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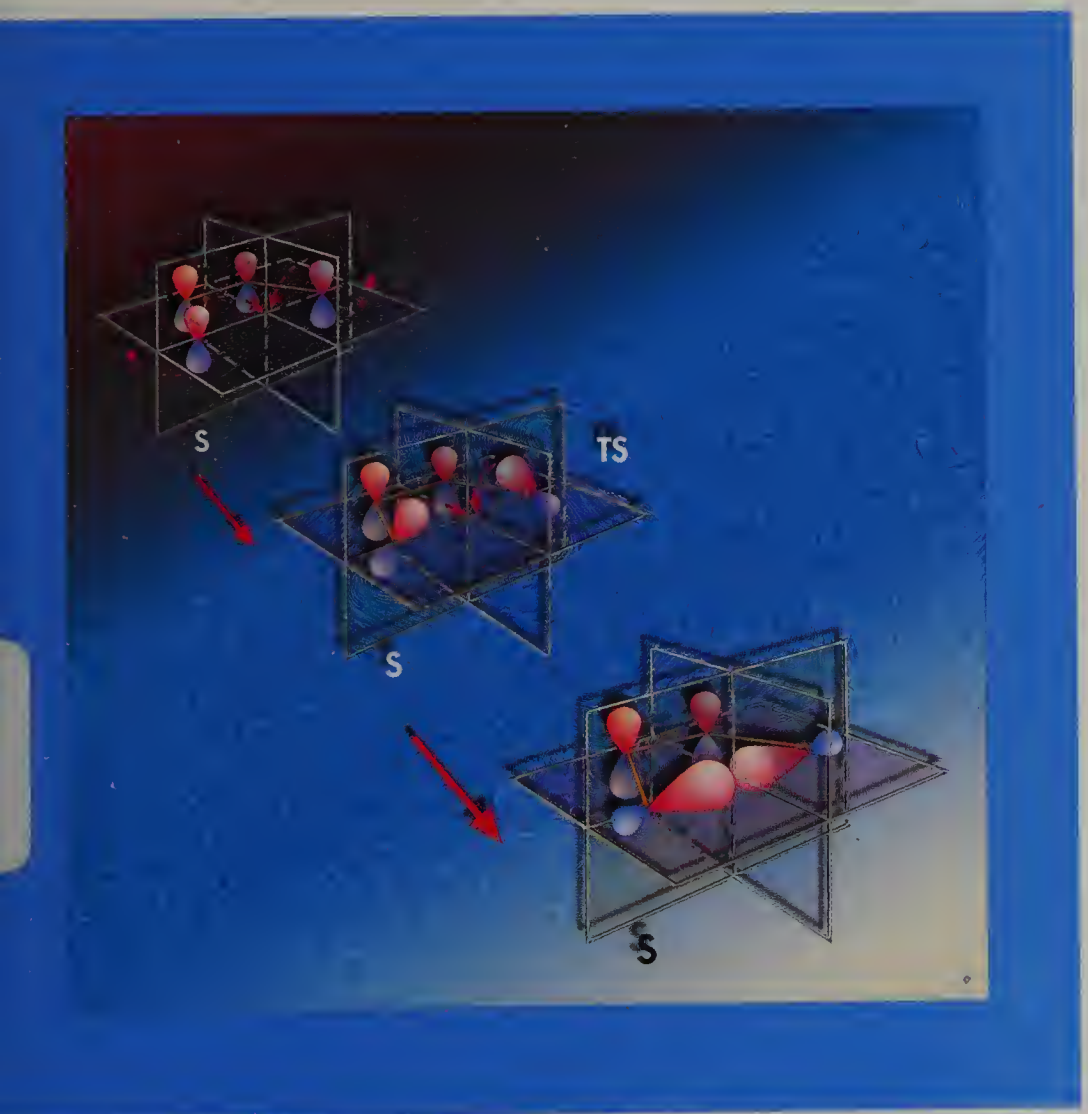
Electrocyclic Reactions

From Fundamentals to Research



computer aided lessons

included

Farzana Latif Ansari, Rumana Qureshi,
Masood Latif Qureshi

Electrocyclic Reactions

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Dedicated to

Jabir-ibn-Hayyan

Known in Europe as Geber (died 803), he rejected the Greek style of speculation and stressed upon the importance of observation and inference. He taught the importance of experimentation in chemistry, as well as organized methods of chemical research. Over 20 types of apparatus were developed by him. These apparatus, and their names, are still in use today. He taught that chemists should have the production of new chemical substances as their motivational force, instead of the search for gold. For this alone, one could call him the father of modern chemistry. Over a hundred scientific papers and a number of books were written by him.

Jabir-ibn-Hayyan studied the geological formation of metals, and showed the method of calcination for the extraction of metals from their ores. He described the process of reduction, evaporation, melting, distillation, sublimation and crystallization. He discovered bismuth, arsenic and antimony. His most important products were lead carbonate, nitric acid and sulphuric acid.

Farzana Latif Ansari,
Rumana Qureshi,
Masood Latif Qureshi

Electrocyclic Reactions

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Preface

Pericyclic reactions, being an important class of organic reactions, deserve extensive theoretical and mechanistic treatment. These reactions were described as *No Mechanism Reactions,* because their mechanism could not be explained since the underlying physical concepts were not properly understood at the time. Pioneering work on the understanding and systematization of these reactions was carried out by Woodward and Hoffmann in the early sixties and the Noble Prize was then awarded to Woodward. Later on, Hoffmann and Fukui were also awarded the Nobel Prize. Woodward and Hoffmann had used the basic idea of the Molecular Orbital Theory and the *Orbital Symmetry Conservation* in a qualitative manner and had derived a set of selection rules for the prediction of the stereochemical course of pericyclic reactions. Alternate approaches, namely, the *Frontier Orbitals approach* and the *Möbius-Hückel approach* were also developed which complemented the theoretical predictions of Woodward and Hoffmann. Contemporary work, however, is on the *Theoretical and Computational approach.* These four approaches could be used to interpret the mechanism of pericyclic reactions.

A thorough understanding of the subject requires a firm grasp of the relevant physical concepts, which makes the subject rather cumbersome. A variety of elegant books and literature are available on the subject. However, students of organic chemistry are not properly equipped with the underlying physical concepts such as Orbital Symmetry, Perturbation Theory and the qualitative aspects of Molecular Orbital Theory in order to fully utilize the available books and literature. Thus the requirement of a book exists that can present the above mentioned concepts in an easily comprehensible manner for post graduate students.

Initially a book on pericyclic reactions was planned to encompass the five known classes of pericyclic reactions, i.e. *Electrocyclic reactions, Cycloaddition reactions, Sigmatropic reactions, Cheletropic reactions* and *Group transfer reactions.*

However, proceeding from the very basics to the latest contemporary research and encompassing all the above five classes of pericyclic reactions would have made the size of the book unmanageable. Therefore, it was found practical to restrict to one class of pericyclic reactions, i.e. Electrocyclic Reactions and to analyze these reactions on the basis of the following different approaches:

i) Orbital Symmetry Conservation Approach
ii) Frontier Orbitals Approach
iii) Möbius-Hückel Approach
iv) Theoretical and Computational Approach

This attempt has culminated in a book titled "Electrocyclic Reactions - from Fundamentals to Research". where an effort is made to explain the underlying concepts using perspective-view illustrations, an elaborate text and the latest research material cross referenced for further research.

An overview of pericyclic reactions highlighting the practical aspects and significance of these reactions is first presented in Chapter 1, in order to orient the reader towards these approaches.

Examples and applications from literature are discussed in Chapter 2 to give an overview of current trends in contemporary research on electrocyclic reactions. After studying the book and understanding the mechanistic interpretations, the reader might like to revise these examples and appreciate them with an enhanced meaning.

The Orbital Symmetry Conservation approach, discussed in Chapter 3, is based on the construction of energy level correlation diagrams and symmetry state correlation diagrams, which help to predict the energetically favourable mechanism of electrocyclic reactions. The related concepts of the symmetry properties of the interacting species are included in Appendix B.

The Frontier Orbitals approach is based on the interactions between these orbitals and their significance in rationalizing chemical reactions is discussed at length in Chapter 4, along with the application of this approach in predicting the favourable mechanism of electrocyclic reactions.

The Möbius-Hückel approach is based on the concept of aromaticity and is discussed in Chapter 5. The aromatic stability of the cyclic transition states is correlated with the feasibility of the pericyclic process.

A unique feature of the book is the inclusion of the Theoretical and Computational approach, and is discussed in Chapter 6. Work on this approach started in the seventies and gained momentum in the eighties. With the advent of powerful computers and sophisticated software some interesting quantitative work is currently carried out. Organic chemists are generally apprehensive of this approach, mainly due to an insufficient background of physics and mathematics. However, the quantitative treatment given does not involve complicated mathematical derivations. Further, Appendix A is added to explain the molecular orbital theory and related concepts.

Another interesting and important feature of this book is the use of a modern educational aid, the computer. In order to exploit the potential of this educational tool, the authors have attempted to hold abstract interactive sessions with the students through the computer. Specific software, supplementing the book, is developed which comprises of a number of CALs (Computer Aided Lessons). These lessons explain the mechanism of electrocyclic reactions on the basis of orbital symmetry conservation. The dynamic molecular models on the computer screen demonstrate reactions that happen too fast and are submicroscopic, thus enhancing concepts beyond those achieved in the laboratory using bulk materials. These visual effects and interactive sessions lead to a better conceptualization and comprehension of this seemingly cumbersome subject.

Any text of this scope has to omit some topics, however, it is hoped that the software and the treatments given here are stimulating enough for a deeper study of electrocyclic reactions.

The authors

Acknowledgements

The authors are indebted to a large number of people and though it is not possible to name all of them, nevertheless, their efforts are indeed acknowledged.

Respects are due to all the numerous scientists whose work has brought the knowledge of pericyclic reactions to its present level. Their contributions to science were freely used, as faithfully as possible, while the faults are all ours.

Special appreciation is due to *Prof. Wolfgang Völter* for all his help, *Prof. Henner Straub* for his valuable suggestions and the Ph.D. students, especially *Miss Humaira Akhtar, Miss Samina Alam* and *Mr. Khosrow Zamani*, for all their contributions.

Thanks are due to the Quaid-i-Azam University, the Pakistan Atomic Energy Commission and the Pakistan Science Foundation, Islamabad, for their financial support and use of their facilities. Thanks are also due to DAAD (German Academic Exchange Service) for providing opportunities for information exchange.

The greatest sacrifices were given by the authors' families, most of all by their children, starting from the youngest *Fakeha Ansari, Midhat Ansari, Zahra Qureshi, Omer Qureshi* and the eldest, *Sarah Qureshi*. They may not understand their contribution at this stage, but they will, as they grow up.

Special mention is due to one of the authors' husband, *Javed Siraj Ansari*, whose understanding and cooperation made all this possible, and to whom all the authors are deeply indebted.

Finally, gratitude is due to the elders for all their prayers towards success.

Farzana Latif Ansari, Rumana Qureshi, Masood Latif Qureshi,
Islamabad, Pakistan.

Foreword

Pericyclic Reactions, or the so-called *No Mechanism Reactions*, have always been difficult to explain rationally. This is more so because organic chemists, by and large, do not acquire an exhaustive mathematical background, and thus find it hard to physically conceptualize these mechanisms. Even though a variety of literature on the subject exists, there are few that would capture the interest of a non-mathematician.

This book on Electrocyclic Reactions, is a major breakthrough in presenting the subject in an easy to understand manner. Each chapter of the book begins with an emphasis on the physical picture, rather than the traditional mathematical treatment. The presentation provides clear enunciations of basic concepts logically leading up to the interpretation of the mechanisms of complex reactions. The authors have also taken pains to include up-to-date literature interspersed with examples of applications from contemporary research. In spite of all their descriptions without mathematical deliberations, they have laid emphasis on the importance of the computational approach and have given it just a touch of mathematics, to serve as an appetizer for the analytical minded.

The use of educational software in the study of electrocyclic reactions is an innovative approach, where the authors have ventured forth and painstakingly developed CALs (Computer Aided Lessons). These lessons are not only eye-catching, they also captivate the reader in the series of simplified question-answer sessions. The student is led to draw his own conclusions regarding the mechanisms being studied. This is further evidenced in the leading questions strategically placed in the flow of thought, as the concept is gradually built up.

The authors have not only filled a need, they have probably created a trend, and future authors might feel incomplete without including CALs in their books.

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1. Pericyclic Reactions

Many organic reactions are a composite of several sequential steps. The overall sequence, from reactants to products, involves either ionic or radical intermediates that may or may not be isolated but can be detected directly or indirectly by chemical or physical means. Figure 1.1 illustrates the energy changes taking place in a two step reaction involving an I (Intermediate) as R (Reactant) transforms into P (Product). Classical examples of such reactions are unimolecular aliphatic and aromatic nucleophilic and electrophilic substitution reactions.

However, many reactions occur in only one elementary step with the formation of no discrete ionic or radical intermediate of significant half life. Such reactions are described as *concerted reactions*. The term concertedness implies that reorganization of electrons during bond breaking and bond formation takes place in a single step as a smooth continuous process. An energy profile of such a reaction involves the conversion of R (Reactant) to P (Product) via a Ts (Transition state). Bimolecular nucleophilic substitutions, eliminations, valence isomerizations, cycloadditions and some rearrangements (Cope or Claisen) are just a few representative examples of concerted reactions:

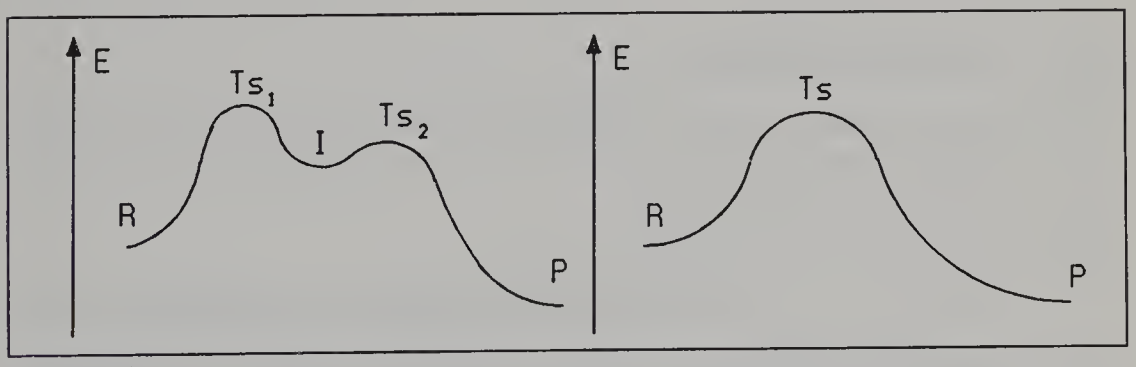


Figure 1.1: *Energy profiles of a stepwise and a concerted reaction.*

These reactions were recognized since long but it was difficult to explain their mechanism on any rational basis. Thus no convincing reasons could be put forward to explain the following observations.

i) Why do S_N2 reactions of alkyl derivatives proceed in a concerted and stereospecific manner to give an inversion of the configuration at the reaction centre?

ii) Why is the Diels-Alder reaction observed as a facile process but not the analogous reaction involving the dimerization of olefins? Also why are these reactions so highly stereospecific?

iii) Why do some conjugated polyenes undergo thermal ring closure to give one stereospecific product? Why do the related polyenes with either one more, or one less, double bond suffer thermal ring closure stereospecifically in an opposite manner?

The answers to these, and many more related, questions were difficult to find at the time because most of the usual probes of establishing reaction mechanisms were of little value, specially when applied to concerted processes. The reasons being the following:

i) In the absence of an intermediate, a detailed description of the transition state is necessary. This was then difficult to obtain.

ii) Structural changes which could throw some light on the mechanism of a reaction were not found to affect, significantly, the rate of these reactions.

iii) Catalysts and solvents then hardly affected the rate of these reactions.

It was essentially due to these limitations that Döring [1] suggested the term *No Mechanism Reactions* for such transformations half in jest and half in frustration.

1.1 General Features

It is observed that many concerted reactions involve transition states wherein all first order bonding changes occur in concert. Woodward and Hoffmann [2] had coined the term *pericyclic* for such reactions.

Salient features of these reactions are the following:

i) Covalency changes occur in a single synchronous step over many centers.

ii) Reagents pass through a conjugated cyclic transition state. The structure of the transition state may be highly symmetrical, but occasionally very unsymmetrical transition states were advocated.

iii) These reactions are not discussed in terms of electrophilic or nucleophilic interactions although there may be an element of charge separation in certain cases.

iv) These reactions are internally self-sufficient, requiring nothing but the thermal or photochemical energy to get them over the hill.

v) They are remarkably stereospecific.

vi) Reaction rates are characterized by large negative entropies of activation suggestive of highly organized transition states.

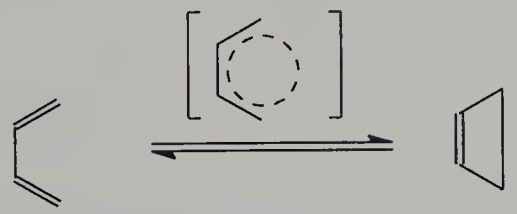
vii) These reactions are in equilibrium, either side of which may involve one or more molecules. The cyclic transition state may be discussed equally well as if arising from either side of the equilibrium.

1.2 Classification

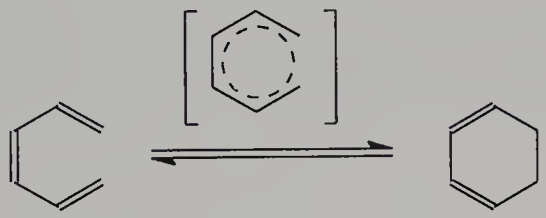
All pericyclic processes may be categorized into the following five main groups:

1.2.1 Electrocyclic Transformations

An electrocyclic reaction is characterized by the opening, or closing, of a ring within a single molecule leading to the conversion of 2σ-electrons to 2π-electrons, or the reverse. The interconversion of butadiene and cyclobutene exemplifies an electrocyclic process (Equation 1.1). Likewise, 1,3,5-hexatriene undergoes an electrocyclic change to 1,3-cyclohexadiene (Equation 1.2).



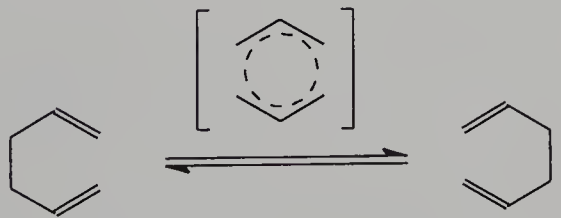
(1.1)



(1.2)

1.2.2 Sigmatropic Rearrangements

A sigmatropic reaction is a process that involves the migration of a σ-bond which is flanked by one, or more, conjugated systems to a new position within the system. Cope rearrangement represents such a process (Equation 1.3). Another example is the intramolecular migration of hydrogen as shown in Equation 1.4.



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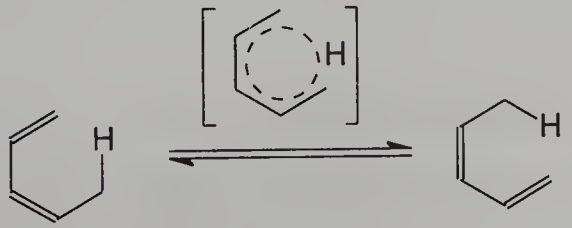
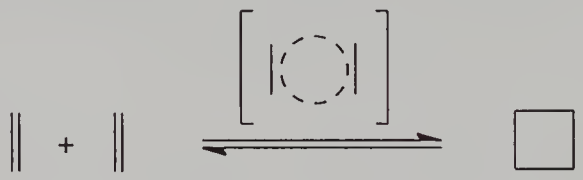


(1.4)

1.2.3 Cycloaddition Reactions

These reactions involve the linking of two or more π-systems to form a cyclic product by transferring electrons from π-bonds to σ-bonds. The Diels-Alder reaction is a prototype of such reactions (Equation 1.5). Another well known example is the dimerization of ethylene (Equation 1.6).

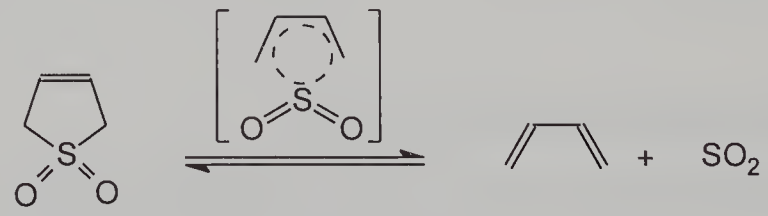
(1.5)



(1.6)

1.2.4 Cheletropic Reactions

These reactions may formally be regarded as a subclass of cycloadditions. The only difference is that on one of the components new bonds are made, or old bonds broken, involving the same atom. Equations 1.7 and 1.8 depict two well known examples.



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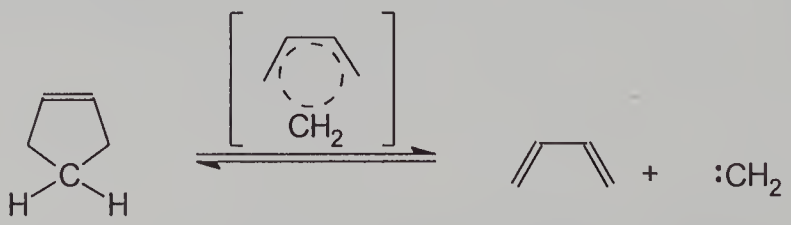
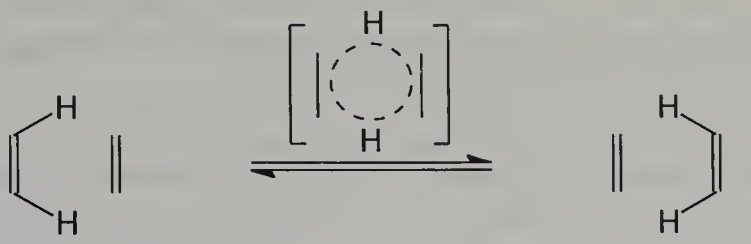


(1.8)

1.2.5 Group Transfer Reactions

Group transfer reactions are characterized by the transfer of a group, or groups, from one molecule to another as shown in Equations 1.9 and 1.10.



