochloride, yielding the free base upon neutralization (Scheme 19, Table X-6).



Scheme 19

TABLE X-6. 2-HYDRAZINOSELENAZOLES (32)



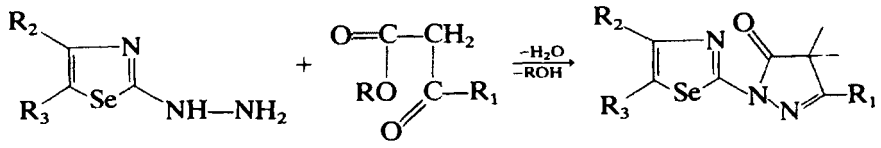
R_2	R_3	m.p. (°C)	m.p. (HCl derivative) (°C)
H	Me	100–2	167–8 (dec.)
Me	Me	115	161–2 (dec.)
Me	COOEt	187 (dec.)	198–210 (dec.)
Ph	H	144–5	166–7 (dec.)
Ph	Ph	199 (dec.)	—
Ph	COOEt	189 (dec.)	179
p-MeC_6H_4	H	166	168
p-$MeOC_6H_4$	H	156	170 (dec.)
p-BrC_6H_4	H	180	187 (dec.)

2-Hydrazinoselenazoles are solids, often in the form of crystals. They possess the characteristic properties common to hydrazines, especially as

reducing agents. Thus they reduce hot Fehling's solution and give, even in the cold, metallic silver from an ammoniacal solution of silver nitrate.

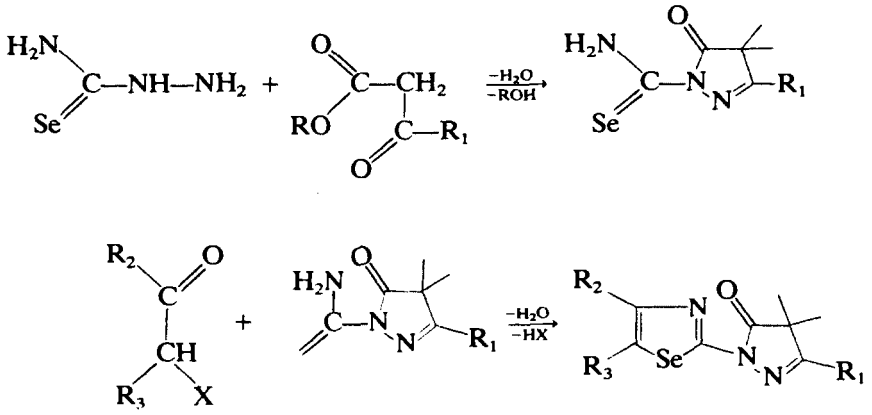
Furthermore, they react with carbonyl derivatives such as acetone and benzaldehyde to give selenohydrazones identical to those prepared from the condensation of selenosemicarbazones with an α-halocarbonyl compound.

Condensation of 2-hydrazinoselenazoles with β-keto esters (R_1–CO–CH_2–COOR) yields 1-(selenazol-2-yl)-3-alkylpyrazol-5-ones (Scheme 20) (34).



Scheme 20

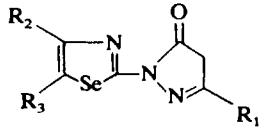
These latter compounds can also be obtained by direct cyclization in a Hantzsch's reaction of the selenosemicarbazone of a β-ketoester, that is, a 1-selenocarbamoyl-3-alkyl-5-pyrazolone (Scheme 21).



Scheme 21

These selenopyrazolones (Table X-7) can undergo further reaction, as described in Section III. 4 (34).

TABLE X-7. 1-SELENAZOL-2-YL-3-ALKYLPYRAZOL-5-ONES (34)

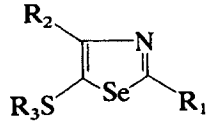


R_1	R_2	R_3	m.p. (°C)	Yield (%)
Me	H	Me	201	58
Me	Me	Me	206–8	62
Me	Me	COOEt	208–9	50
Me	Ph	H	212	76
Me	Ph	Ph	180–1	84
Me	Ph	COOEt	220	41
Me	*p*-BrC_6H_4	H	226	73
Me	*p*-MeC_6H_4	H	210	86
Me	*p*-$MeOC_6H_4$	H	203	75
$C_{17}H_{35}$	Me	COOEt	94–5	44
$C_{17}H_{35}$	Ph	H	90–1	42
$C_{17}H_{35}$	Ph	Ph	73	56
$C_{17}H_{35}$	Ph	COOEt	118–9	8

4. Other Functional Derivatives of Selenazole

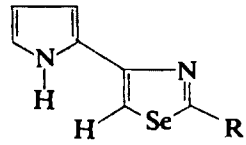
A. *Thioethers*

The preparation of substituted selenazole thioethers (Scheme 22) has already been described (35, 36). These compounds are obtained by the action of a haloketothioether on, for example, selenoacetamide, selenobenzamide, and *N*-ethylselenourea. These selenazoles have not been characterized, but they have been used as intermediates in the preparation of cyanine dyes.



Scheme 22

4-(2-Pyrryl)-selenazoles (Scheme 23), obtained by condensation of 2-chloroacetylpyrrole with selenoamides, are also used in dye chemistry (37).



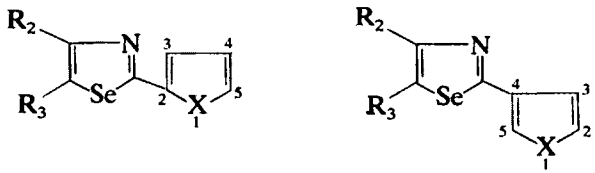
Scheme 23

B. 2-*Mercaptoselenazoles*

2-Mercaptoselenazoles with C_6 to C_{10} cyclic hydrocarbon substituents in the 4-position have been mentioned as giving negative images from photosoluble emulsions (38, 39). Equally cited are other heterocycles such as thiazole, oxazole, or imidazole.

C. *Synthesis of* 2-(2- *or* 4-*furyl, thienyl, or selenienyl)selenazoles*

The general formula of the 2-(2- or 4-furyl, thienyl, or selenienyl)selenazoles is shown in Scheme 24 (40, 105, 106). (Selenienyl-2), (furyl-2), (thienyl-2), and (chloromethyl-4)selenazoles may be prepared by Hantzsch's reaction from selenoamides as described in Scheme 25. Hydrolysis give hydroxymethyl derivatives.



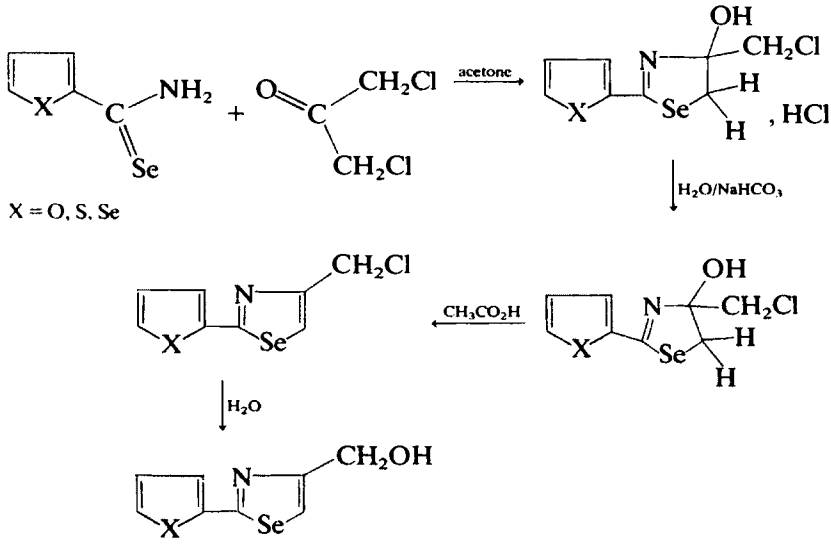
where R_2, R_3 = H, CO_2Et and X = O, S, Se

Scheme 24

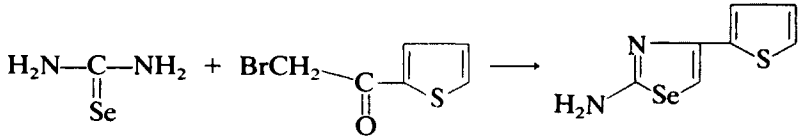
2-Amino-4-(2-thienyl)selenazole (m.p. 132°C, yield = 82%) also has been prepared by condensation of selenourea on 2 bromoacetylthiophene (Scheme 26). In a first step the bromhydrate is obtained (105).

(2- or 4-Furyl, thienyl, or selenienyl)selenoamides on ethyl-α-chloro-α-ethoxalyl acetate as shown in Scheme 27. The diesters may be decarboxylated by a saponification, an acid hydrolysis, and heating to 220°C successively (Scheme 27) (105).

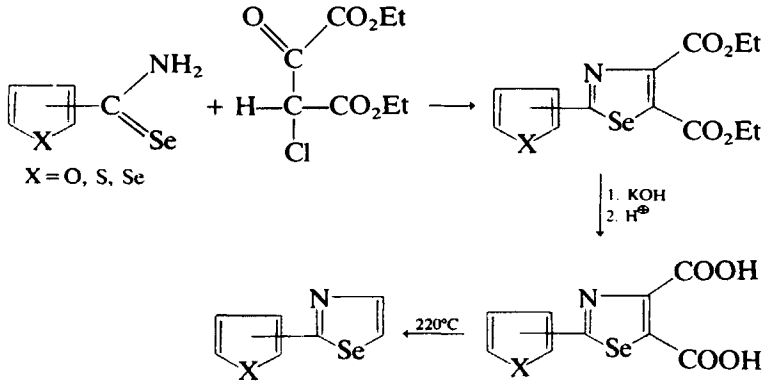
The diesters may react with hydrazine in acidic medium to give 4,7-dioxo-4,5,6,7-tetrahydro[4,5,*d*]azolopyridazine (Scheme 28) (107). The



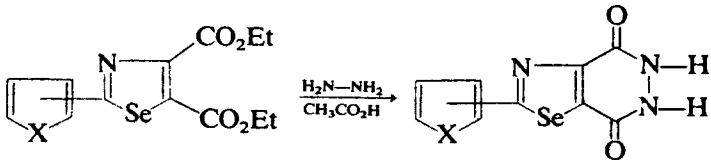
Scheme 25



Scheme 26



Scheme 27



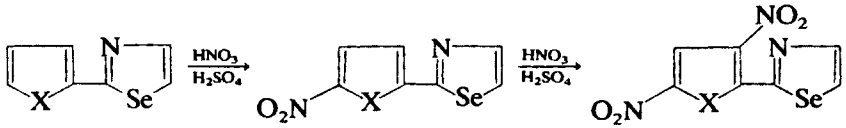
X = O, S, Se

Scheme 28

study of tautomeric equilibrium of azolopyridazines by infrared spectroscopy is in complete agreement with the N–H structure.

The 2-[2-thienyl]selenazole is formylated in the 5-position by action of *n*-butyllithium, dimethyl formamide, and hydrolysis (106).

The nitration of 2-[2-thienyl] and [2-selenienyl] selenazoles is achieved according to Scheme 29 (106).



X = S, Se

Scheme 29

III. REACTIVITY OF THE SELENAZOLE RING AND OF DERIVED COMPOUNDS

A comparison of the reactivity of the heterocycles, selenazole, thiazole, and pyridine, was made by Ochiai (41), who used theoretical considerations to show that the degree of aromaticity was:

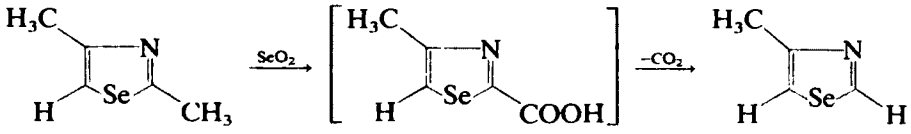
$$\text{selenazole} < \text{thiazole} < \text{pyridine}$$

Furthermore, the strongly metallic character of selenium weakens the C–Se bond and thus favors reactions involving opening of the ring. The basicity of the three heterocycles is approximately in the same order, the nitrogen atom of selenazole and thiazole possessing much the same properties as the heteroatom of pyridine. Of the two carbon atoms ortho to nitrogen, that is, the 2-carbon and the 4-carbon, only the one in the 2-position is fairly active as a result of its interaction with selenium or sulfur. The 4- and 5-positions of thiazole and selenazole are more susceptible to electrophilic substitution than the 3- and 5-positions of pyridine. This is particularly true of the 5-position of selenazole. Thus it can be said that the 2- and 5-positions of the selenazoles and thiazoles

correspond to the para position of benzene, while the 2- and 4-positions correspond to the meta position. The 2-position of selenazole seems to be less reactive towards nucleophilic reagents than that of thiazole (19); however, being based on few experimental results, due to difficulties in preparing suitably substituted selenazoles, this hasty conclusion merits confirmation.

Thus Haginiwa (19) has studied the reactivity of the 2-position of selenazoles towards nucleophilic substitution, especially amination. The reaction of 4-methylselenazole with sodium amide in decalin at high temperature gave only rupture of the selenazole ring. It must be noted, however, that such experiments are limited because of the difficulties resulting from the preparation of 4-methylselenazole or other substrates unsubstituted in the 2-position. All attempts by Haginiwa (19) to diazotize 2-amino-4-methyselenazole led to ring destruction. Similar, later, investigations by Metzger and Bailly (2), who studied the deamination of 2-amino-4-phenylselenazole, were also unsuccessful.

The reaction of 2,4-dimethylselenazole with an excess of benzaldehyde gives a monostyryl derivative exclusively (12). Oxidation of 2,4-dimethylselenazole with selenium dioxide yields 4-methylselenazole (Scheme 30) (4).



Scheme 30

This implies that only the 2-methyl group is sufficiently active to undergo oxidation to a carboxylic acid intermediate that then undergoes rapid decarboxylation.

The greater reactivity of the 5-position of selenazoles, compared to thiazoles, toward electrophilic substitution has also been demonstrated (19). Substituents in the 2-position possessing a mesomeric donor effect increase the reactivity, but, as Haginiwa (19) observed, also increase the tendancy to ring opening.

Thus reactions of the selenazole ring are mainly limited to the 5-position, especially for 2-aminoselenazoles and 2-hydrazinoselenazoles that undergo electrophilic substitution.

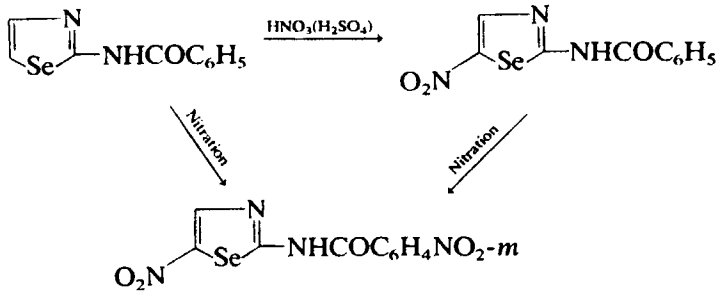
All attempts to prepare selenazole derivatives by the Gatterman (formylation) or Friedel–Crafts (alkylation) methods failed (19, 26), indicating that the electrophilic reactivity of the 5-position is less than that of benzene or toluene.

1. Electrophilic Substitution Reactions

A. *Nitration*

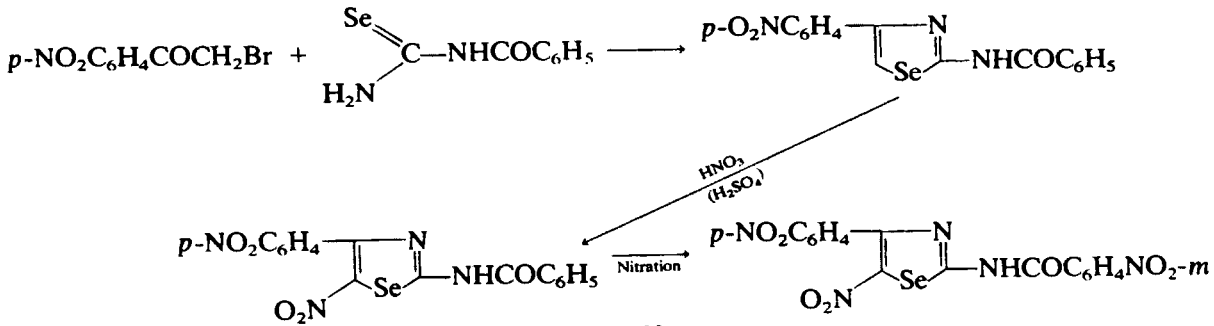
Nitration in the 5-position of 4-methyl- and 2,4-dimethylselenazoles with HNO_3–H_2SO_4 is more rapid than for thiazoles [4-methyl-5-nitroselenazole, m.p. 45°C (19); 2,4-dimethyl-5-nitroselenazole, m.p. 115–120°C (decomp.) (19)]. Direct nitration of 2-amino 4-methylselenazole leads to ring rupture (19).

The 2-benzamido 4-aryl(alkyl)selenazoles (96) form the corresponding 5-nitro derivatives under mild conditions using the nitrate–sulfuric acid method (Scheme 31). The nitro compounds are well-defined, crystalline compounds. They may be most favorably obtained by dissolving the 2-benzamidoselenazoles in acetone and adding concentrated nitric

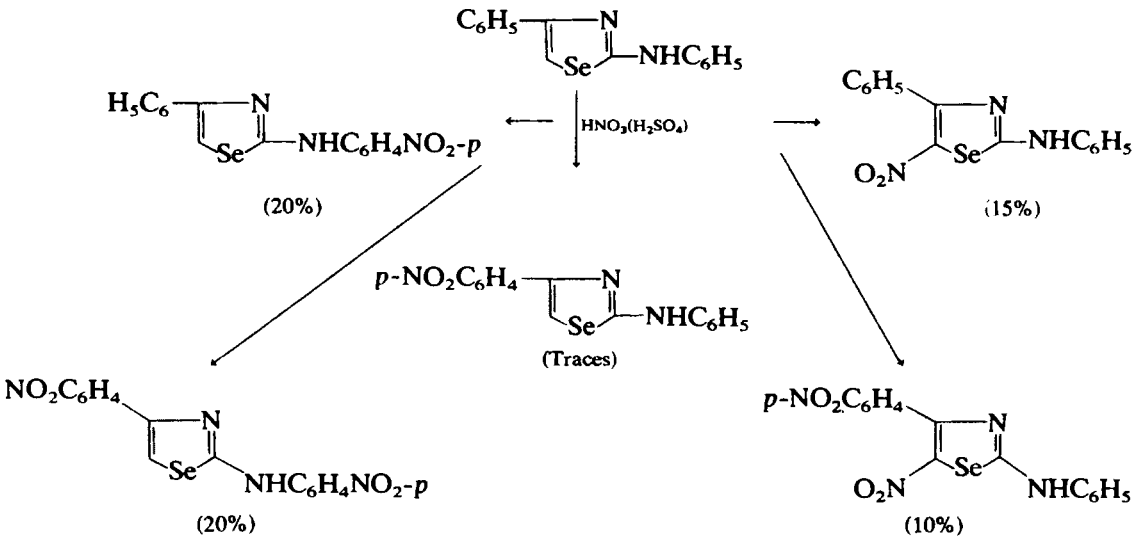


Scheme 31

acid under cooling, whereupon the nitro derivatives are deposited. One can keep them for rather a long time without decomposition. Adding the nitro derivatives very carefully into the sulfuric acid is recommended, because otherwise secondary reactions occur with a violent release of gas. The use of cold mixed nitric and sulfuric acids also affects phenyl groups that may be present (97), leading to dinitro compounds (Scheme 31), or in the case of the 4-phenyl derivative even a trinitro compound. The structure as the 5-nitro derivative was established partly on the basis of the disappearence of the band between 3100 and 3175 cm^{-1} in the infrared spectrum on substitution. It might be assigned to the =C–H stretching vibration in the 5-position in analogy to that in the 2-aminothiazoles. The second part of the structure proof is that compounds of the type in Scheme 31 only form benzoic acid on oxidative degradation. The entry of the second nitro group into the meta position of the



Scheme 32



Scheme 33

benzoyl group, forming compounds of type in Scheme 32, results from the *m*-nitrobenzoic acid obtained by the oxidative degradation. The third nitro group introduced in the dinitro derivative is in the para position of the phenyl group in the 4-position of the selenazole ring. This could be established by an independant synthesis starting with the *p*-nitrophenacyl bromide and the subsequent stepwise nitration of the 2-benzamido-4-*p*-nitrophenylselenazole (Scheme 32). The compound obtained in this way is identical with the trinitro compound formed by direct nitration of the 2-benzamido-4-phenylselenazole.

The nitration of the 2-anilino-4-phenylselenazole (103) is much more complicated. Even careful nitration using the nitrate–sulfuric acid method leads to the formation of a mixture of variously nitrated compounds in an almost violent reaction. By the use of column chromatography as well as thin-layer chromatography a separation could be made, and the compounds could be partly identified by an independent synthesis. Scheme 33 shows a general view of the substances prepared. Ring fission was not observed under mild conditions.

However, prior protective acetylation of the amino group leads to a good yield of the 5-nitro compound [2-acetamido-4-methyl-5-nitroselenazole, m.p. 185°C (19)]. Similarly, 2-diethylamino-4-methylselenazole with nitric acid gives the 5-nitro derivative [yellow needles, m.p. 93°C (26)].