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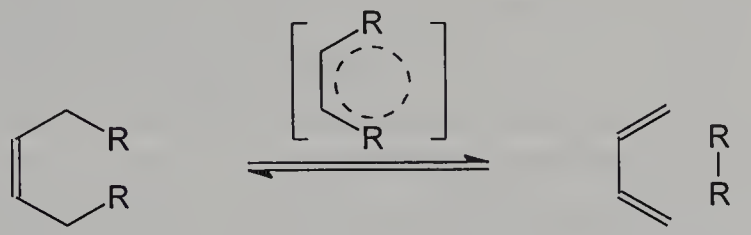


(1.10)

1.3 Analysis

The difficulties encountered during the investigation of the mechanism of concerted reactions in general, and pericyclic reactions in particular, are discussed. Pioneering work on the analysis and systematization of these reactions was carried out by Woodward and Hoffmann [2]. The basic idea of the Molecular Orbital theory was mainly used, in a qualitative way, to predict the stereochemical course of these reactions. Their theoretical framework was later recognized as Woodward-Hoffmann rules. These rules provided not only a rationale for a number of the then-known pericyclic transformations but also enabled startling predictions for the reactions which were not yet scrutinized. The original treatise of Woodward and Hoffmann was based on the principle of *Orbital Symmetry Conservation.* This fascinating idea stimulated the interest of a large body of chemists and led to the development of a number of alternate approaches namely the *Frontier Orbitals Approach* and the *Möbius-Hückel Approach.* All these approaches are asserted to be fundamental and serve to complement the predictions made by Woodward and Hoffmann as they are aspects of the same molecular orbital theory. Besides the three approaches, a set of generalized selection rules were formulated which are based on the concept of suprafacial and antarafacial approach of the reactants. However, the discovery of approximate, as well as precise, computational methods has provided an additional facility to comprehend the subject of pericyclic reactions in terms of the transition state structures. An interesting overview of sixty years (1935-1995) of pericyclic reactions was published by Houk *et al.*[3]. A brief discussion of the more often encountered approaches for analyzing pericyclic transformations follows.

1.3.1 Orbital Symmetry Conservation

The principle of orbital symmetry conservation is the central doctrine of the theory of pericyclic reactions. It implies that the transition state will relatively be of lower energy if the symmetry of the reactant orbitals is retained in passing to the product.

Such a process is said to be *symmetry allowed.* In contrast, the reaction would be disfavoured if the symmetry of the reactant and product orbitals was not the same. Such a process would be termed as *symmetry forbidden.*

It is also possible to treat pericyclic reactions in another way, i.e. a two-sided correlation diagram approach. This approach was first applied by Longuett-Higgins and Abrahamson to pericyclic reactions [4 a-d]. The passing of the reactant orbitals into those of the product is referred to as a correlation of these orbitals, and an orbital energy diagram showing a correlation of the reactant orbitals with the product orbitals is termed as energy level correlation diagram. Only the occupied and unoccupied orbitals corresponding to the bonds being made, or broken, during the course of a reaction are included in the diagram.

If in an energy level correlation diagram, a correlation of the bonding molecular orbitals of the reactants with those of the products is possible with symmetry conservation, then the process is described as a *thermally allowed process*, else as a *forbidden process.*

However, if the reactant is first converted to an excited state then one of its antibonding orbitals gets occupied. If this highest occupied antibonding orbital decays to a lower energy bonding orbital, then the process would be photochemically favourable, else forbidden. Moreover, the thermal reaction yields one stereochemical product only while the photochemical control yields the other isomer. A detailed account of orbital symmetry conservation during electrocyclic transformations, and the correlation analysis of these reactions, would be discussed in Chapter 3.

Another approach, related to the energy level correlation analysis, is called the OCAMS view (Orbital Correspondence Analysis in Maximum Symmetry) and was developed by Halevi [5]. However, the scope of this book limits its detailed discussion.

1.3.2 Frontier Orbitals Approach

During a chemical reaction old bonds are broken and new bonds are formed, either simultaneously, or in steps. In either case, electrons vacate the molecular orbitals of broken bonds, to fill the molecular orbitals of new bonds. This flow of electrons is most important between the HOMO (Highest Occupied Molecular Orbital) and the LUMO (Lowest Unoccupied Molecular Orbital) of the interacting species. These two molecular orbitals are described as the *frontier orbitals.* The significance of these orbitals in rationalizing chemical reactions is well documented [6 a,b]. A chemical reaction occurs when the overlap is maximum between the HOMO and the LUMO of the reacting species, provided the overlapping orbitals have the matching symmetry properties. Thus the course of a chemical reaction is determined solely by looking at the interactions between HOMO and LUMO of the reacting species. This method was developed primarily by Fukui [7] and is a practical representation of the fundamental property that a majority of chemical reactions take place at the position, and in the direction, of maximum overlapping of the frontier orbitals of the reacting species. It provides a simple and practical method to interpret, or predict, the

favourable steric pathway of rather complicated reactions. The application of frontier orbitals theory to electrocyclic reactions would be discussed in Chapter 4.

In addition to the frontier orbitals analysis of pericyclic reactions, Woodward and Hoffmann had also derived a set of generalized selection rules. These rules were based on the concept of the suprafacial and the antarafacial approach of the reactants. These concepts would be discussed in Section 4.3.

1.3.3 Möbius-Hückel Approach

The feasibility of a pericyclic reaction may be correlated with the stability of the transition state of a reaction. This was the approach advanced by Zimmermann [8] who proposed the idea that the concept of aromatic stability of the transition state can be used as a criterion for predicting the favourable mode of a concerted reaction. An examination of the transition states of pericyclic reactions reveals that they differ in their topologies, i.e. some reactions proceed through transition states that have a Hückel topology while others through a Möbius topology. The term Hückel topology refers to a system which is composed of an orbital array with zero, or an even number, of phase dislocations or sign inversions. On the other hand, a Möbius topology refers to an orbital system which is composed of a cyclic orbital array where at least one sign inversion is inevitable.

Hückel systems are stabilized by (4n+2) electrons, because this configuration leads to a closed-shell electronic arrangement. Closed-shell means an electronic arrangement where all electrons are present in bonding orbitals with their spins paired. On the contrary, Möbius systems are stabilized by (4n) electrons leading to a closed-shell configuration. Therefore, Hückel systems are aromatic with (4n+2) electrons and Möbius systems are aromatic with (4n) electrons (Table 5.5). Pericyclic reactions prefer Hückel geometries when (4n+2) electrons are involved and Möbius geometries when (4n) electrons are involved. The rules for photochemical reactions are just the reverse of those formulated for thermal processes (Figure 5.34).

1.3.4 Theoretical and Computational Approach

In addition to the most commonly encountered theories discussed in the preceding sections, computational analysis of pericyclic reactions has further facilitated the comprehension of the seemingly cumbersome subject of pericyclic reactions. These methods include the EHMO (Extended Hückel Molecular Orbital), MNDO (Modified Neglect of Differential Overlap), CNDO (Complete Neglect of Differential Overlap) and *ab initio* calculations. These methods help in determining the energetically favourable reaction pathways. The results obtained through these calculations are in agreement with theoretical and experimental observations in most cases. The transition state structures of a number of pericyclic reactions utilizing computational methods were reported by Dolbier *et al* [9] and constitute the subject matter of Chapter 6.

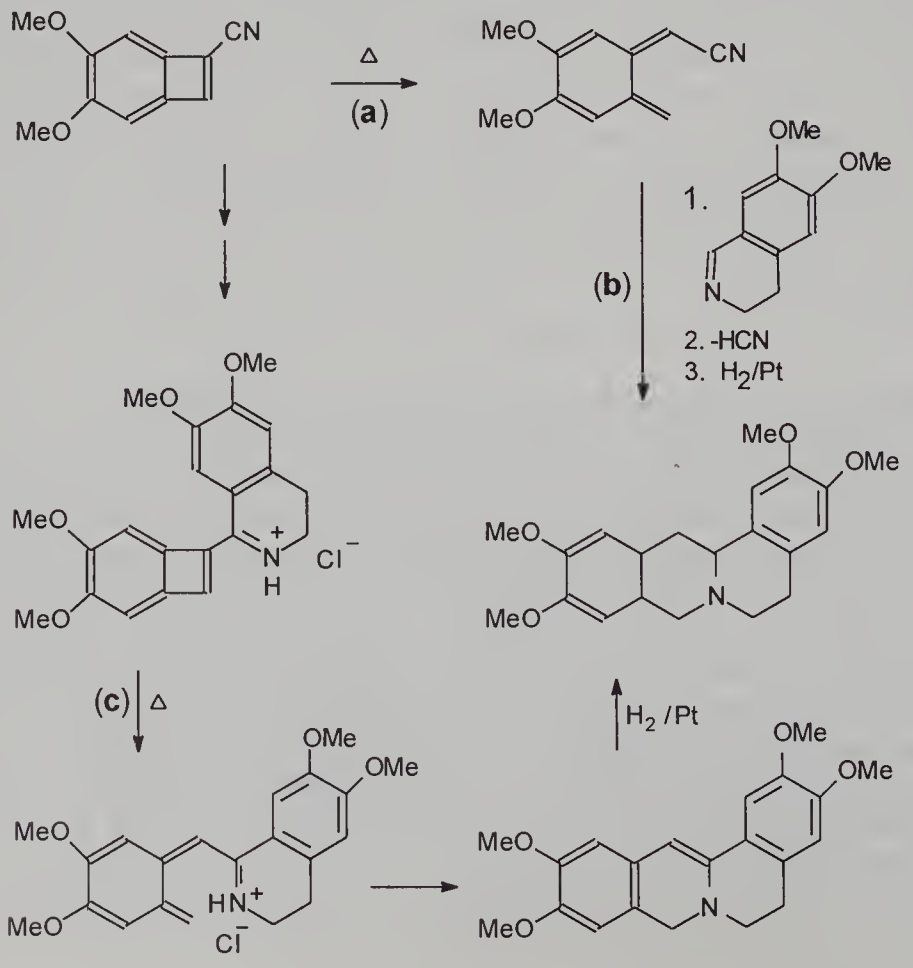
1.4 Significance

The practical aspects of pericyclic reactions in synthesis are important for several reasons.

In the first place they are generally independent of external influences, so that the unanticipated effects of solvents, concentrations, catalysts etc., which frequently complicate other reactions, rarely deflect the course of pericyclic reactions.

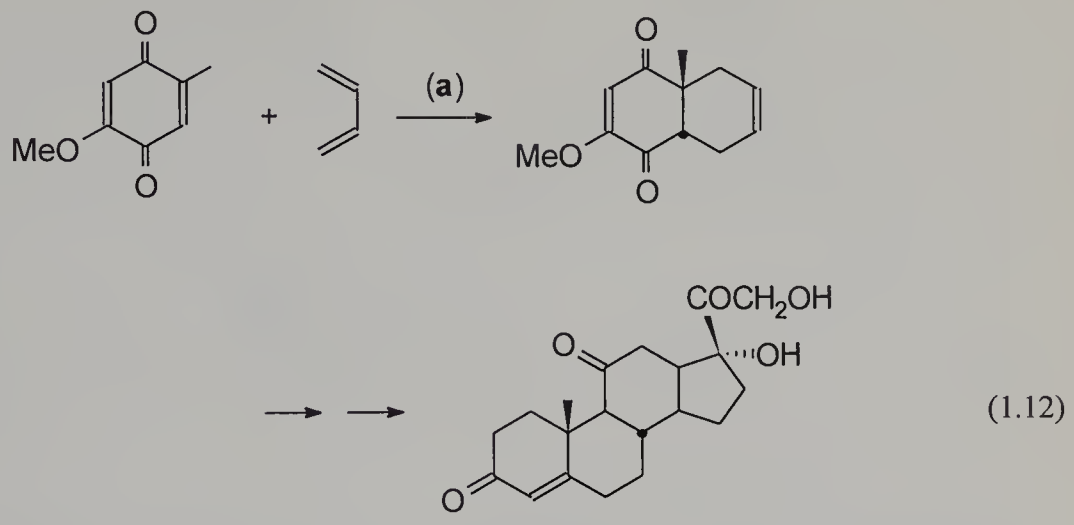
Secondly, many of these reactions create new carbon-carbon-σ-bonds and hence are available for carbon skeleton construction. The synthesis of a wide variety of heterocyclic systems involve pericyclic transformations. The principles of 1,5-electrocyclizations and 1,3-dipolar additions are very important and govern the stereospecific synthesis of a variety of heterocyclic compounds. These reactions will be discussed in detail in Chapter 2. Moreover the synthesis of a wide variety of natural products exploits essential pericyclic transformations [10].

For example the synthesis of xylopinine [11a] involves a series of pericyclic changes including an electrocyclic ring opening of benzocyclobutene (**a**), a cycloaddition reaction (**b**) and an electrocyclic ring opening of a benzocyclobutene (**c**). These changes are shown in Equation 1.11.



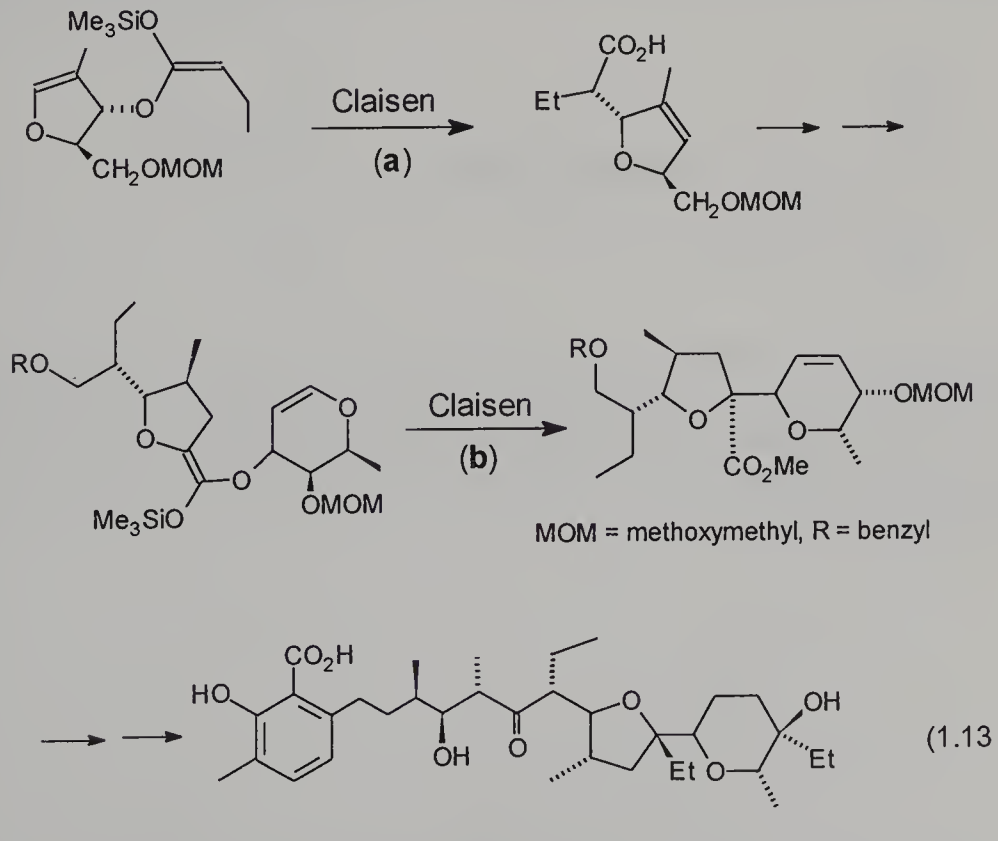
(1.11)

A stereospecific synthesis of the steroid, cortisone, by Woodward [11b] is based upon the Diels-Alder reaction (a) as shown in Equation 1.12.



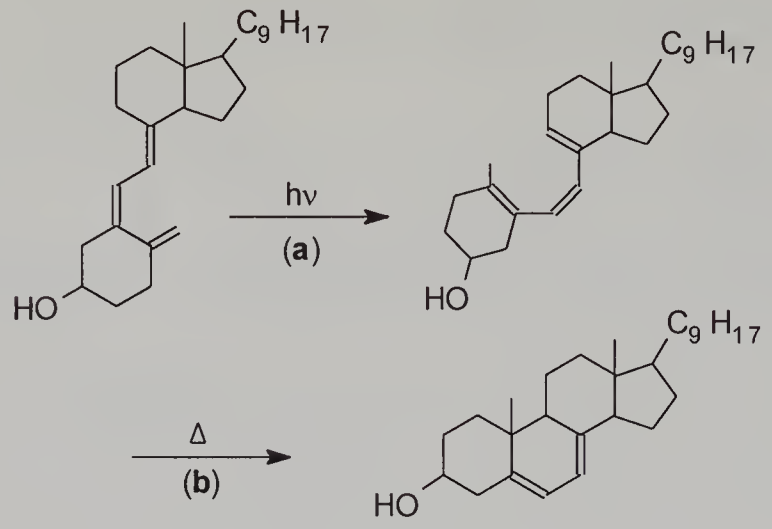
(1.12)

Two essential steps (a) and (b) in the synthesis of lasalocid A [11 c,d] require sigmatropic shifts as shown in Equation 1.13.



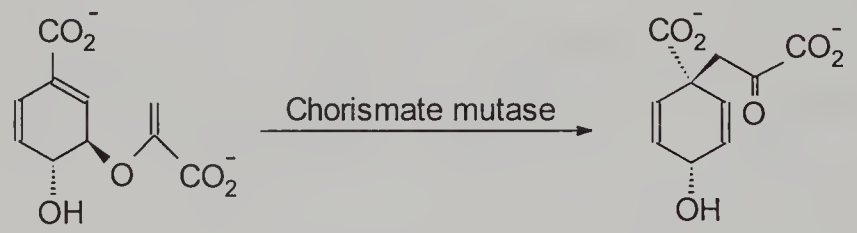
(1.13

There are also pericyclic reactions involved in important biological processes. Ergosterol undergoes a series of photochemical and thermal pericyclic reactions to form Vitamin D_2 [12 a-c]. The first step is a sigmatropic rearrangement (a) while the second step is an electrocyclization of a triene (b) as shown in Equation 1.14.



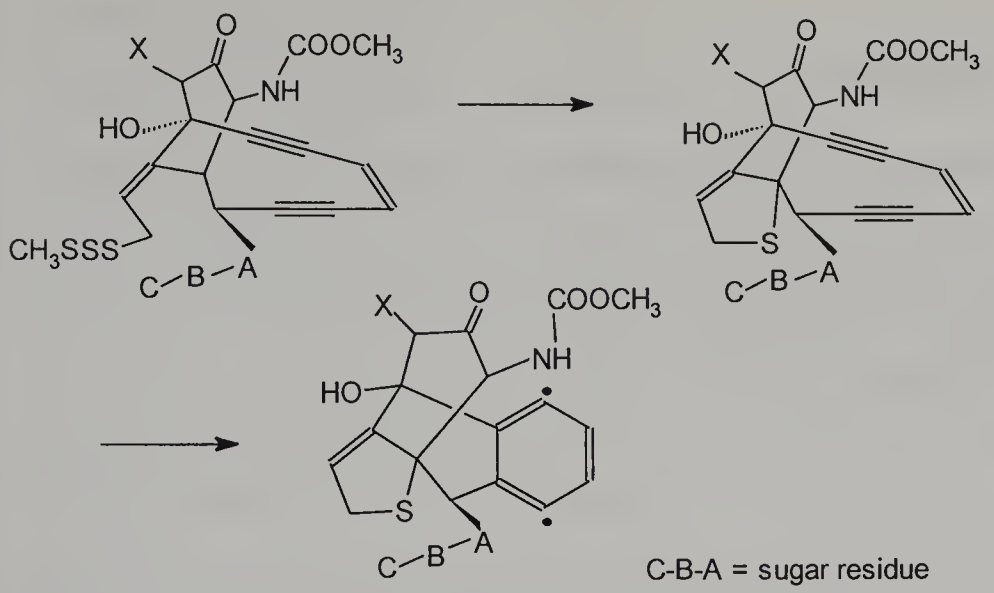
(1.14)

The Chorismate prephenate rearrangement [13 a,b], which occurs in the biosynthesis of aromatic aminoacids in plants, may be considered formally as the Claisen rearrangement and is catalyzed by the enzyme chorismate mutase (Equation 1.15).



(1.15)

The electrocyclic formation of a biradical that reacts with DNA is the origin of activity of the esperamic and calicheamicin series of antibiotics (Equation 1.16). This biradical mechanism has generated worldwide interest in these types of reactions and in the use of thermal rearrangements to generate reactive intermediates for biological action [14 a-k]



(1.16)

The significance of pericyclic reactions is evident. Extensive efforts are being made to carry out in-depth mechanistic studies of these reactions and would be discussed in the following chapters.

1.5 References

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2. Electrocyclic Transformations

During the course of synthesis of vitamin B_{12}, Woodward obtained a cyclic product (1) which, upon heating, cyclized to (2) as was hoped but with the stereochemistry opposite to that expected on the basis of steric and electronic factors (4). Furthermore the same compound, on irradiation, reopened to a triene (3) which upon heating gave the desired product (4). This pretty set of observations provided the first hint concerning the electronic factors which govern the stereochemical course of pericyclic reactions in general and electrocyclic reactions in particular [1 a,b].

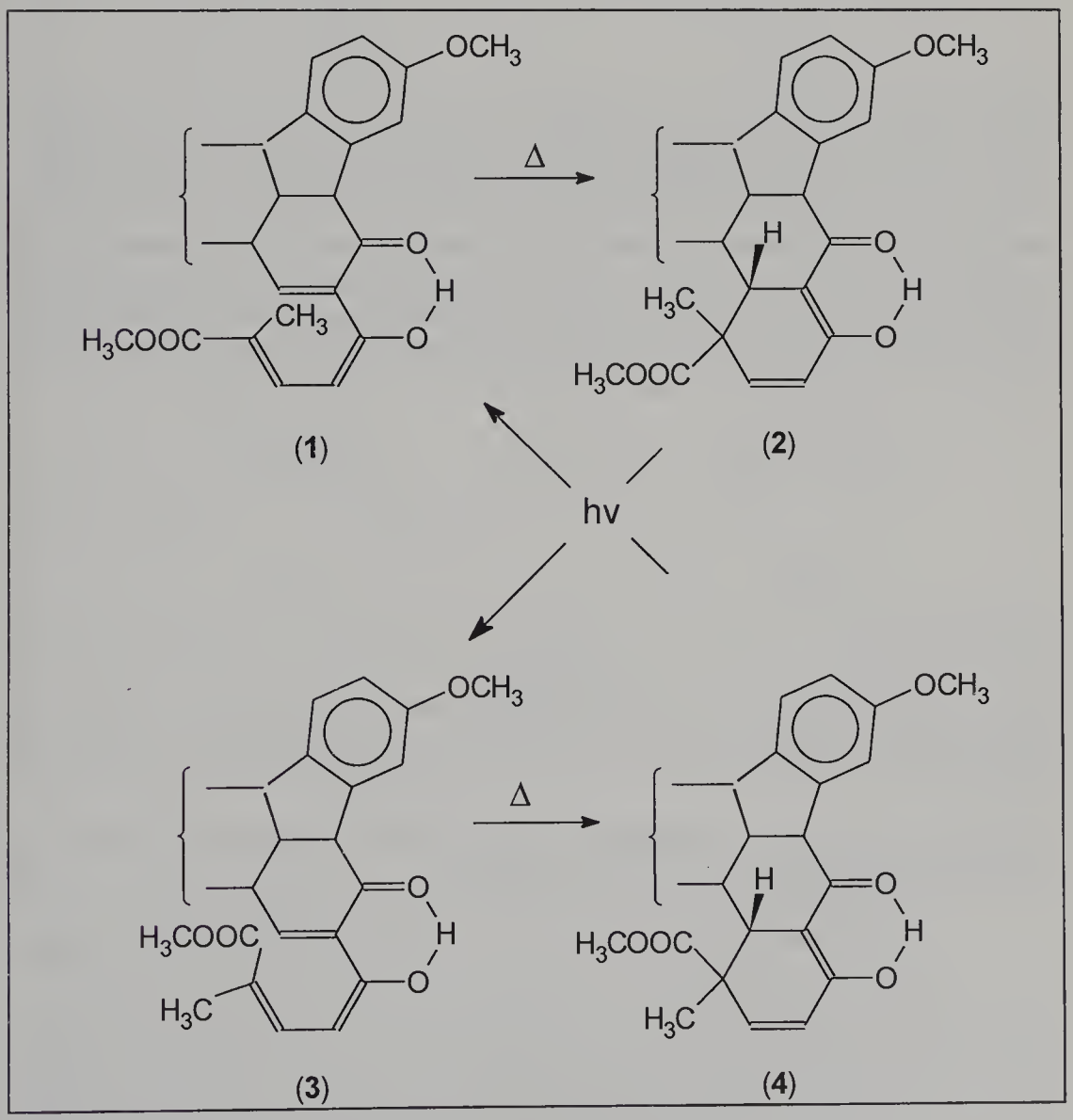


Figure 2.1: *Electrocyclic reactions during the synthesis of vitamin B_{12}.*

2.1 Mechanism

An electrocyclic process involves the cyclization of an (nπ)-electron system to an (n-2)π +2σ electron system and the reverse process.

(162) **(163)**

These reactions are usually reversible and the observance of the ring opening depends upon the thermodynamic stability of the open chain and the ring forms. These reactions may be induced by heat, ultravoilet irradiation or metal catalysts. Moreover they are found to be highly stereospecific. The interconversion of *cis*-1,3-butadiene and cyclobutene is one of the most commonly quoted examples of electrocyclic processes. (Equation 2.1). It involves the transformation of a 4π-electron-butadiene system to a 2σ- and a 2π-electron-cyclobutene system. Clearly this cyclization requires the formation of a bond between the terminal carbon atoms 1 and 4.

(2.1)

(5) **(6)**

The desired bond is formed by rotating the two termini *a* and *b* of the diene (Figure 2.2).

The rotation of the two termini in the same direction is termed as conrotation; *conversely, the rotation of the two termini in opposite directions is described as* disrotation.

As long as the diene is unsubstituted or symmetrically substituted, the products of the two modes of rotation are not distinguishable.

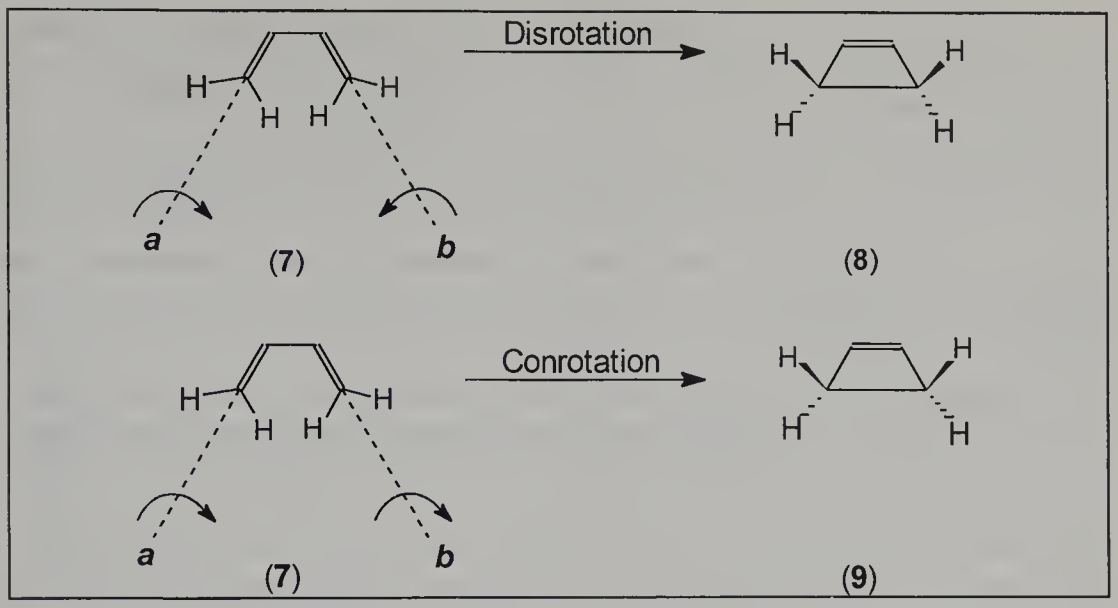


Figure 2.2: *Two idealized modes of an electrocyclic transformation.*

It is possible to keep track of the terminal hydrogen atoms by substitutiing the hydrogen atoms with deuterium, or any other substituent, and the two products would then become distinguishable (Figure 2.3).

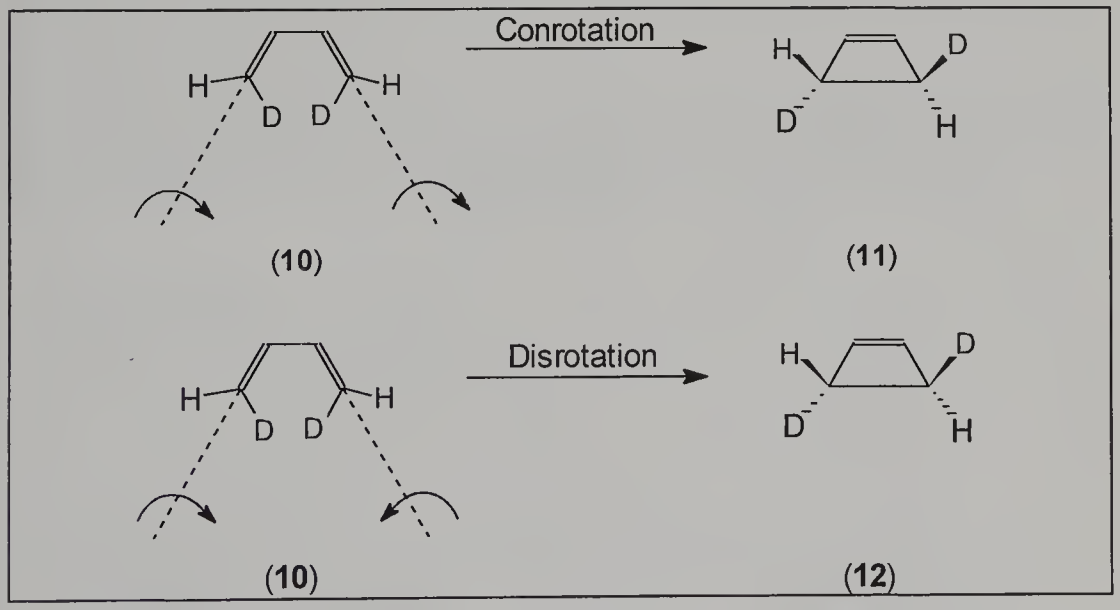


Figure 2.3: *Concerted electrocyclic transformation of a substituted diene.*

The conrotatory mode leads to a *trans* product (11) while that of a disrotatory mode leads to the *cis*-product (12). At this stage, it is not known which of the two paths the reaction would follow. Figure 2.3 depicts an extreme case of a concerted process where both methylene groups rotate by equal amounts as the reaction proceeds. The opposite extreme is a non-concerted, or stepwise, process wherein one methylene group rotates 90° and only after this rotation is complete would the other group begin to rotate. However, the second methylene group is likely to rotate either way giving a mixture of the two products.

Apart from the two mentioned extreme cases, it is also possible to think of a substantial degree of concertedness which implies that the second methylene group should start rotation before the first one has completed 90°. This would involve the destruction of the (4π)-system and the formation of an isolated π- and a new $\sigma_{C\text{-}C}$ - bond. Energy is lost in the breaking of old bonds and gained in the formation of new ones. The lowest energy path would be the one where the new bonds start to form before the old ones are completely broken. Evidently, the new σ-bond cannot be formed to any significant extent until both methylene groups have undergone some rotation.

It is experimentally established that many electrocyclic reactions are highly stereospecific and give 100% of a single stereochemical product. It is observed that both the conrotatory and disrotatory motions can occur in two different ways leading to the formation of stereochemically different products (Figure 2.4). If one mode dominates, then the reaction is said to be *diastereoselective*. During the course of the above reaction, two new saturated centres are formed. With maximum labeling, a total of 4 (i.e. 2^2) stereoisomeric forms consisting of two enantiomeric pairs of diasteromers may be formed (if the polyene is chiral). For example a conrotatory cyclization of (13) yields two enantiomeric cyclobutene derivatives (14) and (15) while the disrotatory process leads to another enantiomeric pair (16) and (17).

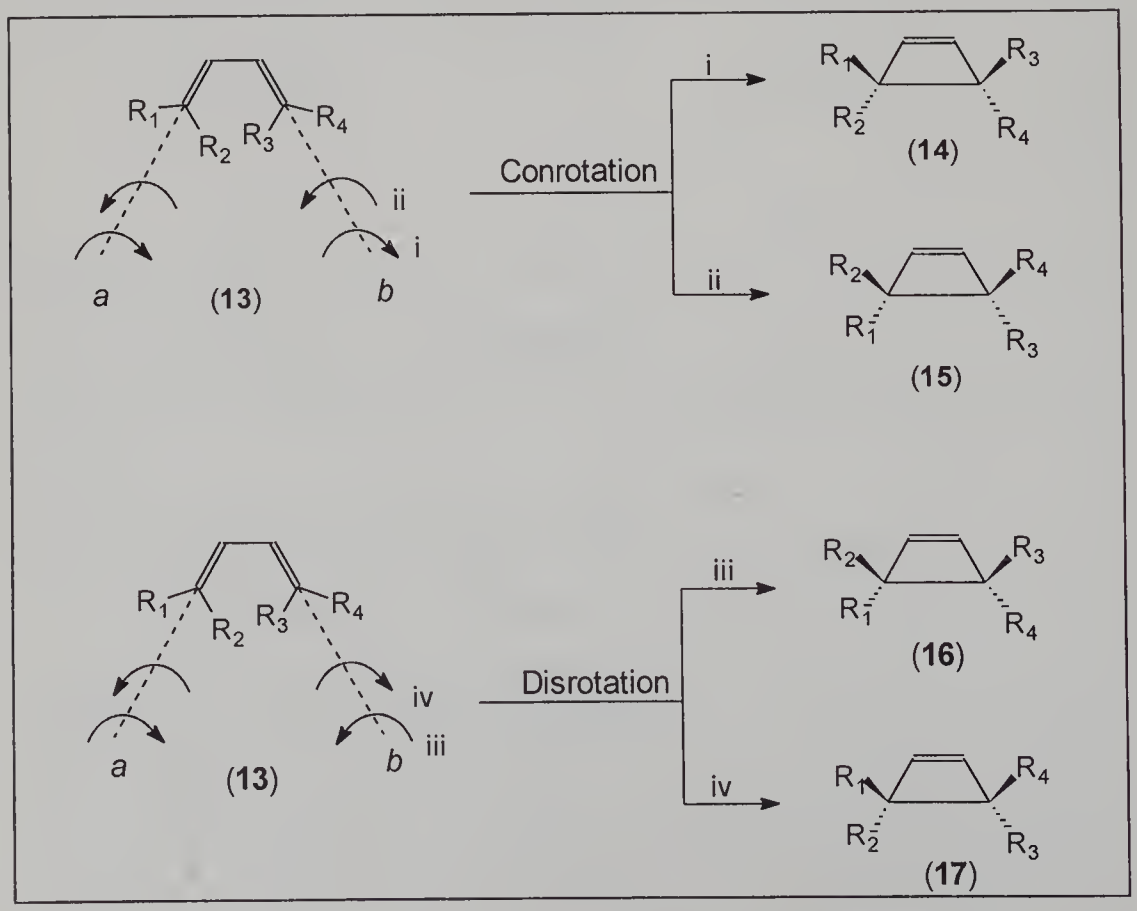


Figure 2.4: *Four different modes of cyclization of a substituted diene.*

With the chiral diene the following four possibilities exist;

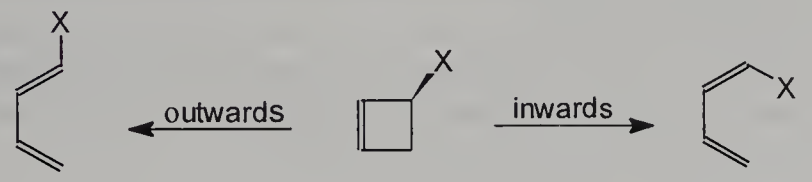
i) both terminii rotate clockwise.

ii) both terminii rotate anticlockwise.

iii) terminal *a* clockwise and *b* anticlockwise.

iv) terminal *a* anticlockwise and *b* clockwise.

Extensive theoretical studies were carried out on the ring opening of substituted cyclobutenes [2 a-c] and it was observed that mono-substituted cyclobutenes undergo a thermally allowed conrotatory ring opening by an inward (19), or by an outward (20), rotation of the substituent X (Equation 2.2).

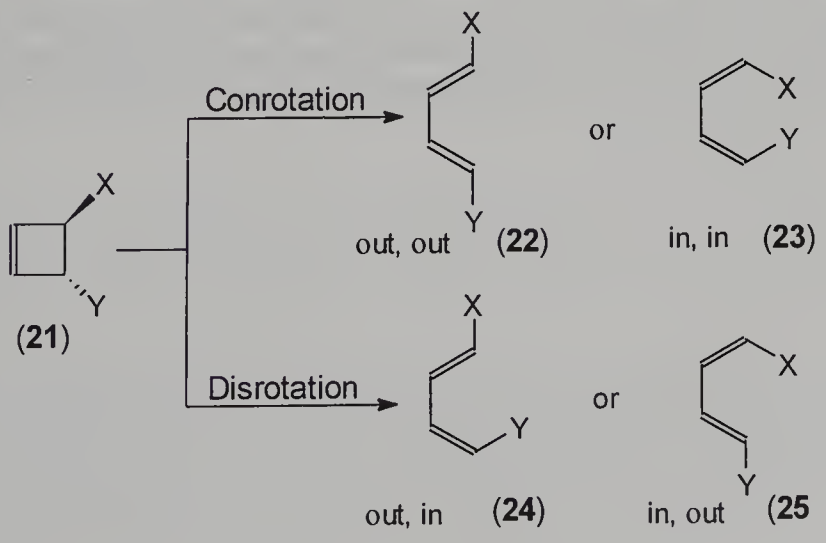


(2.2)

(20) **(18)** **(19)**

The two possible products of the conrotatory ring opening of a 1,4-disubstituted cyclobutene (21) are shown in Equation 2.3 while the products of the two disrotatory alternatives are given in Equation 2.4.

According to recent theoretical predictions made by Dolbier *et al* [2d], the tendency for an outward rotation increases as X becomes a better π-electron-donor and an inward rotation occurs when X becomes a strong electron-acceptor (Chapter 6).



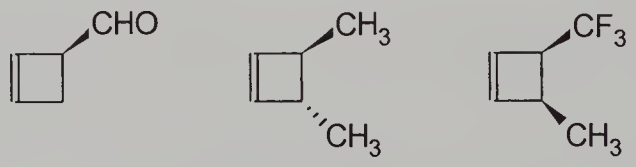
(2.3)

(2.4)

Problem 2.1:

Predict the stereochemistry of the products, formed as a result of two possible conrotatory movements in each of the following compounds.

(Hint: generalization by Dolbier).



Woodward and Hoffmann have established the following set of selection rules for electrocyclic transformations [3 a-c].

An electrocyclic reaction would be allowed, in the ground state, as a disrotatory process if the number of delocalized electrons in the polyene is (4n+2), and as a conrotatory process if the polyene contains (4n) electrons.

The rules get reversed for the photochemical reactions.

Photochemical electrocyclic transformation of a polyene with (4n+2) electrons would be allowed through conrotation while that of a polyene with (4n) electrons would be through disrotation.

Electrocyclic changes are observed in ionic systems and the number of electrons in the polyene would be decisive in determining the stereochemical course of these reactions. Moreover, the radical ions also undergo electrocyclic changes as do the neutral and ionic systems.

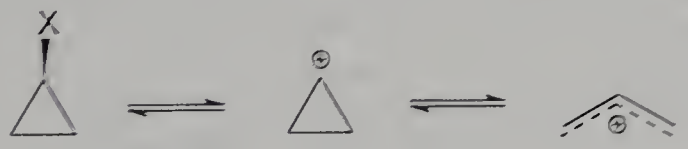
The selection rules developed by Woodward and Hoffmann are confirmed through *Orbital Symmetry Conservation, Frontier Orbitals Approach, Möbius-Hückel Approach* and through *Computational and Theoretical Analysis*. The detailed analysis of these reactions on the basis of these four approaches makes the subject matter of the following chapters.

2.2 Thermal Electrocyclizations

As mentioned earlier, electrocyclic transformations may be affected either thermally or photochemically. The thermal and photochemical reactions are discussed under separate headings. Moreover the behaviour of radical ions undergoing electrocyclic transformations are discussed separately. Typical examples of electrocyclic reactions can be discussed by arbitrarily classifying them with respect to the relative position of the newly formed σ-bond.

2.2.1 [1,3] Electrocyclic Reactions

The simplest electrocyclic reaction is the ring opening of cyclopropyl cation (26) to an allyl cation (27).



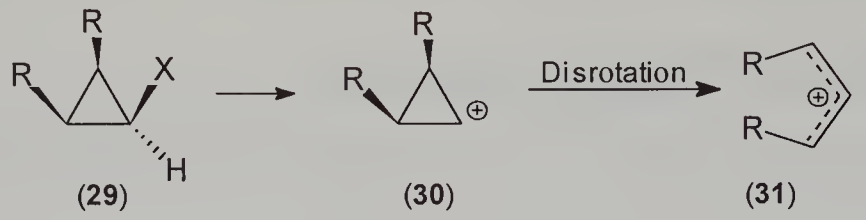
(2.5)

(26) (27) (28)

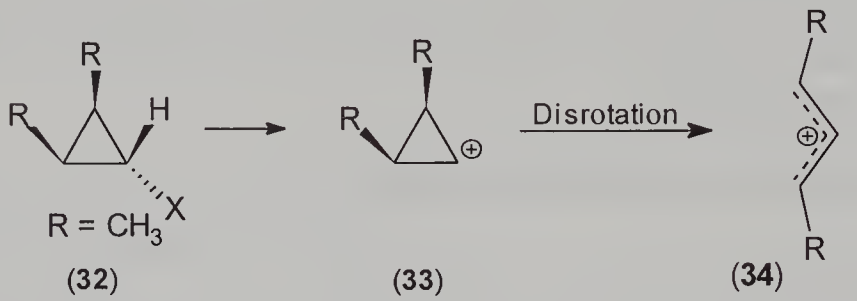
The reaction appears to be irreversible because only the ring opening of cyclopropyl cations is experimentally observed. Even if both reactions are allowed, the formation of cyclopropyl cation must be disfavoured thermodynamically as compared to the allyl cation because of the ring strain in the former system. Cyclopropyl cations are reactive intermediates which are generally formed from stable covalent compounds. Since this electrocyclic transformation involves two electrons, i.e. a $(4n+2)$-electron system, the interconversion takes place through disrotation in accordance with Woodward-Hoffmann's predictions. For example the hydrolysis of 2,3-disubstituted cyclopropyl halides is observed experimentally.

For the *cis*-2,3-disubstituted cyclopropyl cations (30) and (33) obtained by the hydrolysis of the corresponding halides (29) and (32), the disrotatory and conrotatory modes afford two geometrically different allyl cations (Equations 2.6 and 2.7).