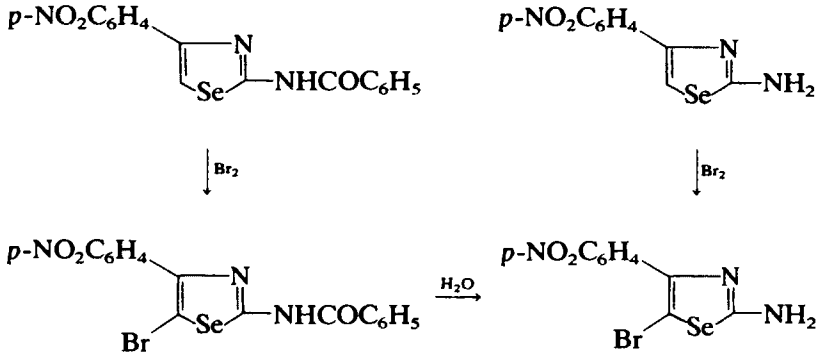
B. *Sulfonation*

2-Alkyl selenazoles have been sulfonated. Thus 2,4-dimethylselenazole with fuming sulfuric acid (5% SO_3) at 100°C gives 2,4-dimethyl-5-sulfonylselenazole [m.p. 238°C (decomp.) (26)], which is relatively unstable, decomposing to give metallic selenium.

C. *Halogenation*

As a further electrophilic substitution the bromination of selenazoles has been investigated. This is not as complicated as nitration. Bromination was carried out in several solvents and with various amounts of bromine. In spite of the great variation in conditions, monobromo derivatives containing the bromine atom in the 5-position are always formed. This could be established, for example, by the bromination of the 2-amino-4-*p*-nitrophenylselenazole (Scheme 34) and its 2-benzamino compound (98). The 2-benzamido bromo compound gives the same bromo

derivative by hydrolysis as it does by the direct bromination in Scheme 34. This simultaneously shows halogens in the 5-position possessing a very low reactivity, because the hydrolysis is done without displacement of bromine. Further displacement reactions were also unsuccessful (Scheme 34).



Scheme 34

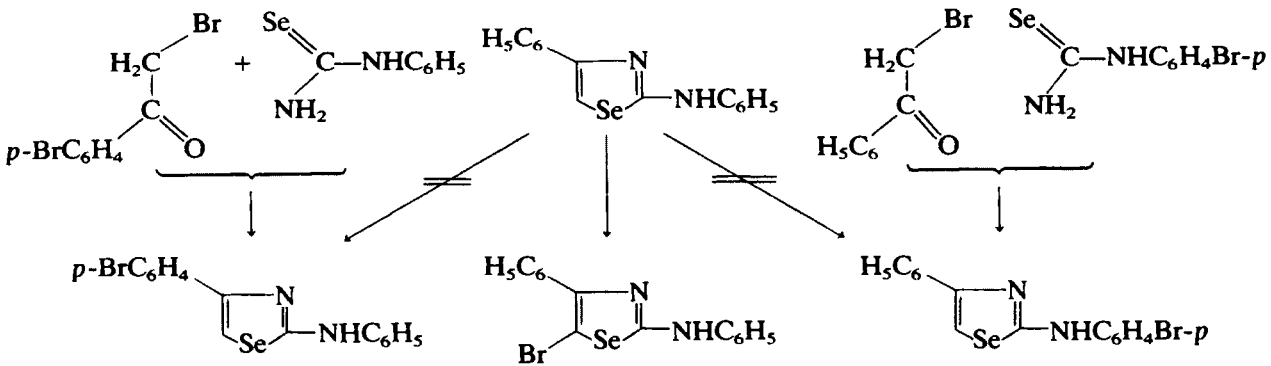
The 2-anilinoselenazoles follow an analogous reaction path. The entry of bromine into the 5-position is in agreement as seen in Scheme 35. The 2-anilino-4-phenylselenazole gives a 5-bromo derivative by bromination. It is not identical with either of the bromo derivatives prepared by direct synthesis (Scheme 35) (99).

Bromination of 2,4-dimethylselenazole with cold bromine gives an unstable monobrominated derivative initially (m.p. 168°C), which is easily converted to a product [m.p. 205°C (decomp.)] considered by Haginiwa to be 5-bromo-2,4-dimethylselenazole hydrobromide (19).

Unlike nitration, 2-amino-4-methylselenazole can be directly brominated, using bromine in carbon tetrachloride solution, to give 2-amino-5-bromo-4-methylselenazole hydrobromide [m.p. 180°C (decomp.)] (19). The free base cannot be isolated. Use of excess of bromine can lead to destruction of the molecule.

2-Acetamido-5-bromo-4-methylselenazole (m.p. 196°C) was obtained by the same method (19).

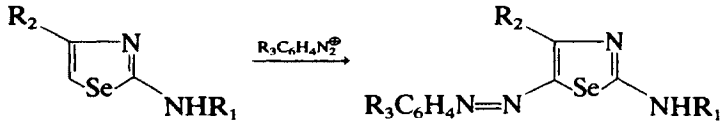
2-Amino-5-bromoselenazole has been used as an intermediate in the synthesis of pharmaceutical compounds (42).



Scheme 35

D. *Diazo Coupling*

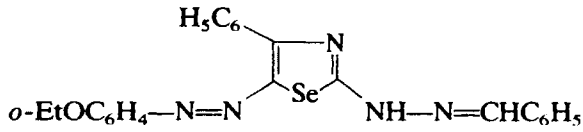
The high reactivity of the 5-position in 1,3-selenazoles toward electrophilic substitution was also observed on azocoupling. By reacting molar quantities of an aqueous solution of a diazonium salt with an ethanolic solution of a 2-arylamino selenazole, for example, the corresponding 2-arylamino-5 azoselenazoles are formed in a smooth reaction (100). They deposit from the deeply colored solution and form intensely red-colored compounds after their recrystallization from a suitable solvent (Scheme 36).



Scheme 36

Coupling of 2-diethylamino-4-methylselenazole with phenyldiazonium chloride gives the corresponding 5-phenylazo compound [orange granules, m.p. 101°C (26)].

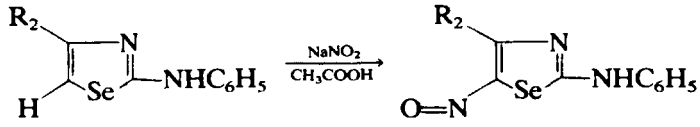
Bulka et al. (43) have demonstrated the electrophilic reactivity of selenazoles possessing an hydrazone in the 2-position and nonsubstituted in the 5-position toward diazonium salt to give 5-phenylazo derivatives preferentially. For example, the main product of the coupling of 2-benzylidene hydrazino-4-phenylselenazole with diazo-*o*-phenetidine is the 5-(*o*-ethoxyphenylazo)-selenazole (Scheme 37) (ruby red prisms, m.p. 206°C, yield 67%). A formazan is obtained as by-product. (See Section III.6) (43).



Scheme 37

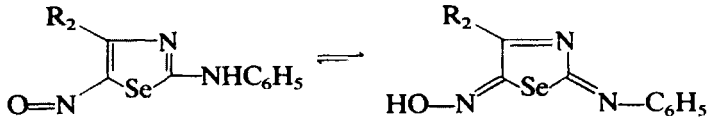
E. *Nitrosation*

Treatment of 2-(arylamino)selenazoles with sodium nitrite in glacial acetic acid at room temperature gives the corresponding nitroso compounds instantaneously (Scheme 38) (29). These compounds give rise to

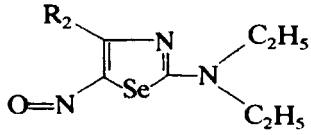


Scheme 38

the tautomeric equilibrium in Scheme 39. They possess properties notably different from analogous aromatic nitroso derivatives not having a mobile hydrogen on the exocyclic nitrogen, as, for example, 2-diethylaminoselenazoles that have the unambiguous 5-nitroso structure (Scheme 40), and properties similar to *p*-nitrosodialkylanilines.

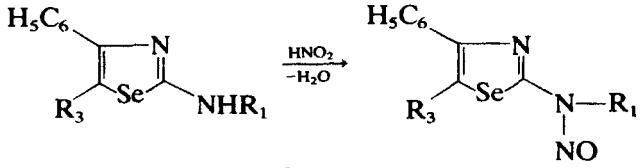


Scheme 39



Scheme 40

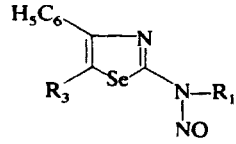
N-nitrosamino derivatives are only obtained when the 5-position is blocked, for example, with 2-arylamino-4,5-diphenylselenazole or 2-arylamino-5-phenylselenazole (Scheme 41). Differents compounds have been prepared (Table X-8) (29).



Scheme 41

Diazotization of 2-arylamino-4-phenylselenazoles with phenyldiazonium chloride gives 2-arylamino-4-phenyl-5-phenylazoselenazoles (Scheme 42) (29).

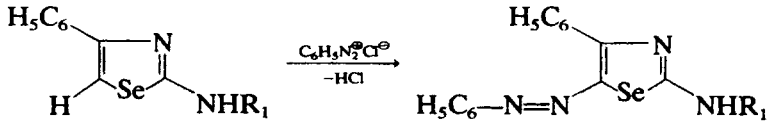
TABLE X-8. N-NITROSAMINO 5-PHENYL-SELENAZOLES (29)



R_3	R_1	m.p. (°C)
H	Ph	176
H	o-MeC_6H_4	183
H	p-MeC_6H_4	161
Ph	Ph	193

In conclusion, in terms of electrophilic reactivity a *methyl* group in the 2-position is equally reactive in the two categories of heterocycles (selenazole and thiazole). Of the two positions ortho to nitrogen, only the 2-position is activated. The 5-position is sensitive to electrophilic reagents and resembles more closely the para position of a benzene ring.

With respect to thiazole, the selenazole system displays a lesser nucleophilic reactivity in the 2-position and a greater electrophilic reactivity of the 5-position, but undergoes fission of the cycle more easily.



R_1 = Ph (m.p. 211°C)
R_1 = o-MeC_6H_4 (m.p. 204°C)
R_1 = p-MeC_6H_4 (m.p. 207°C)

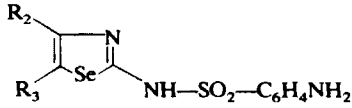
Scheme 42

2. Sulfanilamidoselenazoles

Much of the development of the chemistry of sulfanilamidoselenazole derivatives is a result of the important role played by sulfonamides in chemotherapy and more particularly the good activity of sulfathiazole against bacterial infections. Backer and De Jonge (44) prepared these derivatives by reaction of 2-amino-4-methyl- and 2-amino-4-phenyl-selenazoles with *N*-acetylsulfanilic acid chloride in pyridine. Alkaline

hydrolysis of the resulting *N*-acetylsulfanilamides gave the corresponding 2-sulfanilamidoselenazoles. The principal compounds thus prepared are shown in Table X-9 (16, 45, 46).

TABLE X-9. 2-SULFANILAMIDOSELENAZOLES

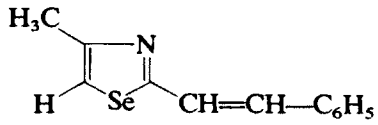


R_2	R_3	m.p. (°C)	m.p. (acetyl derivative) (°C)	Ref.
H	H	206	—	45
Me	H	222–3, 235	228–9, 225	16, 46
		236–7 (dec.)	—	44
Ph	H	231–2	238–9	16, 46
		209.5–210.5	244–5	44
Me	COOH	231–2	238–9	16, 46

The investigations of Jensen and Schmith (45) indicate that in vitro activity of 2-sulfanilamido and 4-methyl-2-sulfanilamido selenazoles against pneumonial infections is comparable to that of sulfathiazole or sulfadiazine. Frisk (47) found that the activity of the selenium compounds was much lower than that of sulfathiazole.