This is directly observed by NMR spectroscopy at -100°C in a strong acidic medium. The rearrangement must proceed in a single step since in each mode only one allyl cation is observed. This indicates that the ring opening is synchronous with the departure of the leaving group [4 a-d].



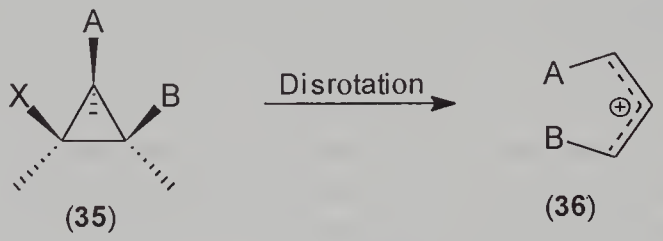
(29) (30) (31) (2.6)



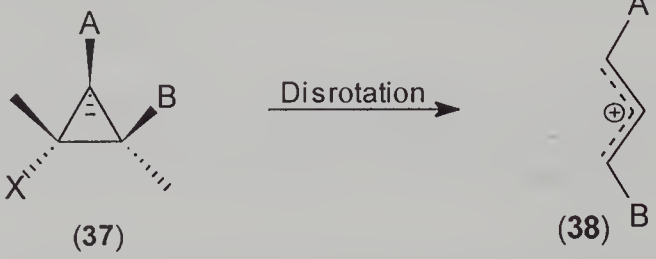
(32) (33) (34) (2.7)

As explained earlier, there are two possible modes of rotation both for disrotation and conrotation depending on whether the substituents rotate outwards or inwards, hence two stereochemically different products are possible. In the case of the cyclopropyl- allyl cation system, an all-*cis*-derivative (35) generates an all-*cis*-allyl cation (36) by an inward rotation of the substituents (Equation 2.8).

These observations were confirmed experimentally as the *anti*-derivatives solvolyze faster than the corresponding *syn*-derivatives [5 a,b].

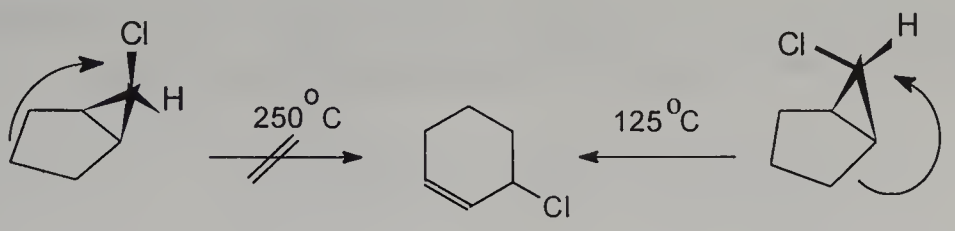


(35) (36) (2.8)



(37) (38) (2.9)

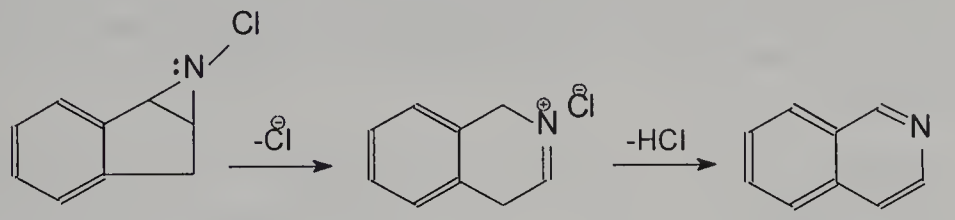
Conversely, the *anti*-derivative (37) forms an all-*trans* cation (38) during an outward disrotatory process (Equation 2.9). The process shown in Equation 2.9 is favoured if A and B are bulky groups. Woodward and Hoffmann confirmed this in several systems [6]. One such example is provided by the isomeric 6-chloro-bicyclo [3.1.0] hexanes (39) and (40), the *endo* (39) is found to convert in a disrotatory manner into 3-chlorocyclohexene (40) after heating for three hours at 125°C but the *exo*-isomer (41) was found unchanged even under more vigorous conditions. This indicates that the leaving group has to be *endo* for smooth ring opening to take place in a disrotatory mode [7 a,b].



(2.10)

Exo (41) (40) *Endo* (39)

The allyl-cyclopropyl-isomerization is very important, specially in the synthesis of bicyclic systems (42) where it leads to ring expansion (43) [7].



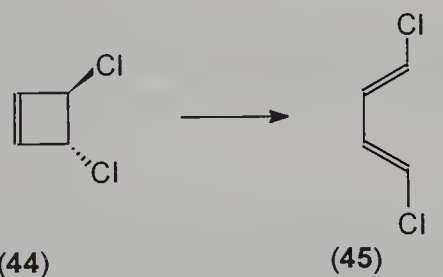
(2.11)

(42) (43)

The reaction has also found extensive application in the synthesis of large heterocyclic systems, specially five-membered ring systems, starting from three-membered heterocyclic systems. This would be discussed in the following sections.

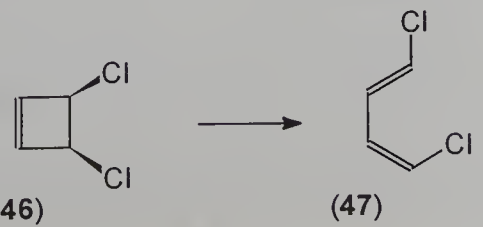
2.2.2 [1,4] Electrocyclic Reactions

1,3-Butadienes and cyclobutenes are related by a reversible [1,4] electrocyclic transformation. The two reactions may be carried out separately. In a thermal process, only the ring opening of cyclobutene is observed as a spontaneous process since cyclobutenes are thermodynamically less stable as compared to dienes. Consequently only photochemically can the ring closure of dienes be carried out in high yield. Typical examples of electrocyclic transformations occur with isomeric *trans*-and-*cis*-3,4-dichlorocyclobutenes (44) and (46) respectively [8].



(2.12)

(44) (45)



(2.13)

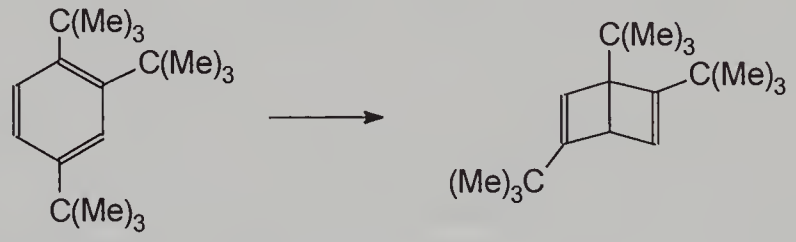
(46) (47)

A spectacular example of an electrocyclic transformation is provided by direct synthesis of Dewar benzene from benzene (Equation 2.14) [9].

(2.14)

(48) **(49)**

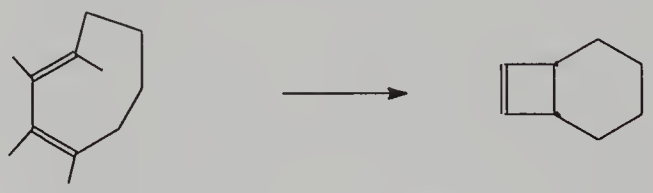
The process seems to be disfavoured by the high energy gap between the stable aromatic compound (48) and the strained bicyclic derivative (49). However, the presence of bulky groups on the benzene ring at *ortho*-and *para*-positions facilitates an electrocyclic transformation because the non-bonding interactions between the bulky tertiary butyl groups are reduced to a considerable extent in the non-benzenoid isomer (51) [10 a,b].



(2.15)

(50) **(51)**

An example of the reverse process is provided by the conrotatory cyclization of the strained *cis,trans*-1,3-cyclooctadiene (52) which takes place at 80°C [11].



(2.16)

(52) **(53)**

Fused ring cyclobutenes (54) are converted to monocyclic dienes (55) under more drastic conditions because these cyclobutenes are thermally stable, specially those in which the cyclobutene ring is fused to a five- or a six-membered ring [12].

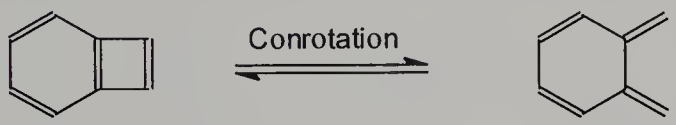
(2.17)

(54) **(55)**

Problem 2.2:

Offer a rationale for the following experimental observation.

Benzocyclobutene is reported to undergo electrocyclic transformation as shown (Equation 2.18) [13].

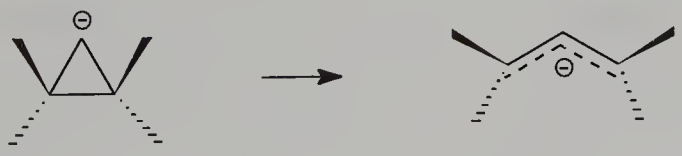


(56) (57) (2.18)

Problem 2.3:

Vinyl heptafulvene is synthesized by an electrocyclization of dihydrofulvene. Predict the mode of both the forward and backward reactions.

The allyl anion, an electronic prototype of butadiene, was predicted to undergo conrotatory cyclization in accordance with Woodward-Hoffmann rules, although no clear-cut example was known at that time. Today the reaction is well established but the evidence for conrotation is still unsatisfactory because substituted allyl anions are capable of free rotations. In order to inspect their original structure, they must transform immediately to stable derivatives with retention of configuration.



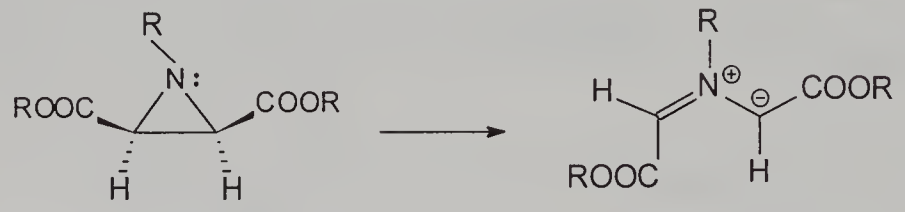
The allyl anion is also an electronic prototype of a 1,3-dipolar compound but lacks the right blend of nucleophilic and electrophilic characters. The replacement of the middle -CH by a heteroatom gives rise to a zwitterion which is isoelectronic with the allyl anion, if the lone pair on the heteroatom is also included. Thus, the replacement of -CH by -NR gives rise to an azomethine ylide which is a 1,3-dipolar compound. The same relationship holds for aziridines and cyclopropyl anions.

The three-membered heterocyclic systems such as (58) undergoes a ring opening just like a cyclopropyl cation system to form a 1,3-dipolar compound (59) [14].

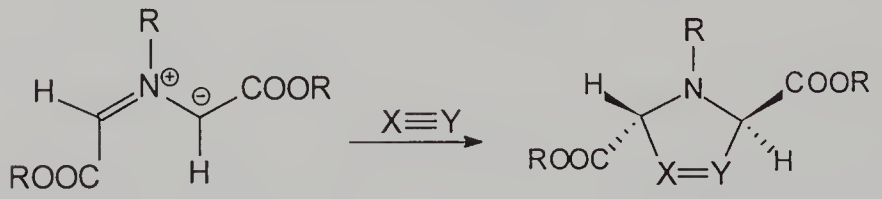
(58) (59)

X = N, O, S etc.

Many *cis*- and *trans*-diesters e.g. (60) and (63) undergo thermal electrocyclic ring openings to form the intermediate 1,3-dipolar compounds (61) and (64) which being isoelectronic with the diene may be trapped by a dienophile to form the adducts (62) and (65) respectively [15].



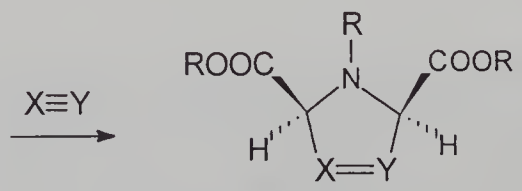
cis (**60**) *trans* (**61**)



(2.20)

trans (**61**) *trans* (**62**)

trans (**63**) *cis* (**64**)



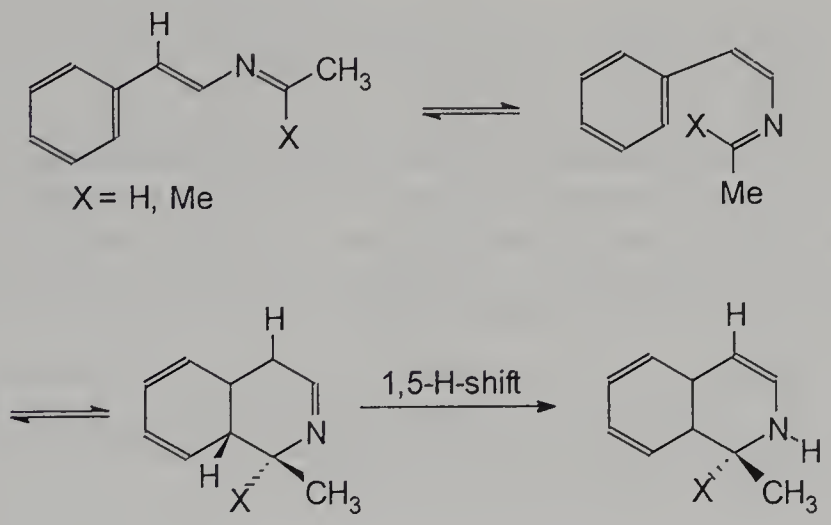
(2.21)

cis (**65**)

This reaction has found extensive application in the synthesis of five-membered heterocyclic systems from three-membered heterocyclic systems.

Problem 2.4:

The hetero-substituted butadienes e.g. 2-*aza*-1,3-butadiene also undergoes thermal electrocyclization leading to a new approach to N-heterocyclic annelation as shown. Predict the reaction mode of the step involving an electrocyclic change [16].



2.2.3 [1,5] Electrocyclic Reactions

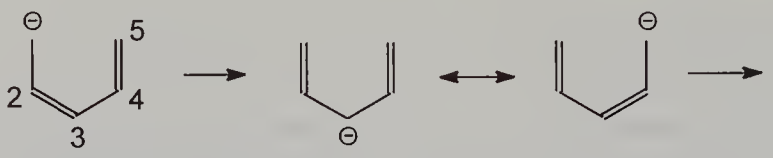
Pentadienyl anions (66) and cyclopentenyl anions (67) undergo a valence isomerization which is described as a [1,5] electrocyclic transformation. The same is true for the corresponding cation and the radical [17].

(66) (67) (2.22)

The pentadienyl system may ideally exist in three planar conformations.

U- *W-* *S-*

The anion (68) possesses six electrons which are present in five *p*-orbitals on five carbon atoms and undergoes electrocyclization as shown in Equation 2.23.

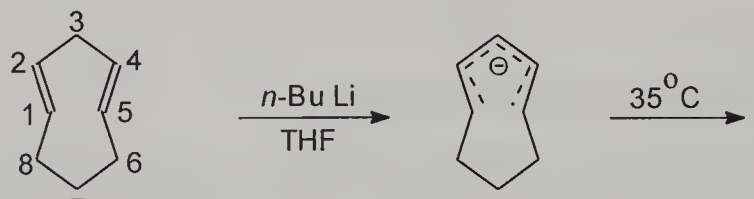


(68)

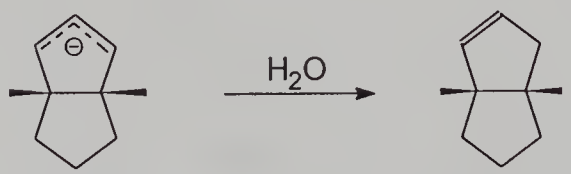
(69) (2.23)

The resonance structures shown indicate the presence of a greater electron density at C1, C3 and C5, of the pentadienyl system. It is usually the *U*-shape of the system which undergoes electrocyclic transformations. The anion possesses six electrons and being a (4n+2)-electron system undergoes thermal change through disrotation, as predicted by the Woodward-Hoffmann rules.

The deprotonation of a 1,4-cyclooctadiene (70) in the presence of *n*-butyl_lithium results in the formation of a cyclopentadienyl anion (71) which undergoes disrotatory electrocyclization at 35°C to a bicyclic-allyl anion (72). This anion afterwards leads to a *cis*-bicyclic product (73) [18].

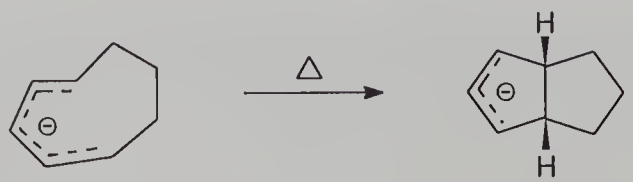


(70) (71)



(72) (73) (2.24)

The only recorded example of the thermal electrocyclization of a pentadienide ion to give a cyclopentenide ion is the disrotatory conversion of a cyclooctadienide ion (74) to the *cis*-bicyclo [3.3.0] octenide ion (75) [19].



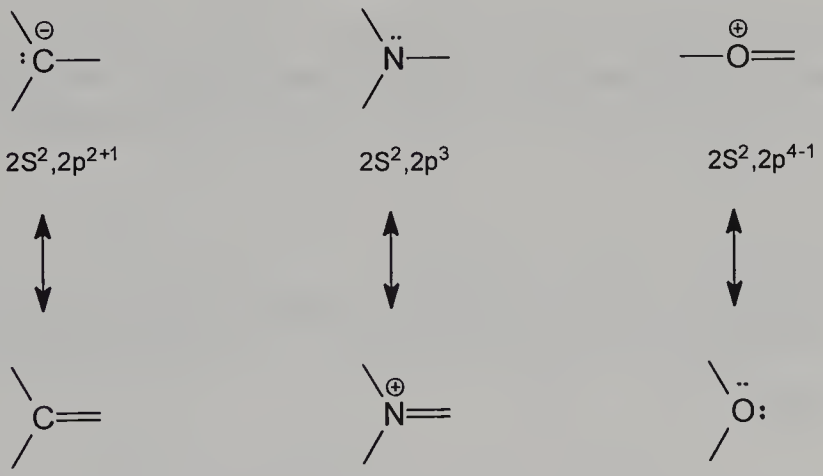
(74) (75) (2.25)

The electrocyclic interconversion of the pentadienyl anion and cyclopentenyl anion is relatively unimportant in all-carbon systems and could not be verified in the case

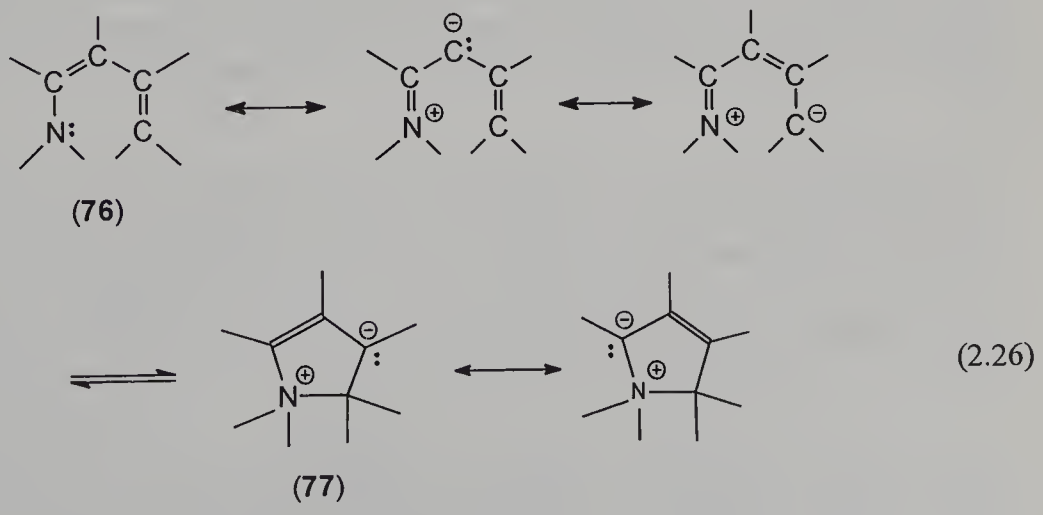
of the parent anion. However, in the heterocyclic series, where a maximum of five carbon atoms of the pentadienyl system are replaced by heteroatoms, a multitude of ring closures and ring openings are observed [20]. The replacement takes place isoionically or isoelectronically. This is explained with nitrogen and oxygen as examples and applies equally well to other heteroatoms.

2.2.3.1 Isoelectronic Exchange

The bonded atoms which have the same total number of electrons in their outermost shell but differ in their nuclear charge are termed as *isoelectronic*. For example, the nitrogen of an amino-function and the oxygen of an ether moiety are isoelectronic with the carbanion. These isoelectronic analogs are shown below:

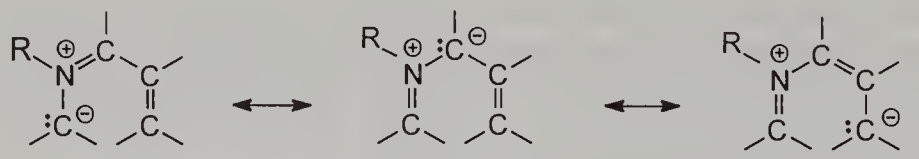


This isoelectronic exchange of a carbon with a heteroatom is possible at any position of the pentadienyl system. As an example the exchange of C1 by nitrogen in a pentadienyl system results in compound (76) which may undergo [1,5]-electrocyclization to form an azole ring system (77). Since the system contains six electrons thermal cyclization takes place through disrotation [20].

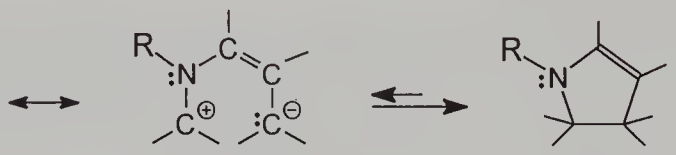


(2.26)

Isoelectronic substitution by -NR at 2–position results in an iminium zwitterion (78) which undergoes cyclization to a cyclic enamine (79) [20].