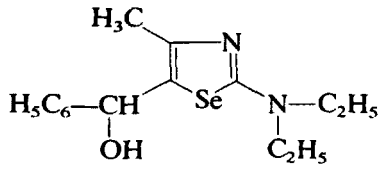
3. Condensation with Carbonyl Derivatives

The reactivity of 2-methylselenazole toward carbonyl compounds is the same as its thiazole homolog. Reaction of 2,4-dimethylselenazole with benzaldehyde in the presence of anhydrous zinc chloride as catalyst gives 4-methyl-2-styrylselenazole [m.p. 74–75°C (19)] (Scheme 43).



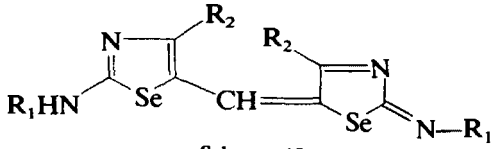
Scheme 43

2-Diethylamino-4-methylselenazole with benzaldehyde in the same conditions as for Scheme 43 yields 2-diethylamino-4-methyl-5-phenylcarbinyl selenazole (m.p. 254°C) (Scheme 44) (26).



Scheme 44

Using formaldehyde, compounds of type 5-[(2-amino-5-selenazolyl)-methylene]selenazoline are obtained (Scheme 45) (48).



Scheme 45

4. Condensation of Selenated Alkylidene or Benzylidene Hydrazones or Pyrazolones with *p*-nitroso Dialkyanilines

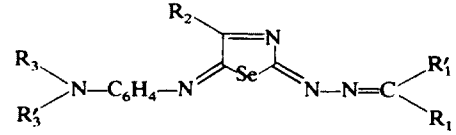
A. *Isopropylidene and Benzylidene Hydrazones*

Isopropylidene and benzylidene hydrazones of selenazole unsubstituted in the 5-position react with *p*-nitrosodimethylanilines or *p*-nitrosodiethylanilines when heated in organic solvents in the presence of acetic acid or pyridine (49). Highly colored crystalline 2-hydrazono-5-(*p*-dialkylaminophenylimino)selenazoles are recovered from the reaction medium (Table X-10).

Seemingly the presence of an aromatic substituent in the 4-position of the selenazole ring is necessary for obtaining well-crystallized products; compounds with an alkyl group in the 4-position are amorphous and quite difficult to obtain as crystals.

The mechanism of the reaction can be interpreted as involving a mesomeric effect of the 2-hydrazone group that leads to a negative charge on the 5-carbon (Scheme 46).

TABLE X-10. ALKYLIDENE OR BENZYLIDENE DERIVATIVES OF 5-(*p*-DIALKYLAMINOPHENYLIMINO)SELENAZOL-2-ONE HYDRAZONES (49)[a]



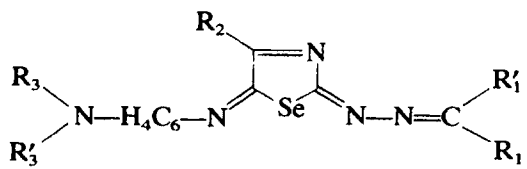
			$R_1 = R_1' = CH_3$	$R_1 = H, R_1' = C_6H_5$
R_2	R_3	R_3'	m.p. (isopropylidene derivative) (°C)	m.p. (benzylidene derivative) (°C)
Ph	Me	Me	154–5	176
p-MeC_6H_4	Me	Me	—	185–6
p-$MeOC_6H_4$	Me	Me	—	165
p-BrC_6H_4	Me	Me	—	207
Ph	Et	Et	125	166–7
p-MeC_6H_4	Et	Et	—	188
p-$MeOC_6H_4$	Et	Et	—	121
p-BrC_6H_4	Et	Et	—	163

[a] λ_{max} (EtOH) = 530 to 580 nm, λ_{max} (acetone) = 520 to 570 nm, λ_{max} (benzene) = 517 to 562 nm.

Electrophilic attack on the 5-position gives formation of an azomethinic bond and elimination of a molecule of water.

The dyes prepared in this way show a positive solvatochromism as the dielectric constant of the solvent increases, indicating that they possess a predominantly nonpolar structure. Substituents on the phenyl group in the 4-position of the selenazole ring have little influence on the absorption spectra.

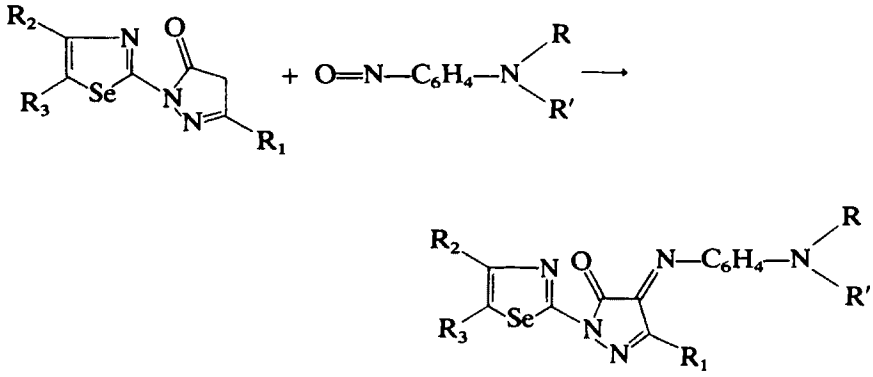
However, benzylidene derivatives show a strong bathochromic shift in comparison with alkylidene derivatives. Thus absorption is a result of the whole conjugated system that is comparable to that of the quinoid dyes. The color of this type of compound is sensitive to acids and bases.



Scheme 46

B. 2-*Pyrazoloneselenazoles*

Reaction of 2-pyrazoloneselenazoles with *p*-nitrosodialkylanilines leads to a series of azomethinepyrazolones (Scheme 47) used as purple magenta dyes in color photography (34). The main regions of absorption are: λ_{max} (EtOH), 535 to 555 nm; λ_{max} (acetone 531 to 552 nm; and λ_{max} (benzene), 521 to 537 nm.



Scheme 47

5. Oxidation to Quinoid Dyes

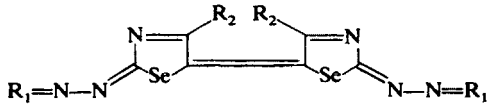
Isopropylidene or benzylidene 2-hydrazinoselenazole derivatives can be converted to highly colored 2,2′-dioxo-Δ-3,3′-biselenazol-5,5′-inylidene-bis-hydrazones (Table X-11) by oxidation with ferric chloride and hydrogen peroxide (33).

Mechanistically, the reaction results from the mesomeric donor effect of the 2-hydrazino group. The coupling between the two molecules takes place in the 5-position (Scheme 48).

The primary dihydro product (**3**) can be obtained by reduction of the quinoid (**4**). Compound **3**, in which $R_1 = C_6H_5–CH=$ and $R_2 = C_6H_5$ can also be obtained by direct condensation of benzylidene selenosemicarbazone with 2,3-dibromo-1,4-diphenyl-1,4-butanedione (Scheme 49).

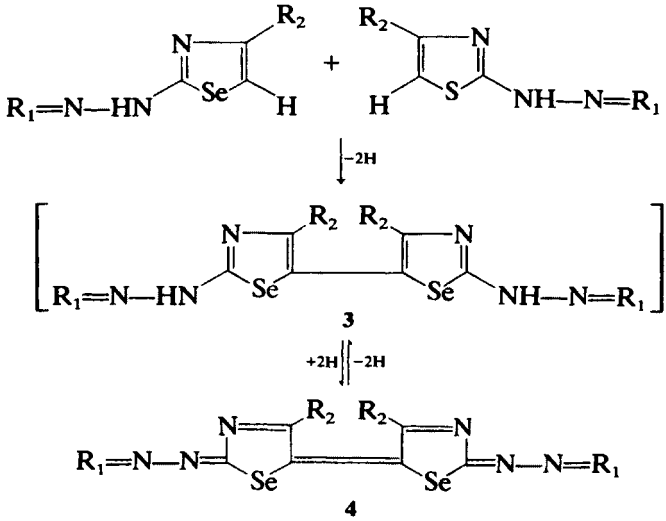
This reaction is proof of the structure of the dye, easily obtained from the dihydro compound (**3**). Yields are low as a result of numerous side reactions. The stereochemical configuration of these quinoid dyes is trans.

TABLE X-11. BIS-ISOPROPYLIDENE OR BENZYLIDENE DERIVATIVES OF 2,2'-DIOXO-Δ-3,3'-BISELENAZOL-5,5'-INYLIDENE BIS HYDRAZONES (33)

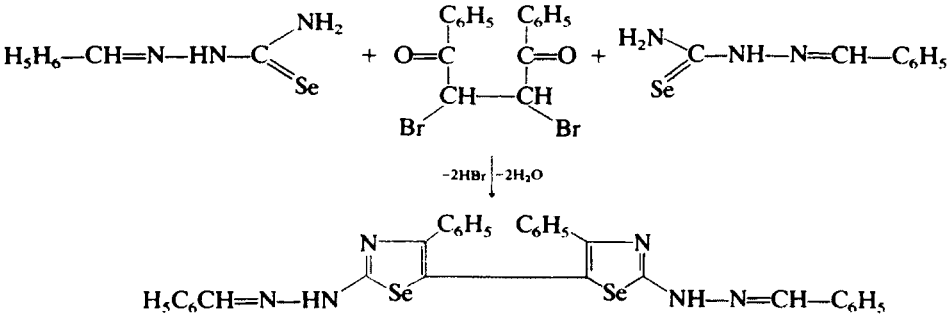


	$R_1 = C(CH_3)_2$ (Bisisopropylidene derivative)		$R_1 = CH(C_6H_5)$ (Bisbenzylidene derivative)	
R_2	m.p. (°C)	λ_{max} (nm) ($CHCl_3$)	m.p. (°C)	λ_{max} (nm) ($CHCl_3$)
4,4'-diPh	246	571	263[a]	578
4,4'-di-*p*-MeC_6H_4	—	—	292	578
4,4'-di-*p*-ClC_6H_4	251	575	270	590
4,4'-di-*p*-BrC_6H_4	252	580	291	593

[a] Bis-α-methylbenzylidene derivative: m.p. = 274°C, λ_{max} ($CHCl_3$) = 590 nm.



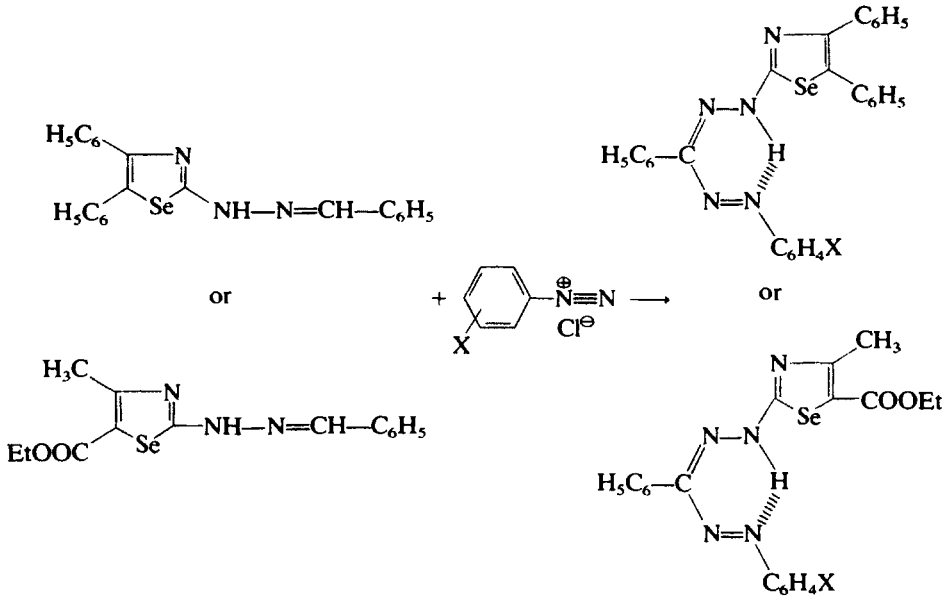
Scheme 48



Scheme 49

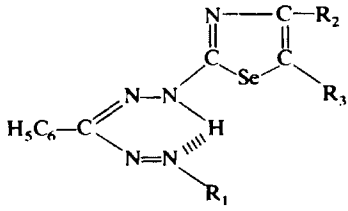
6. Selenazoleformazans

Formazans possessing a selenazole ring can be prepared from benzylidene hydrazones of selenazole. For example, 2-benzylidene hydrazino-4,5-diphenyl- and 2-benzylidenehydrazino-5-carbethoxy-4-methylselenazole with diazonium salts give, by nitrogen coupling [unambiguously since the 4- and 5-positions are blocked (Scheme 50)], formazans (43) (Table X-12). Nitrogen coupling occurs preferentially in the



Scheme 50

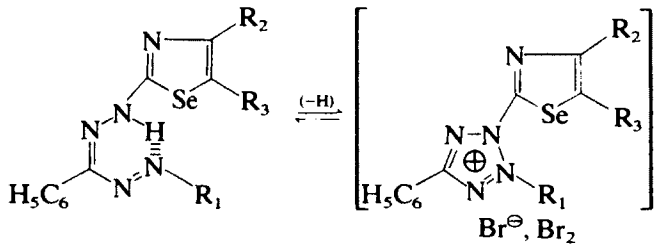
TABLE X-12. FORMAZANS (43)



R_1	R_2	R_3	Yield (%)	m.p. (°C)
Ph	Ph	Ph	60	176
p-MeC_6H_4	Ph	Ph	70	175
o-MeC_6H_4	Ph	Ph	71	185
p-$MeOC_6H_4$	Ph	Ph	75	184
o-$MeOC_6H_4$	Ph	Ph	67	200
p-$EtOC_6H_4$	Ph	Ph	61	172
o-$EtOC_6H_4$	Ph	Ph	83	193
β-$C_{10}H_7$	Ph	Ph	79	201
Ph	Me	COOEt	68	184
p-MeC_6H_4	Me	COOEt	75	175
o-MeC_6H_4	Me	COOEt	53	187
p-$MeOC_6H_4$	Me	COOEt	68	173
o-$MeOC_6H_4$	Me	COOEt	68	192
o-$EtOC_6H_4$	Me	COOEt	57	198
β-$C_{10}H_{17}$	Me	COOEt	77	183

5-position when this latter is free, as this reaction has a higher rate constant.

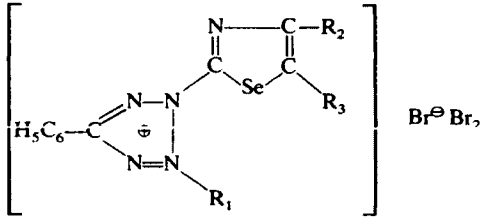
The diazonium salts precursors can be aniline, o- and p-toluidine, o- and p-anisidine, o- and p-phenetidine, or β-naphthylamine. The resulting formazans are crystalline and intensely colored. They are soluble in organic solvents, giving a red-violet coloration that darkens to blue. Dehydrogeneration gives the corresponding tetrazolium salts, which are isolated as perbromides (Scheme 51, Table X-13).



Formazan Tetrazolium perbromide

Scheme 51

TABLE X-13. TETRAZOLIUM PERBROMIDES (43)



R_1	R_2	R_3	Yield (%)	m.p. (°C)
Ph	Ph	Ph	80	177
p-MeC_6H_4	Ph	Ph	64	158
o-MeC_6H_4	Ph	Ph	39	156
p-$MeOC_6H_4$	Ph	Ph	47	156
o-$MeOC_6H_4$	Ph	Ph	51	161
p-$EtOC_6H_4$	Ph	Ph	49	150
o-$EtOC_6H_4$	Ph	Ph	59	173
β-$C_{10}H_7$	Ph	Ph	20	156
Ph	Me	COOEt	90	129
p-MeC_6H_4	Me	COOEt	31	121
o-MeC_6H_4	Me	COOEt	57	128
p-$MeOC_6H_4$	Me	COOEt	49	108
o-$MeOC_6H_4$	Me	COOEt	69	121
o-$EtOC_6H_4$	Me	COOEt	55	120
β-$C_{10}H_7$	Me	COOEt	51	108

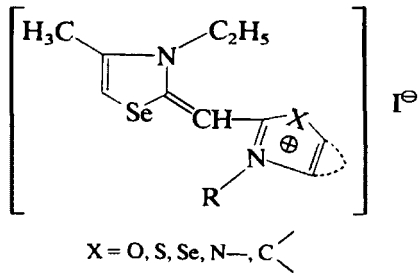
7. Quaternary Salts

Quaternary salts are obtained by alkylation of selenazole bases, the heterocyclic nitrogen atom playing the role of nucleophile with regard to the electrophilic carbon of the alkylating agent.

They are used principally as intermediates for cyanine dyes that serve in photography (5, 6, 35, 36, 50–52). 3-Ethyl-2,4-dimethylselenazolium iodide (m.p. 157–8°C) was prepared as colorless crystals in 87% yield by Brooker et al. (6) by heating 2,4-dimethylselenazole with an excess of ethyl iodide for 48 hr.

By reaction of a corresponding quaternary salt in the presence of a condensation agent such as amyl nitrite or with a heterocycloammonium salt possessing a labile group, such as Cl, I, or SR (6, 11) in the 2-position, cyanine dyes are obtained (Scheme 52).

The heterocycloammonium salts can be made of 5- or 6-membered rings or even be (5+6) or (6+6) condensed systems. Among the cyanines



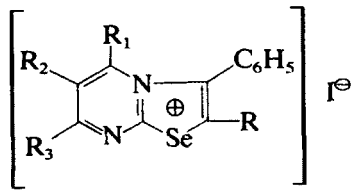
X = O, S, Se, N—, C

Scheme 52

prepared are: 1',3-diethyl-4-methylselenazolo-2'-cyanine iodide, m.p. 256 to 260°C (dec.); 1',3-diethyl-4-methylselenazolo-2'-pyridocyanine iodide, m.p. 232 to 233°C (dec.); and 1',3-diethyl-4-methyl-5',6'-benzoselenazolo-2'-cyanine iodide, m.p. 275 to 277°C (dec.). 2-Methyl-4-phenylselenazole (51) can also be used after quaternization to give such dyes.

Carbocyanines with three methine groups can be prepared using two equivalents of selenazolium quaternary salt and one equivalent of ethyl orthoformate in pyridine solution (53).

Selenazolo[3,2-*a*]pyrimidinium salts (Scheme 53) can be obtained by condensation of 2-amino-4-phenylselenazoles with an excess of β-diketone of the type, $R_1COCHR_2COR_3$.

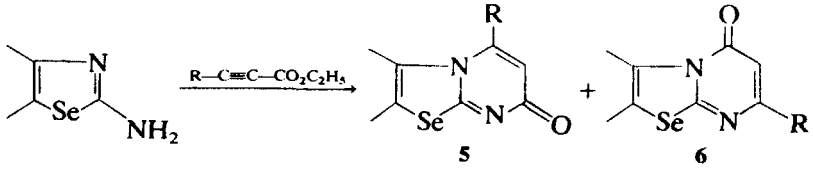


Scheme 53

8. Reactivity of 2-Amino Selenazoles with Ethyl Propiolate (54) and Dimethyl Acetylene Dicarboxylate

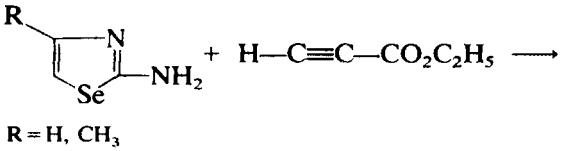
In the reaction of 4-substituted 2-aminoselenazoles with ethyl propiolate and dimethylacetylene dicarboxylate, the major products obtained from such a condensation are substituted 7H-selenazolo[3,2-*a*]pyrimidin-7-ones (**5**) and not the alternative isomeric substituted 5H-selenazoles[3,2-*a*]pyrimidin-5-ones (**6**). Distinction between the alternative structures was based on infrared, ultraviolet, and NMR data (Scheme

54). In the reaction of 2-aminoselenazole with ethyl propiolate, in addition to compound type **7** (50% yield), compounds **8** and **9** were also isolated. Compound **7** is probably formed through the cis isomer of **8** (Scheme 55).

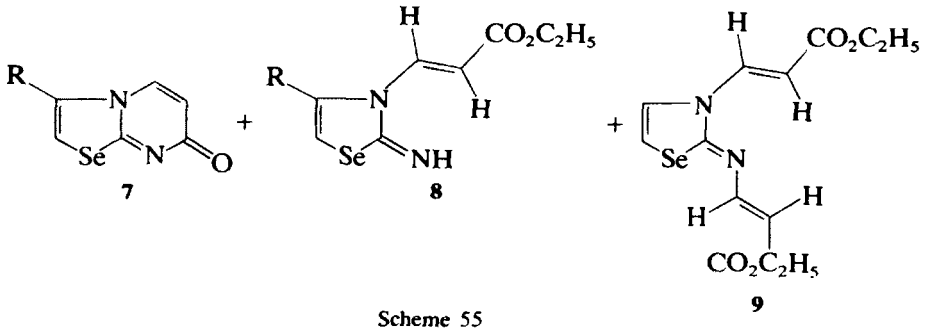


5 **6**

Scheme 54



R = H, CH_3



7 **8** **9**

Scheme 55

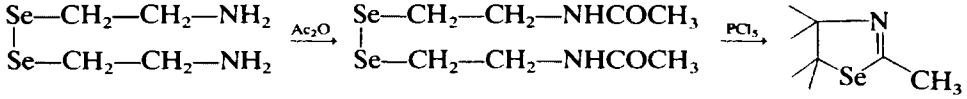
IV. OTHER HETEROCYCLES DIRECTLY DERIVED FROM SELENAZOLE

1. Selenazolines

A. *Alkyl or Aryl-Δ_2-Selenazolines*

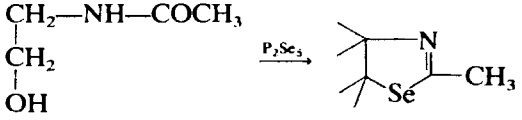
The first compounds with a Δ_2 selenazoline structure were mentioned in the literature in 1892 by Michels (55). He prepared 2-methyl-Δ_2-selenazoline in the course of his investigations into sulfur and selenium

derivatives of ethylamine. The preparative method used was the reaction of acetic anhydride on bis(2-aminoethyl)diselenide to give a diacetyl derivative that cyclizes under the action of phosphorus pentachloride (Scheme 56). 2-Methyl-Δ_2-selenazoline has also been prepared by the action of 2-bromoethylamine hydrobromide on selenoacetamide (56).