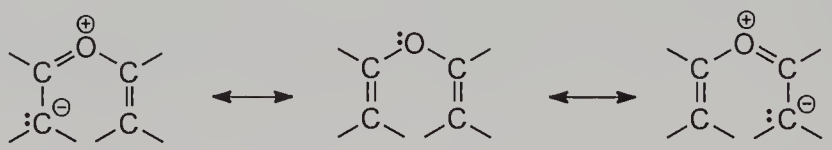
(78)



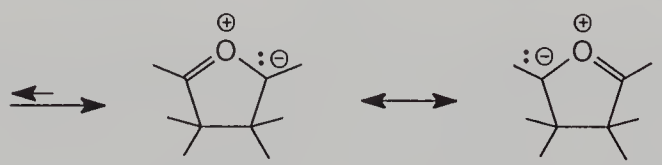
(79)

(2.27)

Just like an isoelectronic exchange of heteroatom at the C2 position, the exchange at C3 is observed. This is exemplified by the exchange of oxygen at C3 leading to a carbonyl ylide (80) which cyclizes to (81) in a disrotatory manner [20].



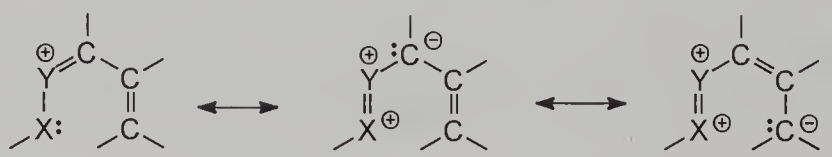
(80)



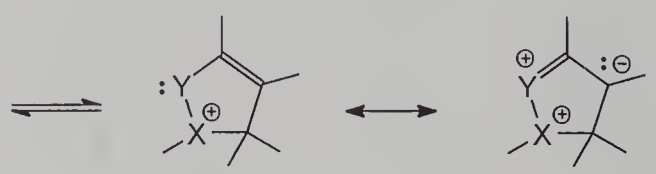
(81)

(2.28)

The multiplicity of the possible [1,5] electrocyclizations is increased further by a double isoelectronic exchange. For example, the exchange of heteroatoms at C1 and C2 positions results in (82) which undergoes a [1,5] electrocyclization as expected [21].



(82)

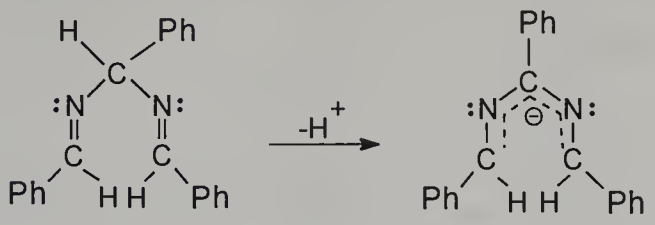


(83)

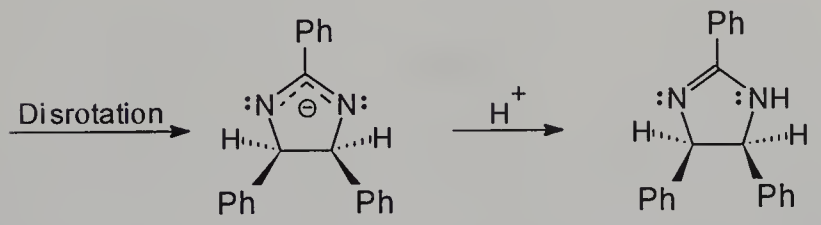
(2.29)

X,Y = N R,O

An exchange of C2 and C4 by two nitrogen atoms leads to another pentadienyl system (84) which undergoes a disrotatory cyclization as expected [22].



(84) (85)



(86) (87)

(2.30)

Only a limited number of examples with double isoelectronic replacements in the 2,3-position (Equation 2.31) and 1,4-positions (Equation 2.32) are reported.

(88) (89)

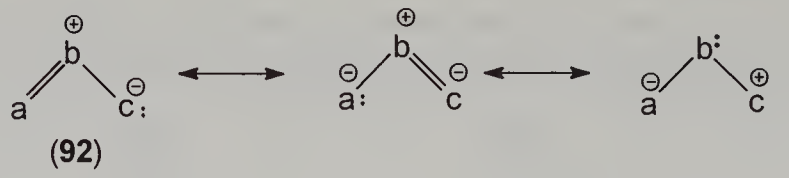
(2.31)

(90) (91)

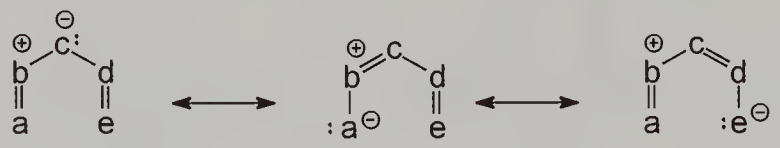
(2.32)

Naturally, 1,3- and 1,5-, relationships of X and Y are also conceivable. Systems with triple isoelectronic replacements are predicted to take place in a dication, however, the examples are not yet reported. It may be noted that the placing of the negative charge on a heteroatom, which is more electronegative than carbon, determines the direction of the electrocyclic reaction. Thus heteroatoms in positions 2 and 4 of the pentadienyl anion favour ring closure while those at positions 1,3 and 1,5 promote ring opening [23 a,b].

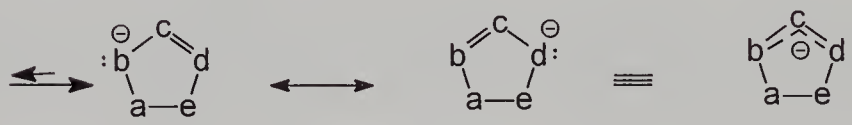
A careful look at the resonance structures of the pentadienyl system (93) reveals that this system is analogous to a 1,3-dipolar compound (92) conjugated with a double bond. The resulting compound is described as a [1,5] dipolar compound which undergoes [1,5] electrocyclization to a five-membered heterocyclic system (94) [24].



(92)

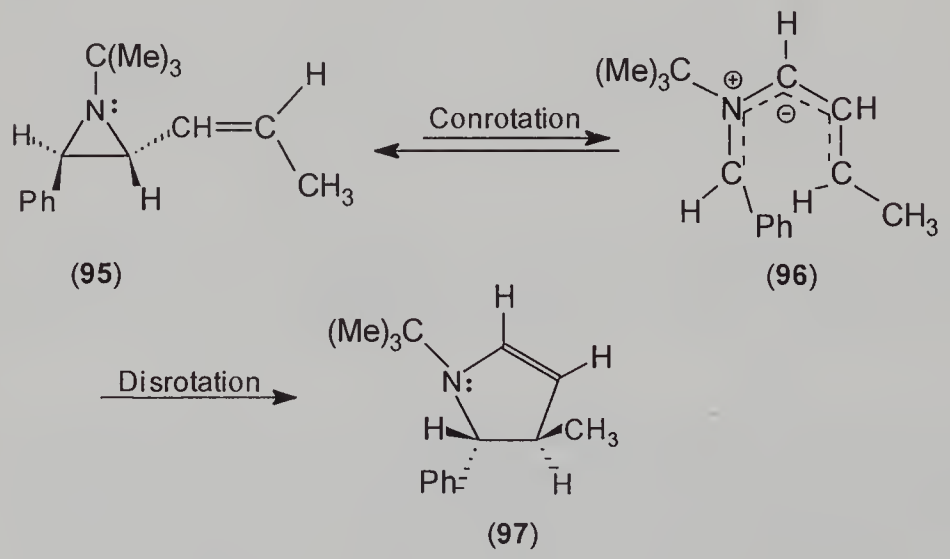


(93)



(94) (2.33)

This is exemplified by the thermal electrocyclic ring opening of vinyl substituted aziridine (95) in a conrotatory manner (4n electron system). The resulting azomethin ylide (96) is a 1,5-dipolar compound which being isoelectronic with the pentadienyl system undergoes thermal [1,5] cyclization in a disrotatory manner to form a substituted azomethine (97) [25].



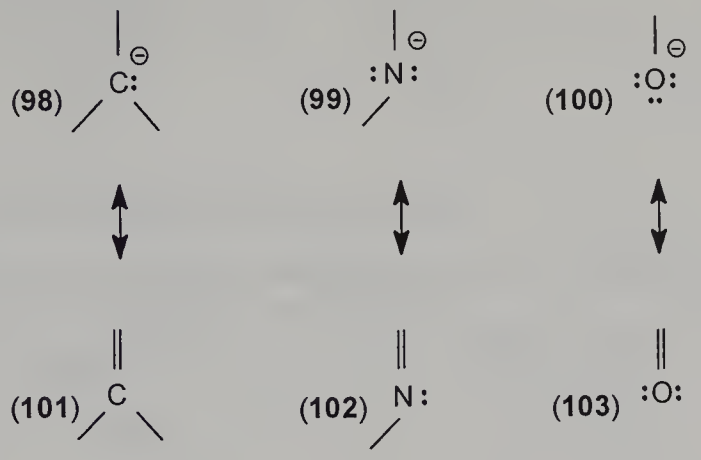
(95) (96) (97) (2.34)

2.2.3.2 Isoionic Exchange

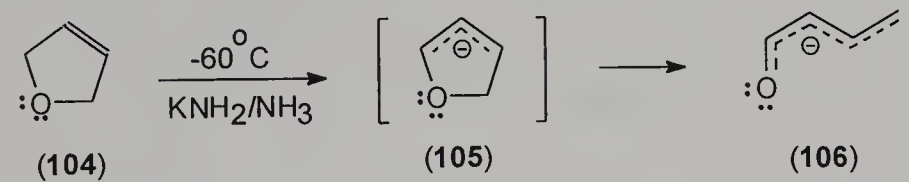
Two bonded atoms are termed as isoionic when they differ in the number of their electrons but bear the same charge. For example, the carbonion (98) has $2s^2$, $2p^{2+1}$ electrons in the outermost shell but the olate function (100) has $2s^2$, $2p^{4+2}$ electrons in its outermost shell. Both bear the same negative charge and are termed *isoionic*.

The carbanionic carbon atom in (98) can be isoionically replaced by an amide anion (99) or an olate function (100). The charge-free olefinic carbon in (101), an imine

nitrogen in (102) and charge free carbonyl oxygen in (103) are the results of isoionic replacements in (98), (99) and (100) respectively.

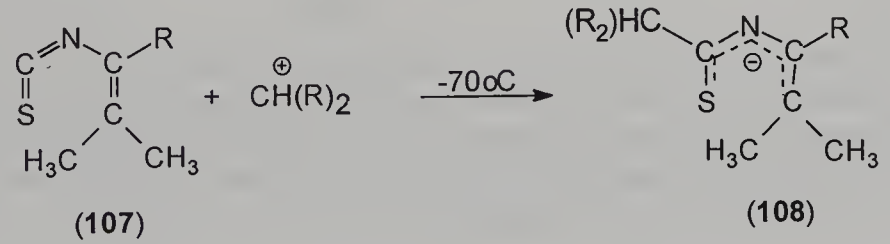


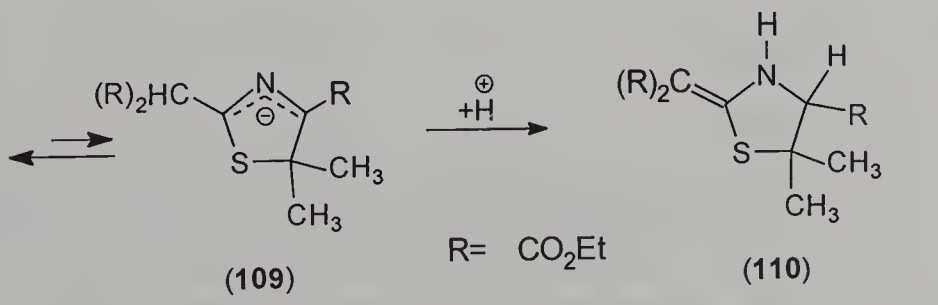
The base-catalyzed ring opening of dihydrofuran (104) serves as an illustration. Only the oxapentadienyl anion profits from the isoionic replacement of CH_2 by oxygen in position C1. The high electronegativity of oxygen stabilizes the open chain (106) but not the cyclic species (105). This stabilization of the open chain form drives the electrocyclic equilibrium in the direction of ring opening [26].



(2.35)

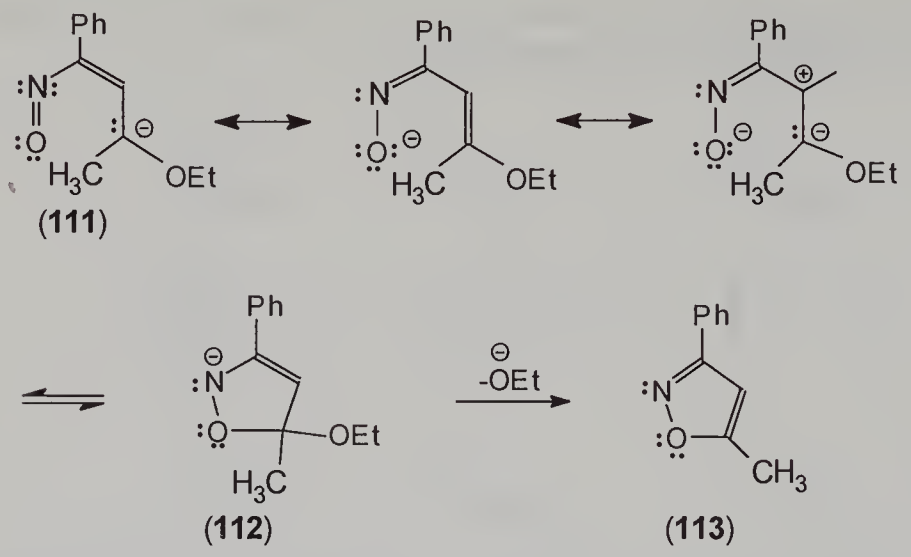
The possibility of the exchange of C1 and C3 with sulfur and nitrogen respectively (107), leads to the synthesis of thiazole (110) via a [1,5] electrocyclic reaction [27].





(2.36)

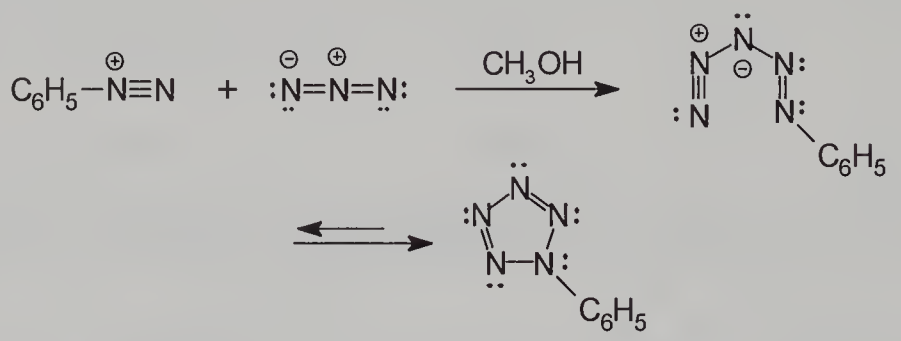
Substitution of heteroatoms at C1 and C2 positions of pentadienyl anion (111) leads to the synthesis of an oxazole (113). It may be noted that during cyclization, the negative charge migrates from the oxygen atom to the nitrogen atom[28].



(2.37)

Problem 2.5:

Benzenediazoazide is formed by the reaction of benzenediazonium salt with an azide ion which leads to a pentazole through [1,5] electrocyclization. Predict the mode of transformation.



Just like pentadienyl-cyclopentenyl anion isomerization, thermal cyclization of pentadienyl cation (114) to form a cyclopentenyl cation (115) is also an electrocyclic process where four electrons are delocalized on five carbon atoms. The reaction proceeds in a conrotatory manner as predicted [29].

(114) (115)

(2.38)

Such cations are prepared by the gas-phase addition of the trienes to their corresponding acids. Kinetic studies on a series of methyl-substituted pentadienyl cations were carried out. Their rate constants, and activation parameters, were determined for this rearrangement in different solvents. However, the stereospecificity in these cations is not 100% and it is believed that some isomerizations probably occur at the dienylic ion stage [30 a,b].

(2.39)

(116) (117)

2.2.4 [1,6] Electrocyclic Reactions

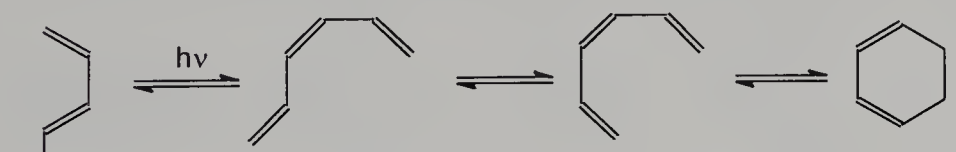
The equilibration of a 1,3,5-hexatriene (118) with that of a 1,3-cyclohexadiene (119) is described as a [1,6] electrocyclic transformation.

(2.40)

(118) (119)

This process differs from a [1,4]-electrocyclic reaction in the following respects.

i) During a thermal ground state reaction, cyclization is possible only from the *cis*-isomer. However, in the excited state, the geometry of the initial triene is no longer important, since both *trans*-, and *cis*-, isomers equilibrate rapidly under photochemical conditions (Equation 2.41).



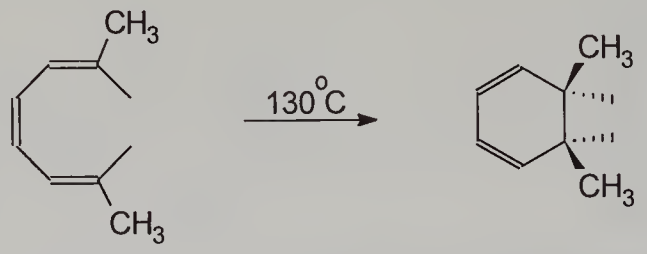
(2.41)

(120) (121) (122) (123)

ii) The free energy difference between the acyclic triene and the cyclic diene is small due to smaller strain in a six-membered ring as compared to a four-membered ring. Moreover the equilibrating trienes efficiently absorb energy in near regions of the UV spectrum. Hence [1,6] electrocyclic processes are reversible under both thermal and photochemical conditions.

iii) Side reactions are more frequent in reversible transformations of trienes than in the reactions of dienes. The most common example is the [1,4] electrocyclic reaction when the triene behaves as a substituted diene.

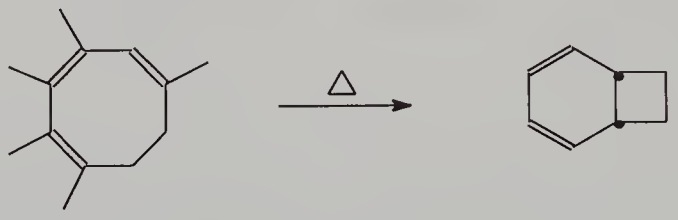
Thermal cyclization of an acyclic hexatriene, a (4n+2)-electron system, takes the predicted disrotatory path. Thus *trans,cis,trans*-octatriene (124) cyclizes to *cis*-5,6-dimethyl cyclohexa-1,3-diene (125) through disrotation.[31 a,b].



EZE

(124) **(125)** (2.42)

The cyclic trienes behave in the same manner, hence 1,3,5-, an all-*cis*-cyclooctatriene (126) equilibrates with the *cis*–fused bicyclic compound (127) during an allowed thermal disrotatory process [32].



(126) **(127)** (2.43)

Cyclooctatetraenes (128) and cyclononatrienes (130) undergo [1,6] electrocyclic reactions in a stereospecific manner to give (129) and (131) respectively [33 a,b].

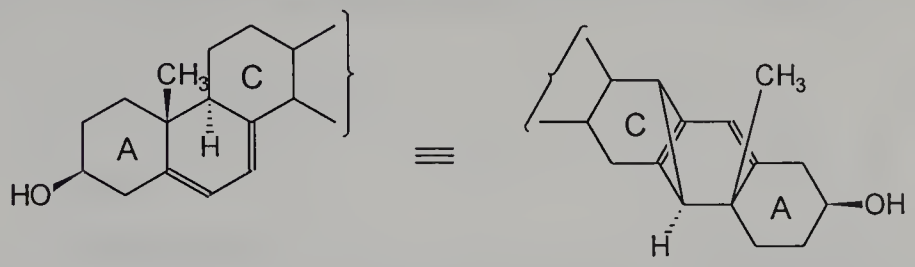
(128) **(129)**

(130) **(131)** (2.44)

Steroid chemistry has furnished ample examples of both thermal and photochemical [1,6]-electrocyclizations as well as the converse process. A number of such transformations are observed during the synthesis of vitamin B_{12} as discussed in the beginning of this chapter. Further examples of the reactions of steroids [34 a.b] illustrate the generality of the selection rules predicted by Woodward and Hoffmann.

Problem 2.6:

Electrocyclic transformations are common in the biosynthesis of steroids. Predict the mode of thermal reaction and draw the structure of the product formed.



The examples already discussed are the all-carbon systems undergoing [1,6] electrocyclizations. The same cyclization processes were observed in heterosystems.

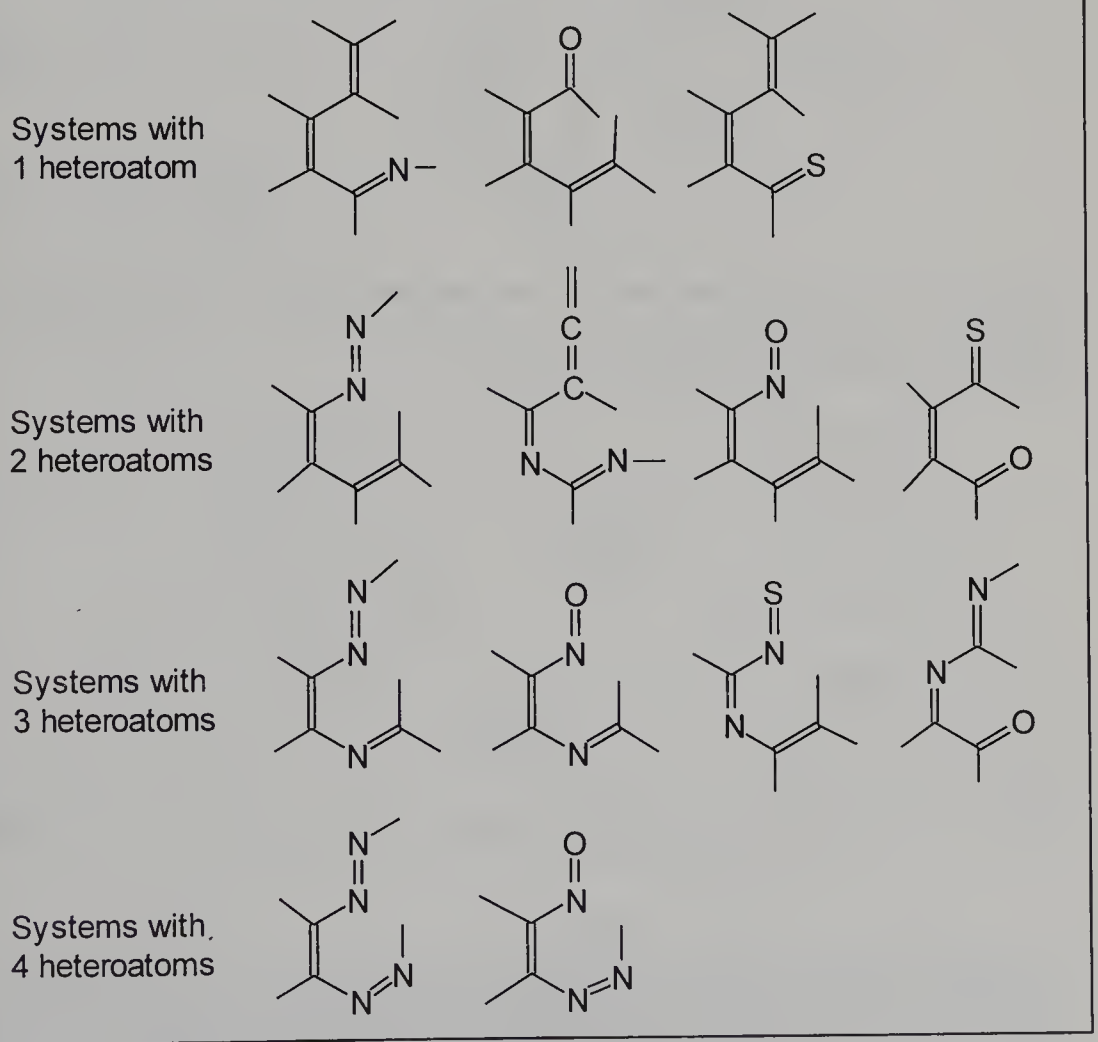
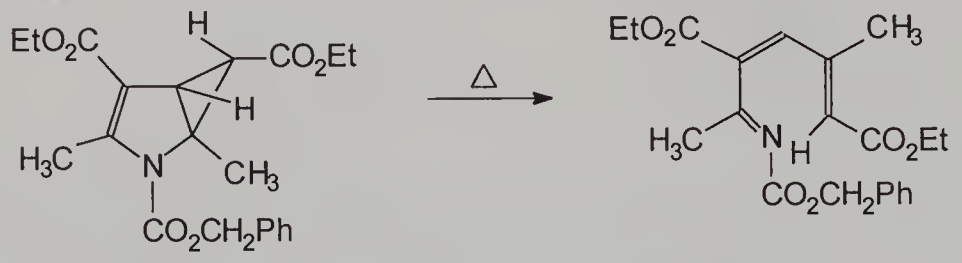


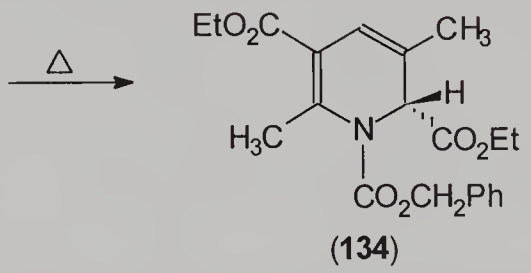
Figure 2.5: *Different hetero-substituted 1,3,5-hexatrienes.*

Thus 1,3,5-hexatrienes containing heteroatoms such as nitrogen, oxygen and sulphur undergo thermal electrocyclizations to give hetero-1,3,5-cyclohexadienes [35]. Depending on the nature of the substrate and the type of heteroatoms, a colourful

variety of products can be formed from the skeletons of the hetero-1,3,5-hexatrienes as shown in Figure 2.5. A few representative examples are discussed.

The thermolysis of homopyrrole (132) gives a quantitative yield of 1,2-dihydropyridine derivative (134) via 1-*aza*-hexatriene derivative (133) [36].

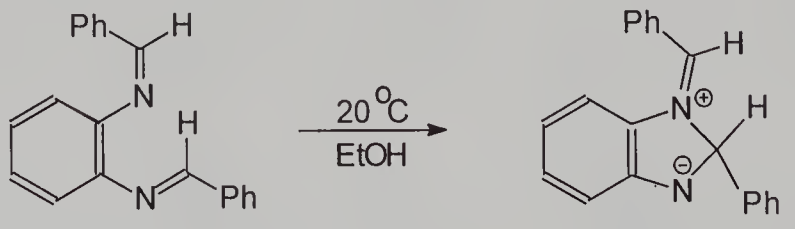


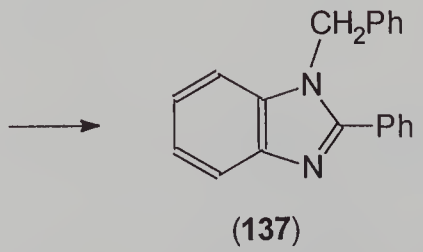


(2.46)

Et = C_2H_5
Ph = C_6H_5

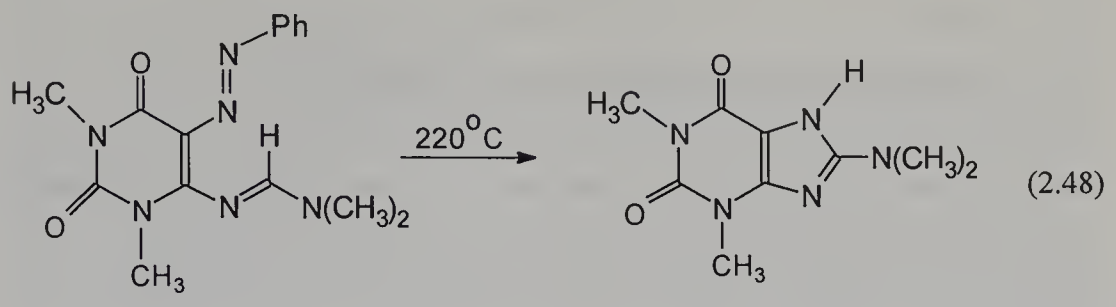
The reaction of *o*-phenylenediamine with benzaldehyde at -20°C yields *bis*-benzylidene (135) which at room temperature undergoes cyclization to 1-benzyl-2-phenylbenzimidazole (137) via (136) [37 a-d].





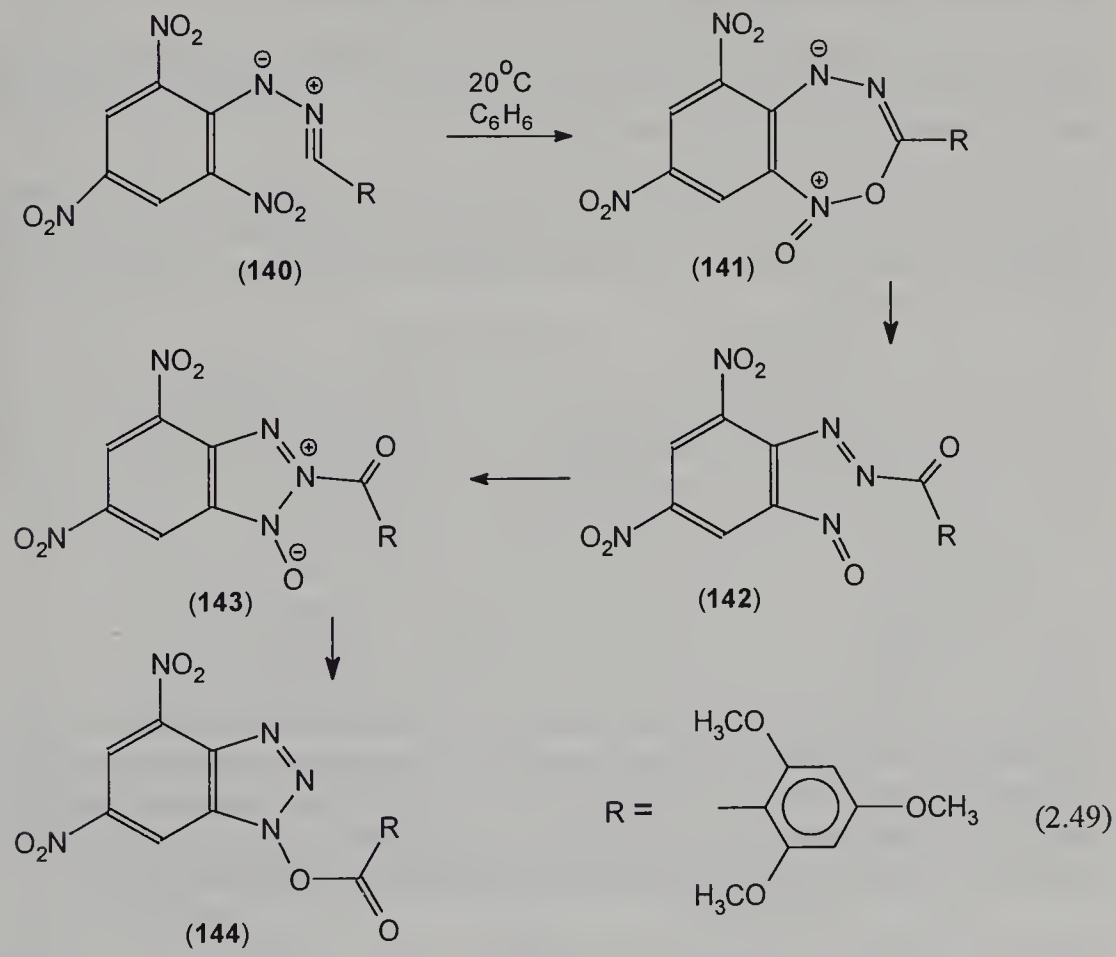
(2.47)

In Equation 2.48 the reaction of 5-arylazo-6-aminouracil (138) with dimethylformamide and dimethylacetal is shown to yield the imidazole (139) [38].



(138) (139) (2.48)

The *o*-nitroso-compound (140) leads to the synthesis of 2-phenylbenzotriazole-1-oxide (144). The formation of an aromatic heterocycle could significantly contribute to the driving force for this cyclization [39].



(2.49)

It is impossible to process the infinite number of possible variables of electrocyclizations and then even to experimentally verify them all. However, hundreds of scattered examples from literature can be tabulated in the classification system introduced.

A few examples of higher order [1,8] electrocyclization and [1,12]electrocyclization are also known [40].

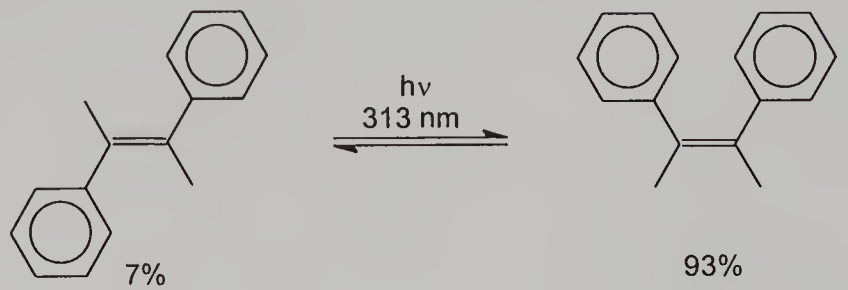
2.3 Photochemical Electrocyclizations

The fundamentals of photochemical reactions are remarkably simple. A molecule is energized to an excited state by the absorption of photons of light and undergoes a chemical reaction while still in that excited state. Photochemical reactions are driven by light energy and thermal reactions use heat energy. Specific molecules require a certain amount of energy to get excited, and a precise wavelength of light provides this energy.

Energy is required to excite a molecule, and the physical process inside the molecule may not produce energy, or enough of it, to excite its neighbouring molecules. Hence there is no chain reaction. A characteristic of photochemical reactions is that they do not generate enough energy to excite their neighbours.

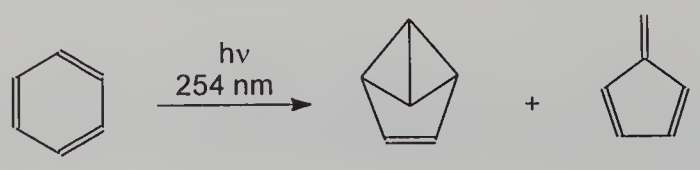
Loss of energy, thermal or photochemical, from the photoexcited species leads to a stable ground state product, and irrespective of the forms of energies involved, the law of conservation of energy is maintained.

For example a mixture of *cis*- and *trans*-stilbenes may be irradiated at 313 nm where only *trans*-stilbene (145) absorbs light. This drives the equilibrium to a nearly pure *cis*-isomer. Contrarily, during a thermal reaction, the equilibrium strongly favours the *trans*-isomer [41].



(145) **(146)** (2.50)

The amount of energy injected into a molecule by the absorption of a photon of light can exceed the amount of energy available in a normal thermal reaction. For example, benzene absorbs 113 Kcal $mole^{-1}$ of energy from a mercury resonance lamp of 254 nm ultravoilet light. With this large injection of energy, benzene is induced to undergo the following unusual rearrangements (Equation 2.51) [42].



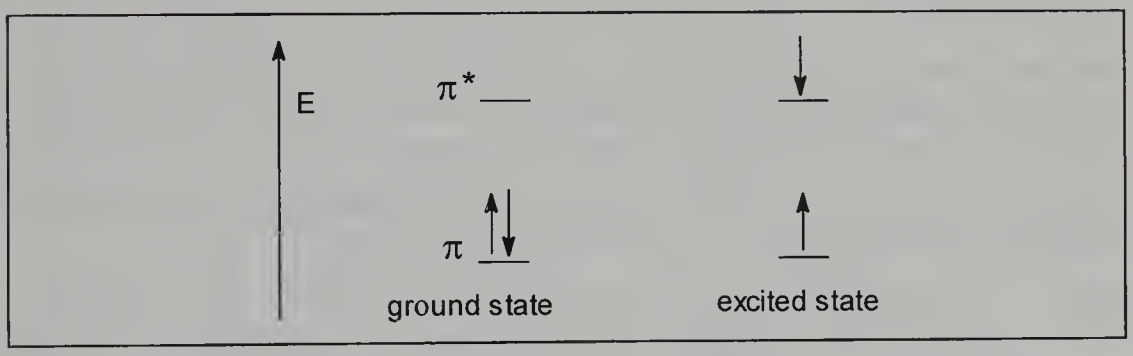
(147) **(148)** **(149)** (2.51)

This photochemical reaction can be performed at room temperature, and the products being stable species can be isolated. Thermally, an equivalent amount of

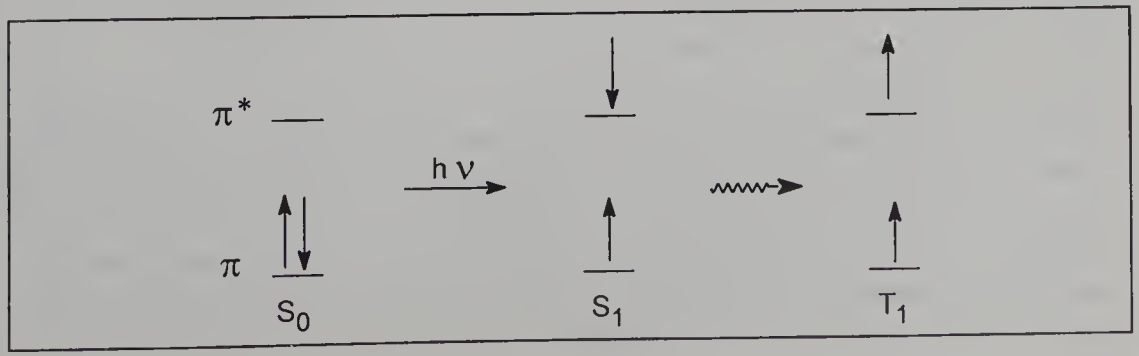
energy would be available only at high temperatures, and at such temperatures the rearranged products might be unstable.

Before proceeding to discuss photochemical transformations, it is worth digressing here to point out some important differences between a molecule in its ground state and the one in an excited state.

i) The electronic configuration of an excited state molecule is different from the electronic configuration of the same molecule in its ground state. Also the distribution of electrons in molecular orbitals is different in the excited state and ground state. For example the electronic configuration of a molecule having a double bond is written as π^2 which is indicative of the presence of two electrons in a π-orbital, while the excited state configuration $\pi\pi^*$ indicates that an electron from a lower energy π orbital is excited to a higher energy π^* orbital by the absorption of light.



ii) Nearly all the stable molecules have an even number of electrons with spins paired in their ground states. This pairing means that the magnetic moments of the electrons compensate each other such that the molecule as a whole has no electron magnetic moment. These non–magnetic states are called *singlets* and the different energy singlet states are abbreviated as S_0, S_1, . . . etc. Excitation of an atom by light absorption does not change the spin of its electron, therefore, only excited singlets are formed by absorption. In an excited singlet the electrons are still spin-paired but present in different orbitals, e.g. π and π^*. Once an electron is excited into an unoccupied orbital, the two unpaired electrons are no longer bound. An excited singlet S_1 may then be converted to another state by inverting the spin of one of the electrons. This creates a new state in which the electronic magnetic moments do not compensate. The new excited state has a net magnetic moment.



The new state is called a triplet state abbreviated as T_0, T_1, . . . etc. In a magnetic field three states appear because the magnetic moment can be aligned in three different ways with respect to the applied field (Figure 2.6).

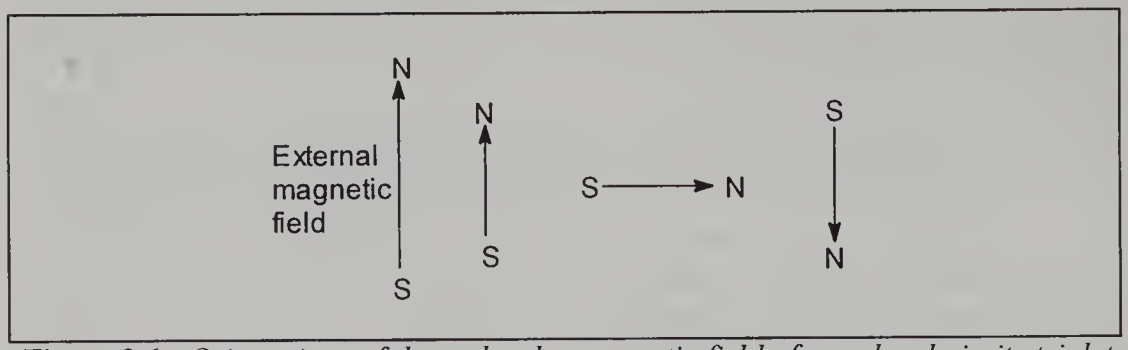


Figure 2.6: *Orientations of the molecular magnetic field of a molecule in its triplet state with reference to an external magnetic field (N and S refer to North and South magnetic poles).*

The two states, i.e. the singlet and the triplet, differ in their energies due to the difference in their multiplicity. A singlet state is usually of higher energy than the triplet state because the two electrons have to occupy the same space.

All the concerted reactions take place in the singlet state and not in the triplet state. The triplet state leads to a non-concerted or stepwise reaction.

iii) The excited molecule has a different geometry than the same molecule in its ground state. Figure 2.7 shows the geometrical changes resulting from the electronic excitation of some molecules.