Scheme 56

Another method, due to Van Dormael (57) involves heating acetamidoethanol with phosphorus pentaselenide (Scheme 57).

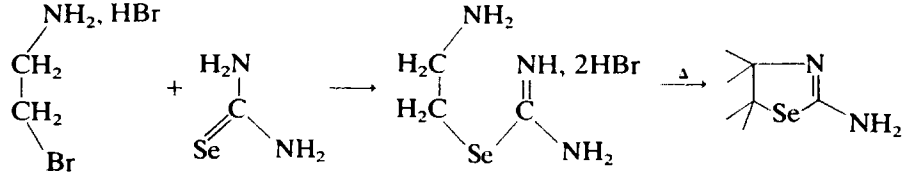


Scheme 57

Other 2-alkyl or 2-aryl-Δ_2-selenazolines have been prepared in the same way starting from suitably substituted *N*-acylethanolamines (58, 59).

B. 2-*Amino*-Δ_2-*Selenazolines*

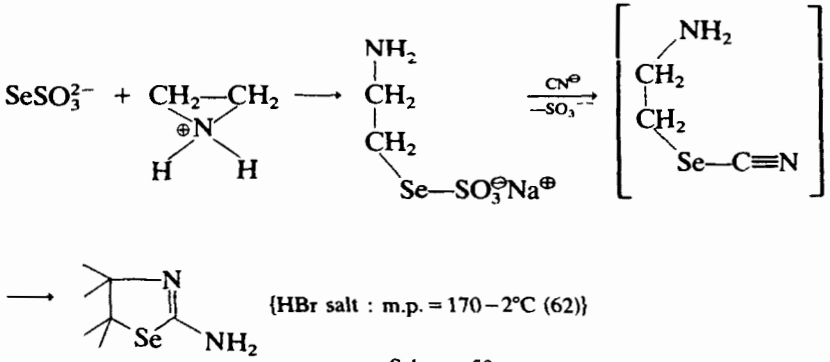
Starting from 2-bromoethylamine hydrobromide and selenourea, Chu and Mautner (60) prepared the salt of 2-(aminoethyl)-selenopseudourea, which cyclizes upon heating in aqueous solution to give 2-aminoselenazoline (Scheme 58).



Scheme 58

2-Amino-Δ_2-selenazoline and its 5-methyl derivative have previously been obtained by Baringer (61) starting from 2-bromoethylamine hydrobromide and 1-amino-2-bromopropane hydrobromide, respectively, by reaction with potassium selenocyanate.

Finally, Klayman (62) also prepared 2-aminoselenazoline by reaction of a cyanide with the sodium salt of 2-aminoethaneselenosulfuric acid (Scheme 59).



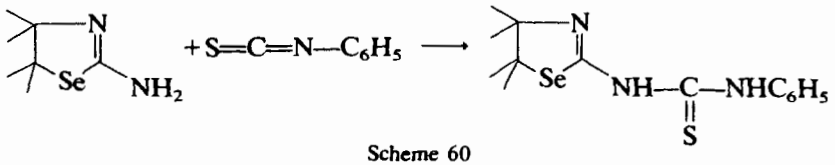
{HBr salt : m.p. = 170−2°C (62)}

Scheme 59

Treatment of 2-aminoselenazoline with aqueous alkaline base (63) or with hydrogen sulfide (64) leads to ring rupture and gives 2-ureidoethaneselenol and 2-thioureidoethaneselenol, which are not isolated but give by oxidation 1,1′-(diselenodiethylene)-bis(2-thiourea) : $(H_2N{-}\underset{\underset{S}{\|}}{C}{-}NH{-}CH_2{-}CH_2{-}Se{-})_2$.

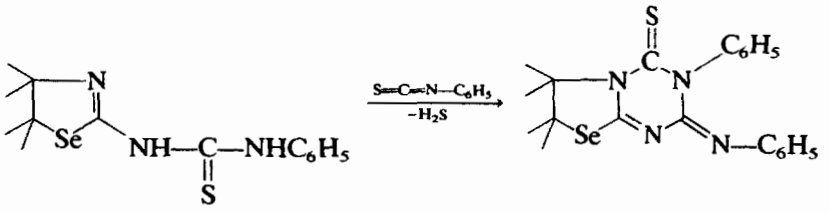
A similar reaction occurs with 2-aminothiazoline (63).

Addition of phenylisothiocyanate to 2-aminoselenazoline leads to 1-phenyl-3-(2-selenazolin-2-yl)-2-thiourea (Scheme 60).



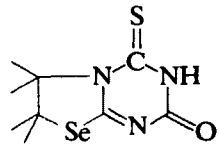
Scheme 60

Heating of this latter compound with an excess of phenyl isothiocyanate in acetonitrile (65) leads to 2-phenylimino-3-phenyl-4-thioxoselenazole[3,2-*a*]tetrahydro-*s*-triazin (Scheme 61).



Scheme 61

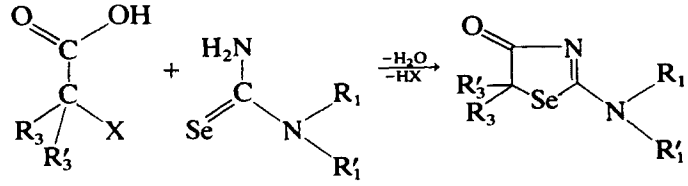
Similarly, the reaction of carbethoxyisothiocyanate (EtO_2CNCS) with 2-aminoselenazoline leads to 2,3,6,7-tetrahydro-4H-selenazolo[3,2-*a*]-*s*-triazin-2-one-4-thione Scheme 62 (66).



Scheme 62

C. 4-*Oxo-Disubstituted* 2-*Amino-*Δ_2-*Selenazolines*

4-Oxoselenazolines with a 2-(disubstituted amino) group are obtained by the action of α-halocarboxylic acid or rather their esters on *N*-disubstituted selenoureas (Scheme 63, Table X-14) (27, 67, 68).



Scheme 63

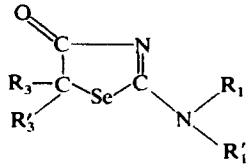
Compounds of this type possess a definite Δ_2-selenazoline structure, while homologous compounds with at least one labile hydrogen on the 2-amino group can exist as a tautomeric equilibrium (Scheme 64).

Such is the case of 2-amino or 2-(monoalkyl or arylamino)-4-oxo-selenazolines. Thus because of this amino$\rightleftarrows$imino tautomerism, these compounds can be called 2-aminoselenazolines or 2-iminoselenazolidines and can be classed either as selenazolines or selenazolidines. This has been a source of controversy that has been resolved by recent spectroscopic studies (67, 68).

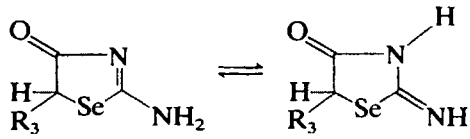
Comrie et al. (68) have thus prepared several compounds of this type by condensation of various selenoureas with α-halocarboxylic acids and have assigned them the "imino" structure (Table X-15a).

Compounds of this type were first obtained from chloroacetic acid and selenourea (1) by Hofmann in 1889, who also assigned them the "imino"

TABLE X-14. 4-OXO-DISUBSTITUTED 2-AMINOSELENAZOLINES



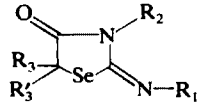
R_1	R_1'	R_3	R_3'	m.p. (°C)	m.p. (HCl or HBr derivative) (°C)	Ref.
H	H	Ph	H	266	—	70
H	H	Ph	Me	240	—	70
Me	H	Ph	H	174–5	—	70
Me	Me	H	H	—	229–231 (dec.) (HCl)	27
Me	Me	Me	H	—	211–212 (HCl) 230–2 (dec.) (HBr)	27
Me	Me	Et	H	—	201–5 (dec.) (HBr)	27
Me	Me	Ph	H	144	—	67, 70
Et	Et	H	H	—	204–6 (dec.) (HCl)	27
Et	Et	Me	H	—	203–5 (HCl)	27
Ph	H	Ph	H	176	—	69
Ph	Me	Ph	H	134–5	—	69



Scheme 64

structure. Guidicelli et al. (67) synthesized tautomeric compounds: 2-amino-4-oxo-5-phenylselenazoline and 2-(methylamino)-4-oxo-5-phenylselenazoline, as well as three compounds possessing a fixed structure: 2-(dimethylamino)-4-oxo-5-phenylselenazoline ("amino" structure), 2-imino-3-methyl-4-oxo-5-phenylselenazolidine ("imino" structure), and 2-(methylimino)-3-methyl-4-oxo-5-phenylselenazolidine ("imino" structure). A study of the ultraviolet spectra in ethanol solution and of the pK_a (67) led to the conclusion that the "amino" structure is predominant in tautomeric equilibria, contrary to the conclusion reached by Comrie et al. (68).

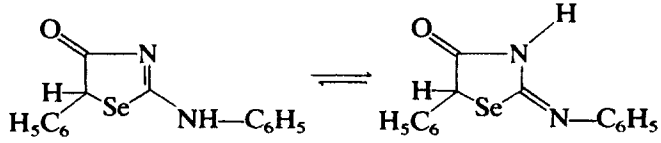
TABLE X-15a. 2-IMINOSELENAZOLIDINE-4-ONES



R_1	R_2	R_3	R_3'	m.p. (°C)	m.p. (HBr or HCl derivative) (°C)	Ref.
H	H	H	H	—[a]	219–224 (HCl) 220–224 (dec.)	68
H	H	Me	H	—	178–180 (dec.) (HBr)	68
H	H	Et	H	178–180 (dec.)	220–4 (dec.) (HBr)	68
H	H	Ph	H	200–4 (dec.) 265–6	—	68
H	Me	Et	H		223 (dec.) (HI)	—
H	Me	Ph	H	115[b]	—	67, 70
Me	Me	Ph	H	98–9	—	67, 70
Et	Et	H	H	50–1	179–180 (HCl)	68
Et	Et	Et	H	oil	154–6 (HBr)	—
Et	Et	Ph	H	96–7	—	—
Ph	H	Ph	H	176[c]	—	70
Ph	Me	Ph	H	98–100	—	69
$CONHC_6H_5$	Me	Ph	H	184–5	—	67, 70

[a] Acetyl derivative, m.p. = 236 to 240°C (dec.); 5-benzylidene derivative, m.p. = 270 to 285°C (dec.).
[b] 2,4-Dione after hydrolysis, m.p. = 96°C.
[c] 2,4-Dione after hydrolysis, m.p. = 164 to 165°C (67), m.p. = 160 to 162°C (71).

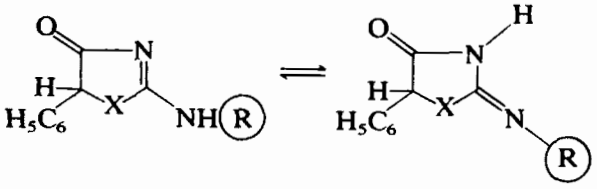
However, in the case of derivatives of the type 2-(phenylamino)-4-oxo-5-phenylselenazoline (Scheme 65), the tautomeric equilibrium is displaced towards the "imino" form (69, 70) This was also shown by the ultraviolet spectra.



Scheme 65

In fact, in this example, the phenyl group takes part in the conjugation of the system and a bathochromic shift is observed.

To sum up, spectroscopic data indicate the "amino" form (**10**) is predominant when R is a hydrogen atom or an alkyl group, while the "imino" form (**11**) is predominant when R is an aryl group (Scheme 66).

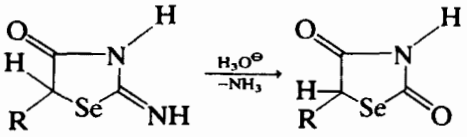


10 **11**

where X = O, S, Se

Scheme 66

The reactivity of these compounds suggests that they exist mainly in the "imino" form, which explains the ease of hydrolysis to give 2-oxo derivatives (Scheme 67) (71).



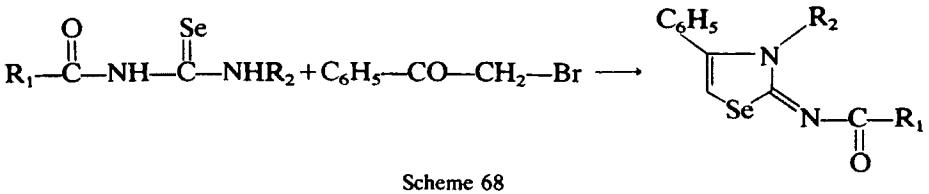
Scheme 67

Hofmann (1) had already demonstrated this type of hydrolysis, which occurs often where the possibility of a tautomerism towards the "imino" form exists. In the case of 2-(dialkylamino) selenazolines, hydrolysis does not take place.

In certain carbocyanines, used as photographic sensitizers in silver halide emulsions, selenazoline rings linked by trimethine bridges are found (56, 72).

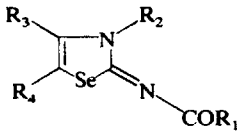
D. 2-*Acylimino*-Δ_4-*Selenazolines* (104)

They were prepared as in Scheme 68, and their characteristics are summarized in Table X-15b.



Scheme 68

TABLE X.15b. 2-ACYLIMINO-Δ_4-SELENAZOLINES 2-ACYLIMINO = Δ_{-4} = SELENAZOLINES



R_1	R_2	R_3	R_4 or Ar	m.p. (°C)	Yield (%)	Ultraviolet λ_{max} (nm)/(log ε)			
C_6H_5	H	C_6H_5	C_6H_5	207–209 (ethanol)	96	237 s (4.46)	279 s (3.82)	287 s (3.75)	345 (4.25)
C_6H_5	H	C_6H_5	*p*-BrC_6H_4	203–204 (nitromethane)	95	235 (4.38)	283 s (3.46)	345 (4.27)	
C_6H_5	H	C_6H_5	*p*-$NO_2C_6H_4$	295–297 (nitromethane)	81	235 s (4.44)	346 (4.27)		

2. Selenazolidines

A. *Alkyl or Arylselenazolidines*

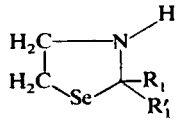
A certain number of selenazolidines were first prepared by Draquet and Renson (73) from aziridine using two different pathways (Table X-16).

The first involves the reaction of aziridine with an aldehyde or a ketone and the treatment of the resulting carbinol with hydrogen selenide (Scheme 69) (Methode I).

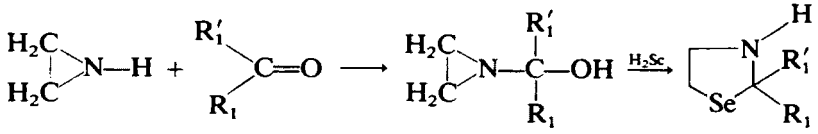
Selenazolidines can also be obtained by first treating aziridine with hydrogen selenide and condensing the intermediate product with a carbonyl compound (Scheme 70) (Methode II).

Similarly 2- and 4-disubstituted selenazolidines were prepared from 2-methyl- and 2,2-dimethylaziridines (Table X-17) (74) and 2- and 3-disubstituted selenazolidines were obtained from *N*-substituted aziridines (Table X-18) (74).

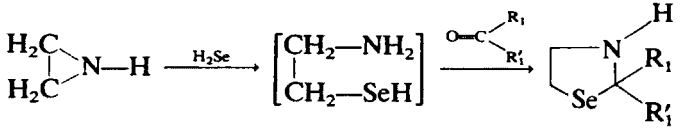
TABLE X-16. 2-ALKYL OR 2-ARYLSELENAZOLIDINES (73)



R_1	R_1'	b.p./mm (°C)	m.p. (°C)	Method	Yield (%)
H	H	76/20	—	I	33
Me	H	72/20	—	I, II	56, 53
Me	Me	80/20	—	I	50
Me	Et	90/20	—	I	57
Et	H	84/20	—	I	52
n-Pr	H	110/20	—	I	60
Ph	H	—	105	I, II	63, 61
p-MeC_6H_4	H	—	98	I	44
p-$MeOC_6H_4$	H	—	96	I	62
o-ClC_6H_4	H	—	65	I	48
$-(CH_2)_5-$		95/1	—	I	82



Scheme 69



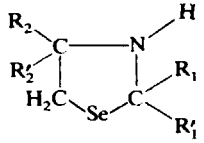
Scheme 70

Treatment of 2,2-dimethylselenazolidines with reactive aromatic aldehydes gives exchange of carbonyl radicals (Scheme 71).

Benzoylation of selenazolidines in aqueous solution leads to opening of the selenazolidine ring and gives dibenzoylselenoalkylamines (Scheme 72) (73).

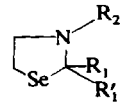
Selenazolidines are acylated on carbon without ring rupture when the reaction is carried out in benzene in the presence of pyridine (73).

TABLE X-17. 2,4-ALKYL OR ARYLSELENAZOLIDINES (74)



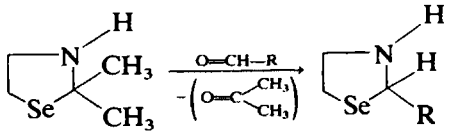
R_1	R_1'	R_2	R_2'	b.p./mm (°C)	m.p. (°C)	Method	Yield (%)
H	H	Me	H	98/40	—	I	55
H	H	Me	Me	75/25	—	I	40
H	Me	Me	H	79/20	—	I	71
H	Et	Me	H	88/20	—	I	65
H	Et	Me	Me	88/20	—	i	56
Me	H	Me	Me	76/20	—	I	48
Me	Me	Me	H	78/20	—	I	40
Ph	H	Me	H	125/0.5	—	I	49
Ph	H	Me	Me	120/0.3	—	I	25

TABLE X-18. 2,3-ALKYL OR ARYL SELENAZOLIDINES[a] (74)

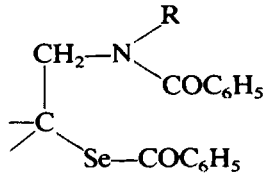


R_1	R_1'	R_2	b.p./mm (°C)	m.p. (°C)	Yield (%)
Me	H	Me	73/20	—	15
Me	H	Ph	102/0.1	—	59
Me	H	Acetyl	99/0.6	—	>90
Me	H	Benzoyl	—	53	>90
Me	Me	Me	76/20	—	21
Et	H	Me	83/20	—	25
Et	H	Ph	108/0.1	—	—
Ph	H	Me	103/0.1	—	17
Ph	H	Acetyl	160/0.4	—	>90
Ph	H	Benzoyl	—	70	>90
Di-*o*,*p*-$MeOC_6H_3$	H	H	—	89	>90
di-*m*,*p*-$MeOC_6H_3$	H	H	—	78	>90
m-$MeOC_6H_4$	H	H	—	79	>90
o-$EtOC_6H_4$	H	H	—	62	>90
p-ClC_6H_4	H	H	—	105	>90
m-ClC_6H_4	H	H	—	98	>90
m-BrC_6H_4	H	H	—	83	>90
$-(CH_2)_5-$		Benzoyl	—	125	>90

[a] By method II.

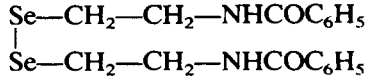


Scheme 71



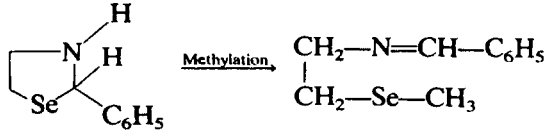
Scheme 72

Hydrolysis and subsequent oxidation by air of benzoylated selenazolidines gives *N,N'*-dibenzoylbis(2-aminoethyl)diselenide (Scheme 73)



Scheme 73

Finally, methylation of 2-phenylselenazolidine leads to benzalamino Se-methylselenocysteamine (Scheme 74).

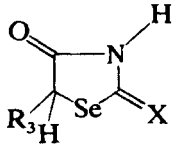


Scheme 74

Methylation takes place on the selenium (73), in contrast to the thiazolidines where it occurs on the heterocyclic nitrogen (75).

B. 2-*Iminoselenazolidin*-4-*ones* (*I*), *Selenazolidin*-2,4-*diones* (*II*), *and* 2-*Alkylidenehydrazones* (*III*)

The general structure of these compounds is described in Scheme 75. Type I compounds can show a protomeric equilibrium and thus can be classed eventually with the 2-aminoselenazolines when this latter structure predominates.

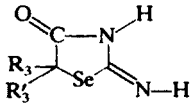


with X = NH (I)
X = O (II)
X = N—N=CHR$_1$ (III)

Scheme 75

- 2-Iminoselenazolidin-4-ones (I) are prepared by condensation of α-halo acids with selenourea in ethanol solution. The free base is obtained at the end of the reaction by neutralization of the hydrohalide (Table X-19) (71).

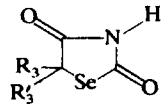
TABLE X-19. 5-ALKYL-2-IMINOSELENAZOLIDIN-4-ONES (71)



R_3	R_3'	m.p. (°C)	Yield (%)
n-Pr	H	184–6	80
i-Pr	H	211–3	61
Bu	H	179–181 (dec.) (HBr)	43
Ph	H	200–4	60

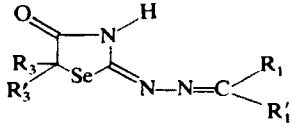
- Selenazolidin-2,4-diones (II) are obtained in the same way as the 2-iminoselenazolidin-4-ones, except that the reactants are under reflux in aqueous solution (Table X-20) (71).
- Selenazolidin-2,4-diones-2-alkylidene (or arylidene) hydrazones (III) are simply prepared by base-catalysed condensation of α-haloacids on selenosemicarbazones of acetone or benzaldehyde (Table X-21) (71).