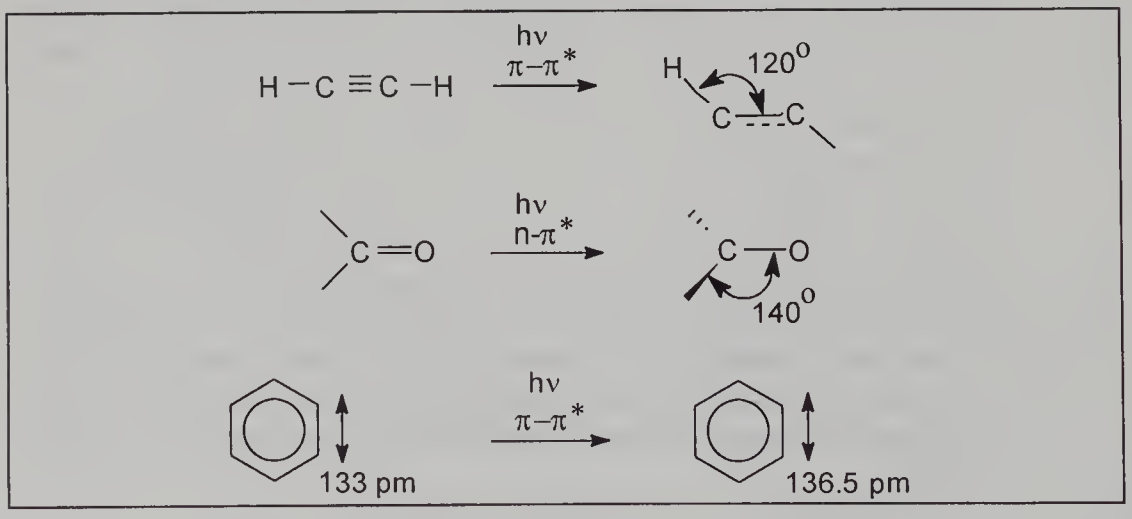
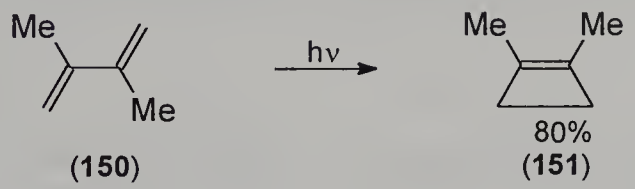


Figure 2.7: *Geometrical changes resulting from electronic excitations.*

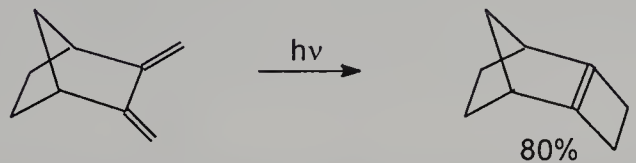
Consider the simplest case of a photochemical interconversion of butadiene and cyclobutene. The reaction takes place in the direction of cyclization because the diene is a strong absorber of light at the wavelength used in the reaction. Thus it is the diene which gets excited during a photochemical conversion of butadiene and cyclobutene. An interesting feature of the photochemical reactions is their ability to lead to higher energy isomers i.e. cyclobutenes. On the contrary, thermal reactions tend to promote the formation of more stable butadienes.

As mentioned earlier, the behaviour of photochemical reactions is opposite to that of thermal reactions and Woodward-Hoffmann rules predict opposite behaviours for the two modes of reactions. Hence polyenes with (4n) electrons opt for the conrotatory mechanism when subjected to thermal conditions and disrotatory when subjected to photochemical conditions.

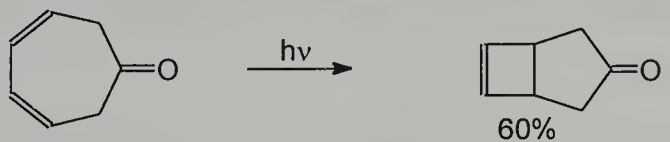
A few examples of the electrocyclization of butadiene system are shown in Equations 2.52 to 2.54 [43 a,b].



(150) (151) (2.52)

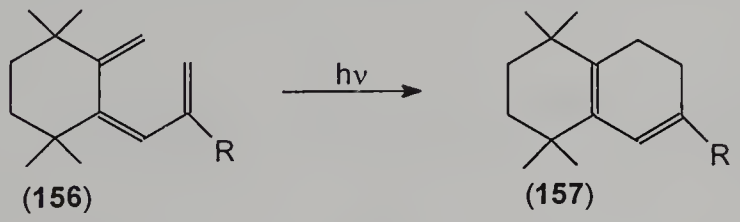


(152) (153) (2.53)

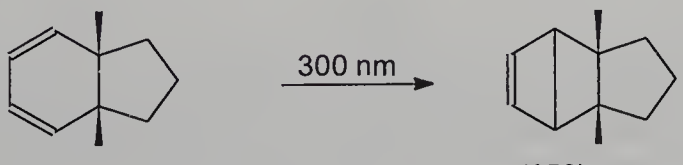


(154) (155) (2.54)

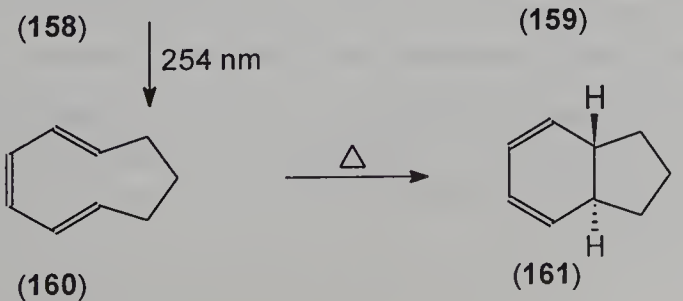
Photochemical cyclizations of some other systems (156,158,160) are further examples of electrocyclization reactions, which involve either four or six electron redistributions [44 a,b].



(156) (157) (2.55)



(158) (159) (2.56)

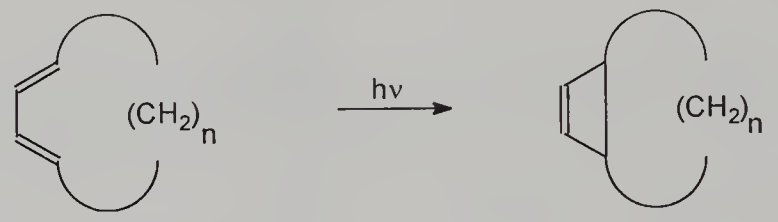


(160) (161) (2.57)

Problem 2.7:

Confirm that the stereochemistry of the products shown in Equations 2.55 to Equation 2.57 are in agreement with the predictions made by Woodward and Hoffmann.

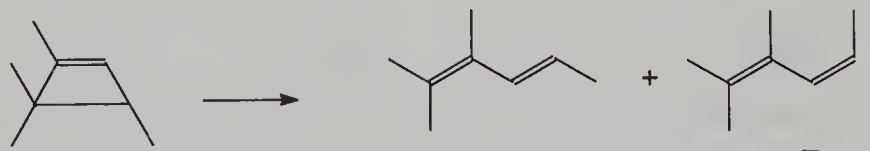
The most instructive examples of photochemical electrocyclic transformations are those where the diene forms a part of the ring (162) thereby leading to the formation of fused cyclobutene (163). The resulting products are very stable [45].



(2.58)

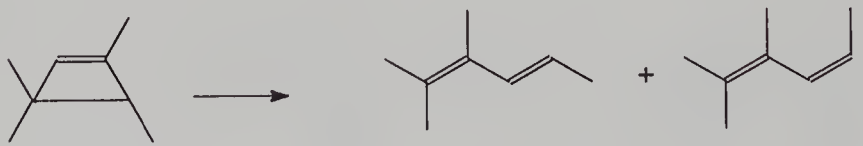
(162) **(163)**

Photolysis of 1,3,4,4- and 1,3,3,4-tetramethyl cyclobutene (164) and (167) resulted in competitive electrocyclic ring opening yielding a mixture of stereoisomeric dienes in each case [46].



(2.59)

(164) E **(165)** Z **(166)**

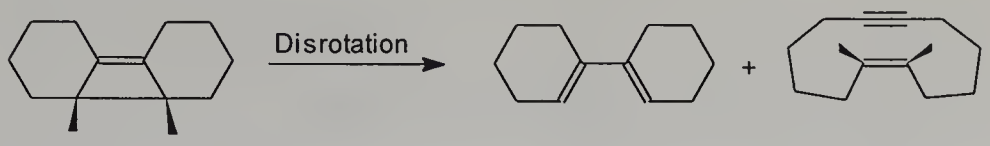


(2.60)

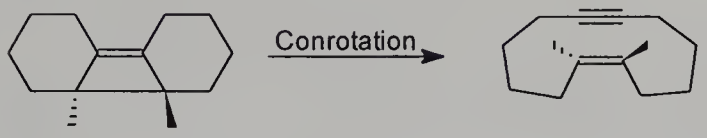
(167) Z **(168)** E **(169)**

Moreover isomerization of the other cyclobutene derivatives was also found to take place. The occurrence of the interconversion process is offered as an evidence for the intermediary of a cyclopropylcarbene. The interconversion of butadiene and cyclobutene is believed to take place stereospecifically via the disrotatory pathway.

The isomeric fused cyclobutenes (170) and (173) are reported to undergo photochemical ring openings with disrotatory and conrotatory pathways respectively. However, the highly strained *trans*-product (174) rapidly isomerizes to the *cis-cis*-isomer (171) [47].

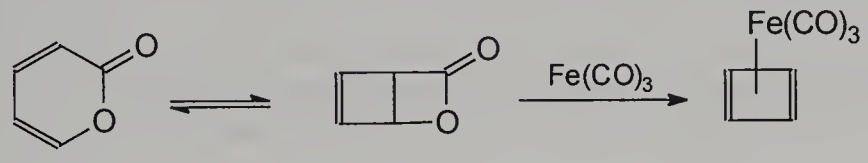


(170) (171) (172) (2.61)



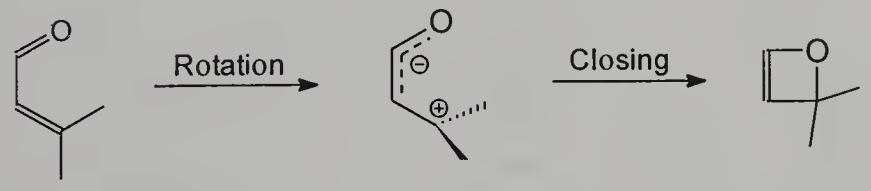
(173) (174) (2.62)

A useful synthetic application of the photochemical ring closure is the photochemical equilibration of 2-pyrone (175) to a bicyclic tautomer (176) which undergoes decarboxylation in the presence of iron pentacarbonyl to give a cyclobutadiene-iron tricarbonyl complex (177) [48].



(175) (176) (177) (2.63)

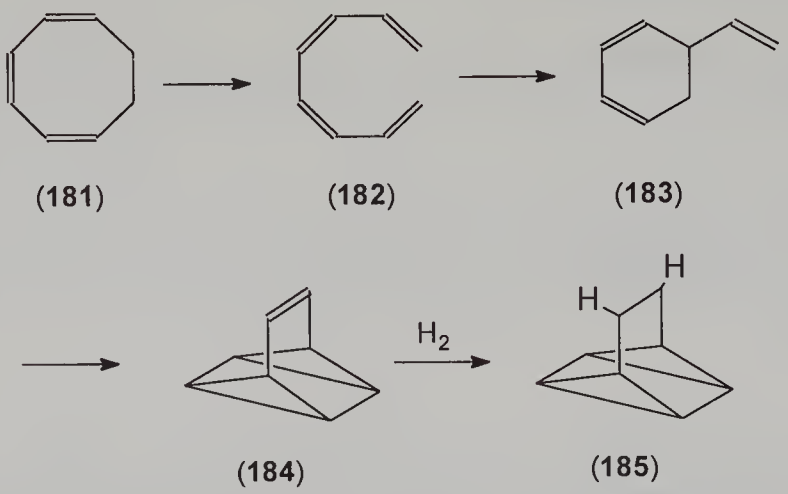
A formal electrocyclic reaction of *s-cis*-acrylaldehyde (178) to 2H-oxete (180) was reported by Morihashi *et al* [49]. The system is isoelectronic with butadiene-cyclobutene system and must proceed along the concerted mechanism in a disrotatory manner. However, an analysis of the potential energy surfaces of the reaction gives an evidence of a stepwise mechanism in which the ring closure occurs after the rotation of the methylene group (Equation 2.64).



(178) (179) (180) (2.64)

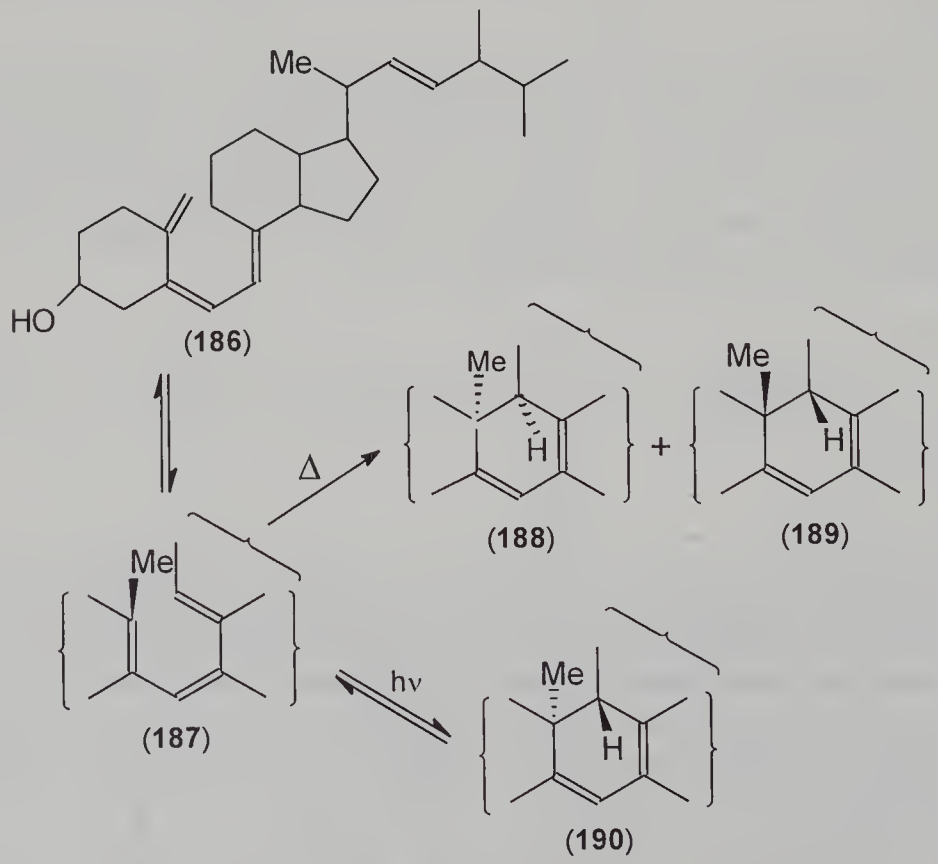
The zwitterion (179) undergoes ring closure easily because of strong attractions between the positive charge and the in-plane lone-pair of electrons on the oxygen.

For 6π-systems the photochemical cyclization of hexatriene is conrotatory which is in sharp contrast to thermal reactions, e.g., photoisomerization of 1,3,5-cyclooctatriene (181) leads to a tricyclic product via a number of intermediate products [50].



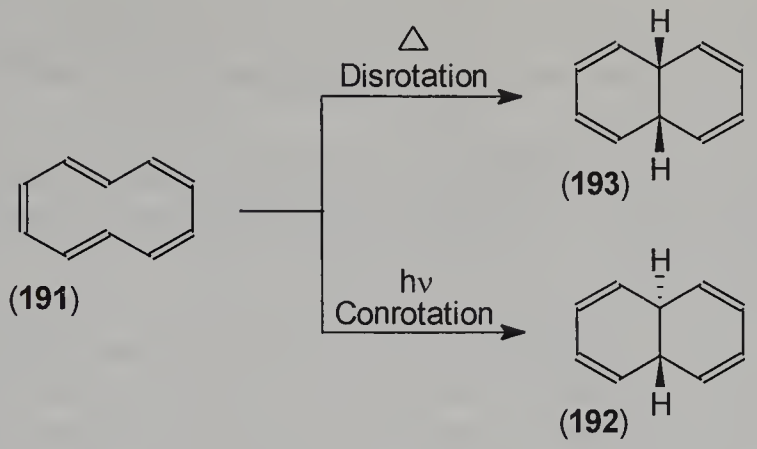
(181) (182) (183) (184) (185) (2.65)

Havinga *et al* [51] noted the difference in the stereochemistry of thermal and photochemical reactions of vitamin D. Calciferol (186) thermally isomerizes to precalciferol (187) which upon heating at 150-200° C cyclizes to give two *cis*-fused products (188) and (189). These two products are the result of two possible modes of disrotatory cyclization. However, on irradiation, precalciferol equilibrates with a different cyclic product which is the *trans*–fused lumisterol (190) formed as a result of a conrotatory ring closure.



(186) (188) (189) (187) (190) (2.66)

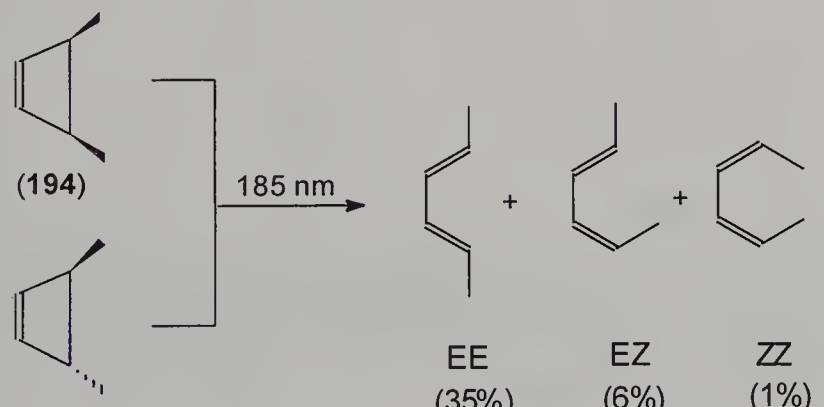
Many examples of this contrasting behaviour are discovered. The all-*cis*-cyclodecapentaene (191) equilibrates with (192) by a conrotatory reaction, but is converted thermally to *cis*-9,10-dihydronaphthalene, by disrotation [52].



(191) (193) (192) (2.67)

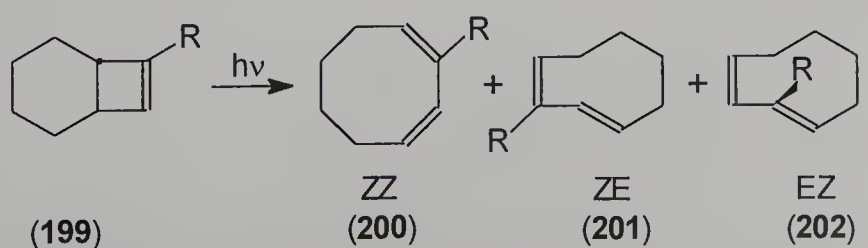
These examples illustrate the stereospecificity observed during photochemical electrocyclic reactions. However, direct photolysis of an alkyl-substituted cyclobutene results predominantly in a non-stereospecific ring opening. This is in sharp contrast to the general belief that the ring opening of cyclobutene is disrotatory.

As an example, photolysis of both *cis*-and *trans*-dimethylcyclobutenes (194,195) takes place in a non-stereospecific manner yielding mixtures of substituted isomeric hexatrienes in the relative yields shown (Equation 2.68) [53].



(194) (195) (196) (197) (198) (2.68)

Another example of the non-stereospecificity observed during electrocyclic reactions is reported where the photolysis of fused cyclobutene (199) at 193 nm in an *n*-pentane solution led to isomeric 2-substituted-1,3-cyclooctadienes (Equation 2.69) [54 a,b].

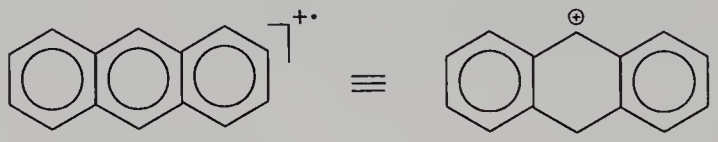


(199) (200) (201) (202) (2.69)

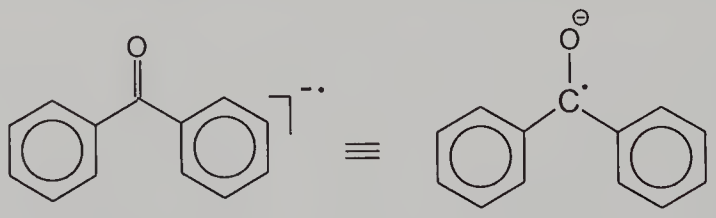
2.4 Electrocyclizations of Radicals and Radical Ions

The studies on the electrocyclic transformations on neutral radicals are also carried out [55]. As an example, the ring opening of cyclopropyl radical to form an allyl radical was studied. However, it was difficult to predict whether the ring opening takes place through conrotation or disrotation (Chapter 6).

Radical ions are an important class of organic reaction intermediates that contain an unpaired electron. They are simply free radicals that also bear a positive, or negative, charge and are accordingly called radical cations or radical anions. In most cases radical ions are derived from a parent organic molecule by the gain, or loss, of one electron. Anthracene (203) and benzophenone (204) are two common examples of radical ions.

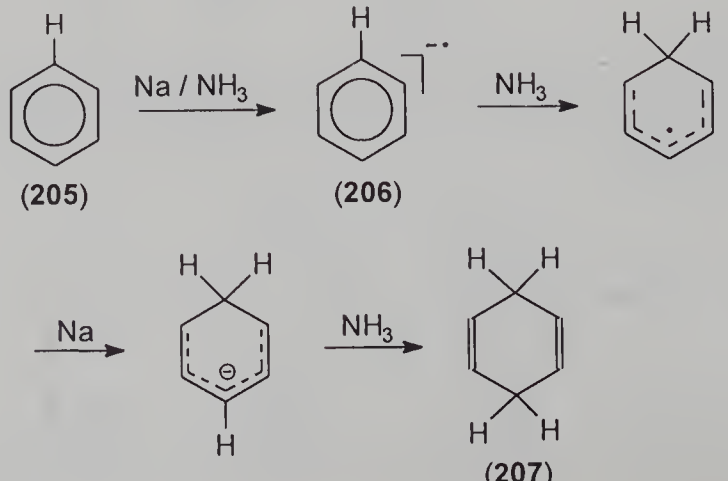


(203)



(204)

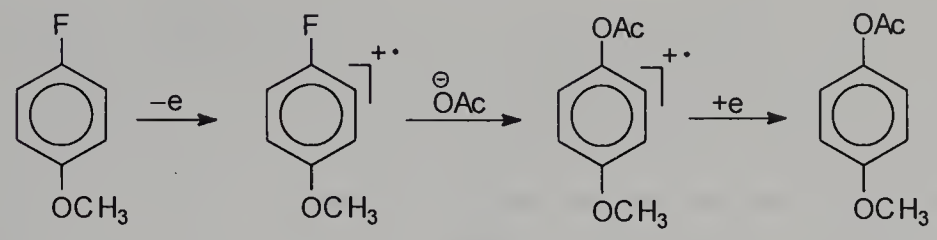
As expected, radical anions may be intermediates in reduction reactions and radical cations are intermediates in oxidation reactions. The synthetically valuable Birch reduction accomplishes a partial reduction of an aromatic ring by an electron transfer from sodium in liquid ammonia.