TABLE X-20. 5-SUBSTITUTED SELENAZOLIDIN-2,4-DIONES (71)



R_3	R_3'	m.p. (°C)	Yield (%)	m.p. (5-derivative) (°C)
Me	H	74–5	82	250–2 (5-benzylidene) 214–6 (5-salicylidene)
Me	Me	82.5–83.5	68	—
Et	H	69–71	75	—
n-Pr	H	55–6	67	—
i-Pr	H	73–4	73	—
n-Bu	H	92–3	89	—
Ph	H	160–2	60	—

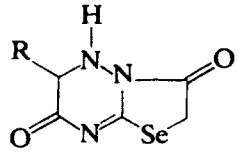
TABLE X-21. SELENAZOLIDIN-2-4-DIONES-2-ALKYLIDENE OR ARYLIDENE HYDRAZONE (71)



R_1	R_1'	R_3	R_3'	m.p. (°C)	Yield (%)	Ref.
H	Ph	H	H	254–6 (dec.)	—	—
H	Ph	Et	H	200–2	64	—
Me	Me	H	H	101–4	61	—
Me	Me	H	Et	103–6	69	—
Me	Me	H	Ph	208	39	—
p-$Me_2NC_6H_4$	H	H	H	—	—	76
p-$MeOC_6H_4$	H	H	H	—	—	76
o-HOC_6H_4	H	H	H	—	—	76

2-Iminoselenazolidin-4-one is benzoylated on the "imino" nitrogen with benzoyl chloride in pyridine solution (77).

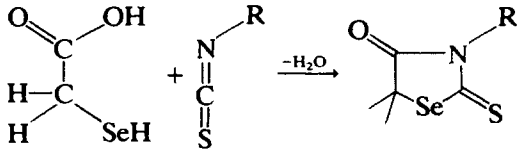
Selenotriazines (Scheme 76) can be obtained starting from seleno-semicarbazide (76).



Scheme 76

C. 2-*Thio*-4-*oxoselenazolidines*

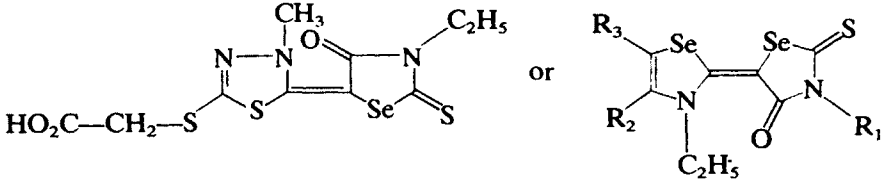
2-Thio-4-oxoselenazolidines substituted in the 3-position, have been described in a number of patents, (79, 80). They are used as intermediates in the manufacture of pharmaceutical products and color sensitizers in photography. They are obtained by action of isothiocyanates on α-hydroselenoacetic acid in the presence of strong base and in the absence of air (Scheme 77).



Scheme 77

The following compounds have been prepared: R = Et, m.p. = 61–2°C; R = Ph, m.p. = 202°C; R = allyl, m.p. = 45–6°C; R = cyclohexyl, m.p. = 159°C; and R = benzyl, m.p. = 120–1°C.

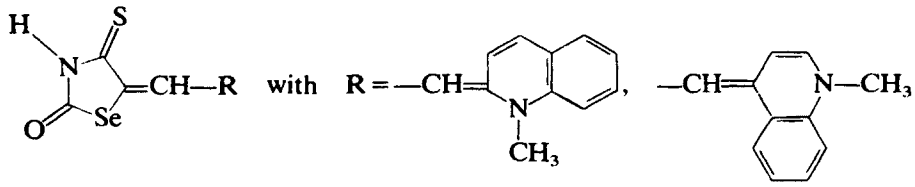
4-Thio-2-oxoselenazolidine can be obtained in 89% yield by treating the 2,4-dione with P_4S_{10} in boiling dioxane (81). This structure is found in heterocyclic indigo-type dyes (Scheme 78).



(Ref. 82) (Ref. 83)

Scheme 78

Merocyanines with selenazolidine nuclei are obtained in 70 to 80% yield from the appropriate derivatives of lepidine or quinaldine (Scheme 79) (84).



Scheme 79

V. PHYSICOCHEMICAL STUDIES

1. Infrared

Comparative studies have been undertaken between different heterocyclic series, especially the azoles, thiazoles, oxazoles, imidazoles, and selenazoles. In a large number of these studies, the heterocycles are condensed with aromatic nuclei.

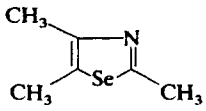
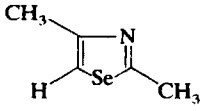
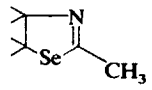
A. *Methylselenazoles*

Bassignana et al. (85) have studied 2,4-dimethylselenazole, 2,4,5-trimethylselenazole, and 2-methylselenazoline. The main infrared absorption bands observed are summarized in Table X-22.

Benzoselenazoles have an additional band at 1590 to 1610 cm^{-1}. The presence of high-intensity infrared bands in selenazolines is further evidence for the assignment of the "selenazole I" vibrations to $\upsilon_{C=N}$ (1650–1680 cm^{-1}) and the "selenazole II" vibration to the group –N=C–Se– (1537–1570 cm^{-1}).

The authors (85) have also mentioned the deformational vibrations (γ) of the out-of-plane group –CH= of a pentatomic heterocyclic nucleus, showing that there exists a relationship between the absorption frequencies of this group and the electronegativity of the heteroatom (86).

TABLE X-22. INFRARED ABSORPTION

Compounds	Selenazole I	$\nu_{C=C}$	Selenazole II	Heterocyclic nucleus
	1650 M	—	1550 M	950 M
	1650 M	1572 W	1531 S	930 S
	1656 s	—	1558 S	930 W

B. *Substituted Selenazolidinediones* (and their sulfur and oxygen homologs)

These compounds have infrared spectra that are greatly complicated by harmonics and combination bands in the region of carbonyl group vibrations.

The two absorption bands in the spectral region, 1690 to 1850 cm^{-1}, of oxazolidinediones, thiazolidinediones, and selenazolidinediones (87), cannot be assigned to two independent carbonyl groups. They are in fact the result of an electronic coupling analogous to that observed with imides (88). The intensity of the out-of-plane vibrational absorption bands (γ_1) favors a planar conjugated group and also undoubtedly a nearly planar ring, even in the case of selenazolidine dimers (bulky heavy atom). The low-frequency C=O vibration (1695–1782 cm^{-1}) is the result of an out-of-phase vibration of the two C=O groups (ν_1), while the high-frequency band (1757–1849 cm^{-1}) corresponds to an in-phase vibration of the C=O groups (ν_2). With the replacement of the oxygen of oxazolidine-2,4-diones by S, Se, or NH, the frequency of the coupled C=O vibrations increases linearly with the increase in electronegativity of the heteroatom. The separation ($\Delta\nu = 37$–79 cm^{-1}) and the relative intensities of these two bands are independent of the substitution and dependent primarily on the

nature of the substitutents on the 5-carbon and on the nitrogen between the 2 C=O groups (89).

C. 2-*Thio*-4-*oxoselenazolidines* (and their oxygen, sulfur, and nitrogen homologs)

Cogrossi (90) studied these spectra in the region 4000 to 400 cm^{-1}. The different characteristic bands have been assigned as follows: $\nu_{C=O}$ at 1708 to 1765 cm^{-1}; the group N–C=S, thioureide I at 1300 to 1550 cm^{-1}, thioureide II at 1200 to 1300 cm^{-1}, and thioureide III at 1100 to 1180 cm^{-1}.

Methyl bonding, methylene scissor, and γ_{Car-N} modes occur at 1460 to 1340 cm^{-1}. Ring bonding and methyl rocking modes are found at 1040 to 1070 and 980 cm^{-1}, respectively. Four bands, at 600 to 700, 550 to 600, 520 to 500, and 430 to 510 cm^{-1} are attributed to the $\beta_{ring}+\delta_{C=O}$, $\beta_{ring}+\delta_{C=O}$, $\beta_{ring}+\gamma_{C=O}$, $\gamma_{C=O}+\beta_{ring}$ modes, respectively.

2. Ultraviolet Spectroscopy

Comparison of the ultraviolet spectra of analogous sulfur and selenium compounds shows that there is very little difference in the absorption curves, except for a slight bathochromic shift in the case of the selenium derivatives.

3. NMR and Mass Spectrometry

Noncondensed aromatic or satured selenated heterocycles are little mentioned in NMR or mass spectrometry literature.

VI. APPLICATIONS OF SELENIUM HETEROCYCLES

1. Dyes

Carbocyanine or merocyanine dyes prepared from selenazole or selenazoline rings have a particular interest in photography.

2-Hydrazono-5-(*p*-dialkylaminophenylimino)selenazoles, pyrazolone azomethin selenazoles, quinoid dyes, and formazans are other important dyes used in photography and the color industry (cf. previous sections).

2. Biological Activity and Radioprotection

A large number of selenium derivatives such as the selenium analog of vitamin B_1 have been tested for physiological activity (91).

Sulfonamides prepared from 2-aminoselenazoles by normal methods sometimes possess activity comparable to that of sulfathiazole (45, 47).

The ability of various selenium heterocycles to check the loss of orthophosphate caused by irradiation of ATP has been studied by Brucker and Bulka (92). They found that only 2-amino-4,5-dimethylselenazole shows radioprotective properties, while other 2-aminoselenazoles, selenosemicarbazides, and acetone selenosemicarbazones possess no such activity but are in addition very sensitive to radiation (93).

A series of selenazolidines substituted in the 2-position have been synthesized to be used as antiradiation agents, but no results are yet available (94).

VII. CONCLUSION

Selenium heterocycles receive far less mention in the literature than do such homologs as oxazole, thiazole, or imidazole. In fact, preparative methods of selenium heterocycles are much more limited than for the other series, mainly because of manipulatory difficulties arising from the toxicity of selenium (hydrogen selenide is even more toxic) that can produce severe damage to the skin, lungs, kidneys, and eyes. Another source of difficulty is the reactivity of the heterocycle itself, which can easily undergo fission, depending on the reaction medium and the nature of the substituents.

Condensed aromatic compounds (benzoselenazoles) are considered much more stable, and they are in fact more commonly used in the area of cyanine-type photographic dyes.

Despite the inconveniences, a certain number of studies have been carried out, particularly concerning dyes containing azomethine groups, such as hydrazones, pyrazolones, formazans, and selenazoles quinoids. Saturated heterocycles, that is, selenazolines and selenazolidines, have also been tackled. Selenium derivatives for pharmacological or physiological applications are little developed by comparison with their thiazole homologs.

Finally, as far as physicochemical or theoretical studies are concerned, except for a few infrared studies, especially comparative ones on azoles (O, S, Se), little work has been done. This is particularyl true of recent

spectrometric techniques (NMR and mass spectrometry) and in the field of quantochemical studies.

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