(205) (206) (207)

(2.70)

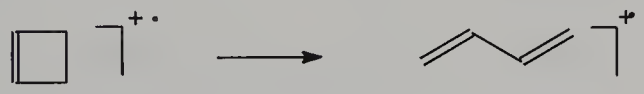
Analogous possibilities may be envisaged for reactions of radical cations. An example is the displacement of a fluoride ion by weakly nucleophilic acetate ion after oxidative initiation of a chain process.



(2.71)

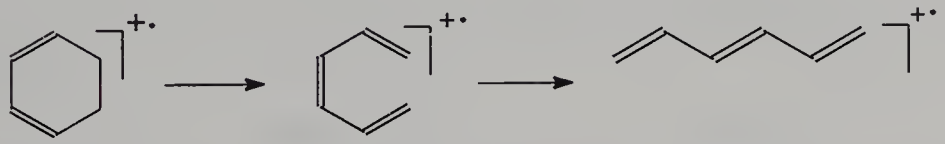
(208) **(209)** **(210)**

Organic radical cations are best known in connection with mass spectrometry. However, several methods are developed for generating them in low temperature matrices [55]. As a result of recent studies, it is becoming apparent that radical cations undergo a facile photochemical rearrangement as shown [56 a-c, 57].



(2.72)

(211) **(212)**



(2.73)

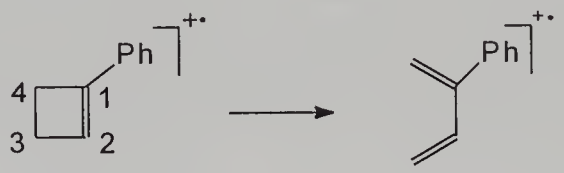
(213) **(214)** **(215)**

These examples reveal that the reactions of radical cations are analogous to electrocyclic reactions of neutral as well as ionic systems. Examples of radical cations undergoing other pericyclic reactions familiar in the chemistry of uncharged molecules are also known. Although an understanding of the electrocyclic ring opening is well developed, relatively little is known of similar ring opening processes of radical cations. Moreover the effect of removing an electron in the course of most electrocyclic reactions is still not understood. Electrocyclic ring opening of a thermally activated neutral cyclobutene and its derivatives to the corresponding 1,3-butadiene is known to proceed thermally and stereospecifically in a conrotatory manner. However, it proceeds photochemically in a disrotatory manner. The experimental activation energy is 32.9 Kcal $mole^{-1}$ for the thermal process.

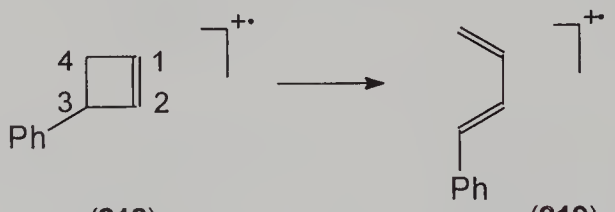
Moreover, theoretical methods have enabled qualitative predictions of the influence of substituents on the ring opening of cyclobutene. Using these methods, it is observed that any substituent at C1 or C2 of cyclobutene decreases the rate of

conrotatory ring opening. On the other hand, substitution at C3 or C4 positions increases the rate of reactions. These predictions have received considerable experimental support [58a-c].

Parallel studies were carried out on the ring opening of radical cations of 1-phenyl cyclobutene (216) and 3-phenyl cyclobutene (218) to determine the effect of substituents using mass spectrometric techniques. It was observed that substitution at the double bond of cyclobutene stabilizes the cyclobutene radical cation compared to the unsubstituted moeity, whereas phenyl substitution at C3 position enhances the rate of electrocyclic reactions. The estimated activation energy of the ring opening of 1-phenyl cyclobutene radical cation is less than 14 Kcal $mole^{-1}$. It is assumed that the effect of ionization is to reduce the energy barrier of the electrocyclic ring opening of cyclobutene [59].



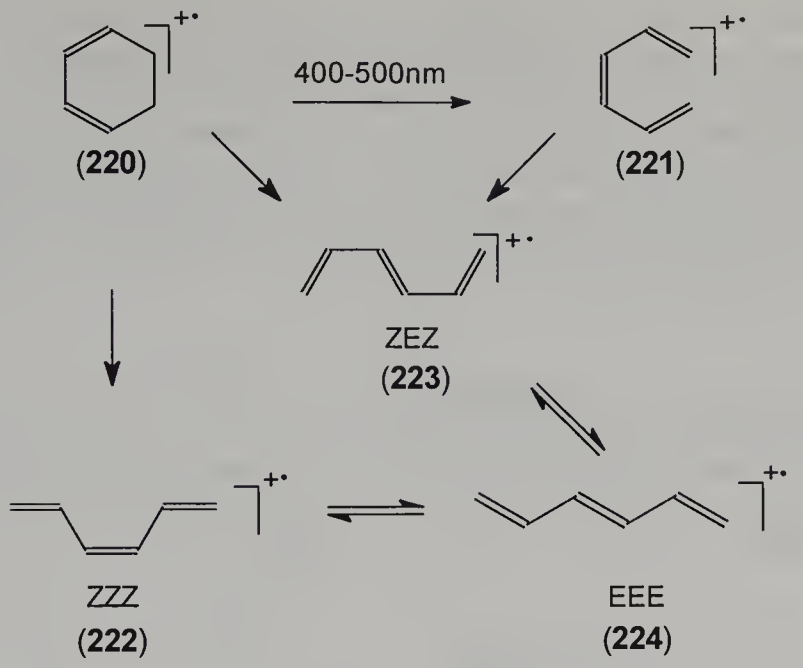
(216) **(217)** (2.74)



(218) **(219)** (2.75)

The same researchers found the activation energy of the isomerization of gaseous-phase 1-methyl and 3-methyl cyclobutene radical cations to be 16 Kcals $mole^{-1}$ and 4 Kcal $mole^{-1}$ respectively. These values are considerably lower than those of the corresponding electrocyclic reactions of neutral molecules. Moreover, the effects of substitution parallel those found for neutral cyclobutenes.

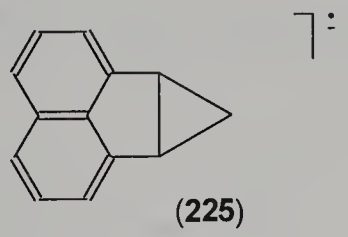
The cation radical of 1,3-cyclohexadiene (220) isomerizes to the radical cation of an all-*trans*-1,3,5-hexatriene (221) after photoexcitation using visible light. The conversion involves three intermediate cations of hexatriene having the conformations *cis,cis,cis*- (222), *cis,trans,cis*- (223) and *trans,trans,trans*- (224). These intermediates are very sensitive to light and interconvert as shown in Equation 2.76 [60 a-c].



(2.76)

There exist a large number of examples of electrocyclic reactions of radical cations, but space limitations preclude their discussion.

A few examples of the electrocyclic reactions of radical anions are reported. One such example is the ring opening of napthocyclopropane (225). A proposed mechanism involves the ring opening of the cyclopropane ring in the radical anion (225) [61].

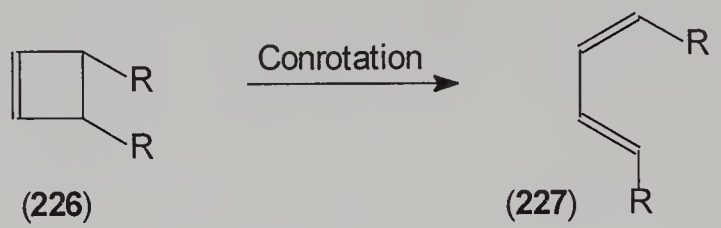


2.5 Metal Catalysis

The Woodward-Hoffmann rules dividing molecular transformations into allowed and forbidden categories have proved to be a powerful tool for understanding a large body of pericyclic reactions.

However, several examples [62-65] have been reported which indicated that pericyclic reactions, which are symmetry forbidden by the Woodward-Hoffmann rules become allowed under the influence of appropriate transition metal complexes. It has also been demonstrated that in the presence of catalytic amounts of certain metal ions, or metal complexes, various strained derivatives of cyclobutene can undergo facile disrotatory ring openings to yield derivatives of butadiene. An explanation for the apparent breakdown of the Woodward-Hoffmann rules is offered in terms of the formation of intermediate organometallic π complexes. The subsequent energetics involved for the ring opening reactions of these complexes

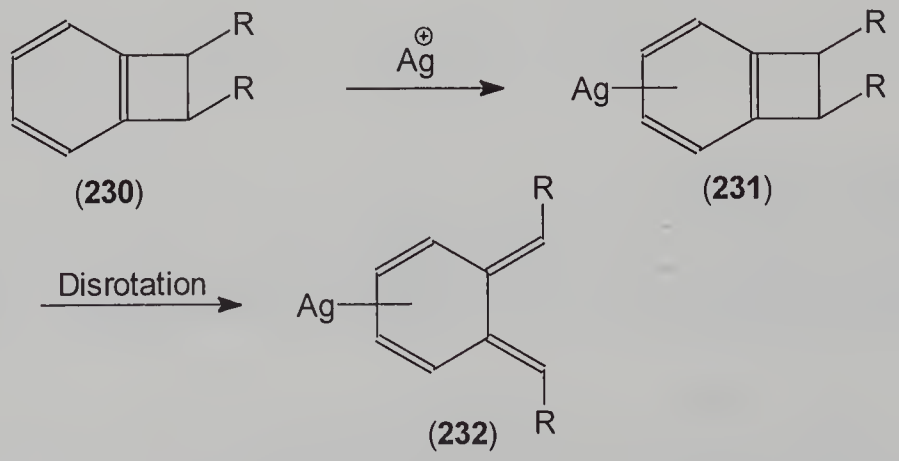
were also considered. Many reports appear on an observed, increased yield of the allowed reactions, as well as the rate enhancements in the presence of metal catalysts. The opportunity to achieve enantioselective transformations by adding chiral ligands is also an attractive feature of this strategy. For example, the Woodward-Hoffmann rules state that thermal isomerization of cyclobutene to butadiene takes place through conrotation, rather than by disrotation. However, the process may become allowed through disrotation by the addition of metal ions (Equations 2.77 and 2.78) [66].



(226) (227) (2.77)

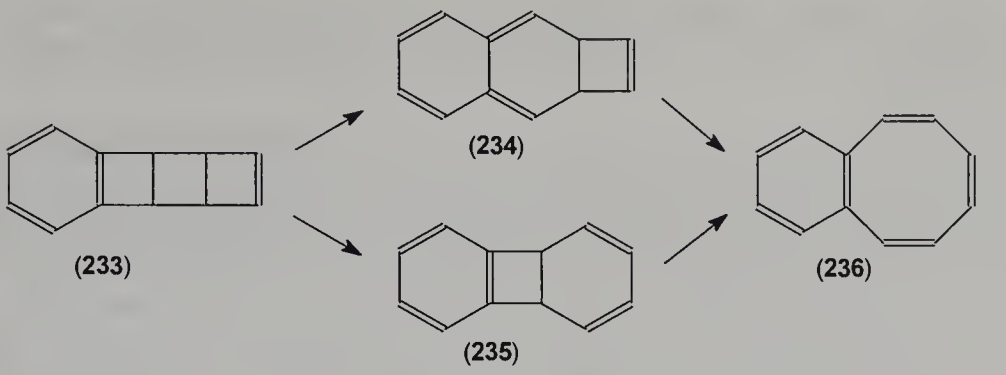
(228) (229) (2.78)

Similarly, the disrotatory conversion of the silver complex of benzocyclobutene (230) to xylylenes (232) is an allowed process, whereas, in the absence of metal ions, it is forbidden [66].



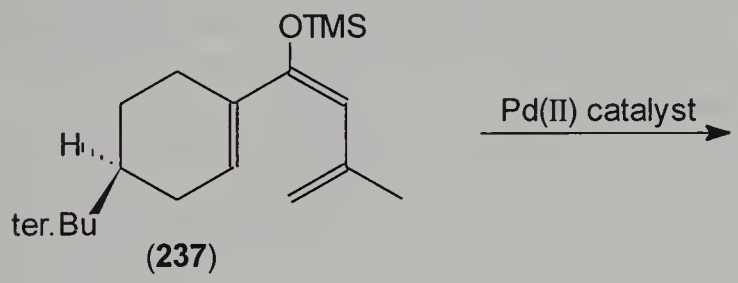
(230) (231) (232) (2.79)

Similar types of isomerizations have been observed with other strained cyclobutene derivatives, e.g. the isomerization of benzotricyclooctadiene (233) to benzocyclooctatetraene (236). As indicated, the metal catalyzed isomerization should, in principle, proceed by two different pathways; one involving a benzocyclobutene-o-xylylene isomerization (234), while the other a cyclobutene-butadiene isomerization (235). Both processes involve disrotatory ring openings [66].

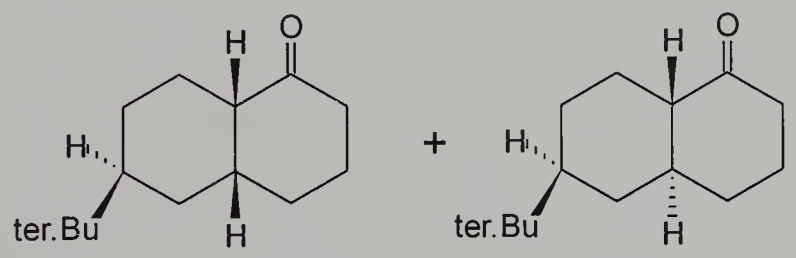


(2.80)

Stereochemical problems were addressed in palladium catalyzed 1,6-electrocyclic ring closure of silyl enol ether (237), with a modest level of stereoinduction, in order to afford a diastereomeric mixture of *cis-trans* isomers [67].



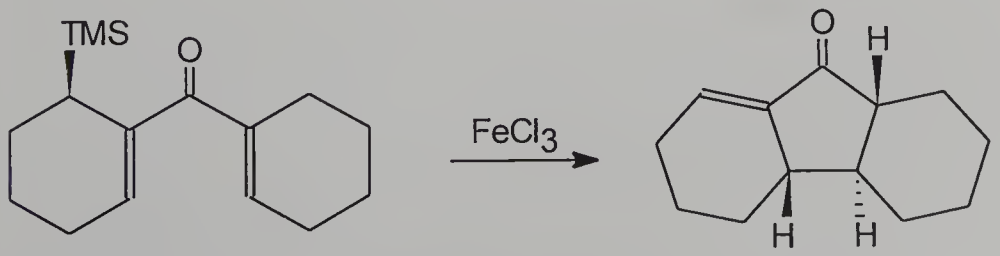
(237)



(238) (239)

(2.81)

The use of Lewis acid catalysts during electrocyclization is examplified by a conrotatory 1,5-electrocyclic ring closure of scalemic divinyl ketone (240) in the presence of iron (III) chloride catalyst [68 a-c]. The mechanism of the reaction remains the same, i.e. conrotatory, but the rate acceleration is observed.



(240) (241)

(2.82)

These results stimulate further investigations into transition metal catalyzed electrocyclizations, and have the potential for future development of metal catalysts for such processes.

The electrocyclic reactions of π-electron systems play a pivotal role in the synthesis of a wide variety of carbocyclic and heterocyclic systems. Substituted cyclobutenes undergo thermally allowed conrotatory electrocyclic ring opening reactions and provide a method for the stereoselective construction of 1,3-dienes. On the other hand, hexatrienes undergo thermally allowed disrotatory electrocyclic ring closure, and provide a method for the construction of cyclohexadienes and related ring systems. Apart from the predictable control of the diene geometry, and the control of the configuration of the vicinal stereogenic centers on cyclohexadiene rings, it is the electrocyclic pathways that hold the potential for diastereoselective C–C bond construction. These are the potential targets for future investigations.

The mechanism of electrocyclic reactions would be discussed in terms of the Orbital Symmetry Conservation, the Frontier Orbitals Method, the Möbius-Hückel Approach and the Computational and Theoretical Analysis which constitute the subject matter of the following Chapters.

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3. Orbital Symmetry Conservation

According to Heisenberg, *physicists learn from mathematicians that the symmetry of a problem, as a rule, produces a conservation law. All the conservation laws that are known in physics, for example, the conservation of energy, momentum, angular momentum etc., rest upon fundamental symmetry as the underlying natural law.* So is the case with chemical phenomenae.

Pericyclic reactions belong to a class of chemical processes which are concerted and are known to obey the same natural law of conservation of symmetry. A systematic study of the application of this law, to pericyclic reactions, was pioneered by Woodward and Hoffmann [1] who enunciated the principle of orbital symmetry conservation as follows:

Concerted reactions occur readily when there is congruence between orbital symmetry characteristics of reactants and products; only with great difficulty, when such congruence is absent, or to put it more succinctly, orbital symmetry is conserved in concerted reactions.

Reactions which conserve orbital symmetry are termed as *allowed* and the reactions that do not maintain this symmetry conservation are designated as *forbidden.* The allowed processes take place readily and rapidly under normal conditions, while the forbidden processes may take place very slowly, with great difficulty or through non-concerted mechanisms. This principle was greeted with great enthusiasm as not only did it provide a rationale for no mechanism reactions, but also permitted clear predictions in many interesting cases which need to be scrutinized.

3.1 Basic Concepts

Before applying the principle of orbital symmetry conservation to electrocyclic reactions, a few important concepts need elaboration.

3.1.1 Conrotation and Disrotation

As mentioned earlier in Chapter 2, electrocyclic reactions are pericyclic processes that involve cyclization of conjugated polyenes which may be induced either by heat (*thermal)* or light (*photochemical*). Consider the simplest case of the thermal interconversion of s-*cis* butadiene and cyclobutene involving the transformation of a 4π-electron-butadiene system to a 2π- and a 2σ-electron-cyclobutene system. The *p*-orbital system of butadiene is made up of four 2*p* orbitals lying perpendicular to the plane of the molecule. Clearly this cyclization requires the formation of a bond between C1 and C4 which is possible by an overlap of *p*-orbitals on the carbon atoms.

(3.1)

The desired overlap can be affected by rotating the two termini *a* and *b* of the diene as shown in Figure 3.1.

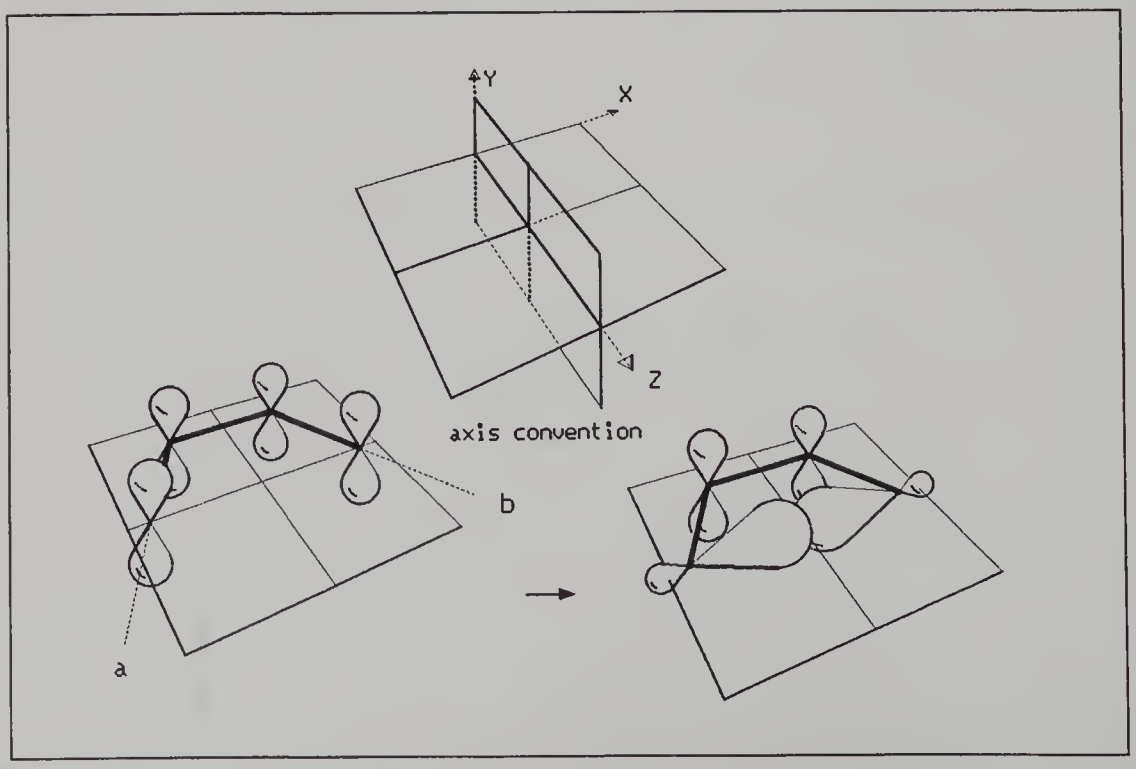


Figure 3.1: *Pertinent orbitals of butadiene and cyclobutene.*

There are, in principle, only two distinct modes of rotation. *When the two termini of a polyene rotate in the same direction, the process is described as conrotation; conversely, if the two termini of the diene rotate in the opposite directions the process is termed as disrotation.* Figure 3.2 shows a conrotatory and a disrotatory cyclization of butadiene. Only one of the two alternatives for both processes are shown. Thus, for a conrotatory process, both termini of the diene are shown to rotate in a clockwise direction, or as an alternate, the rotation of both the termini in an anticlockwise direction. However, during a disrotatory process, terminal *a* rotates clockwise and *b* in an anticlockwise direction while the other alternative is the reverse rotation of the terminals as shown in Figure 3.2 (Chapter 2).

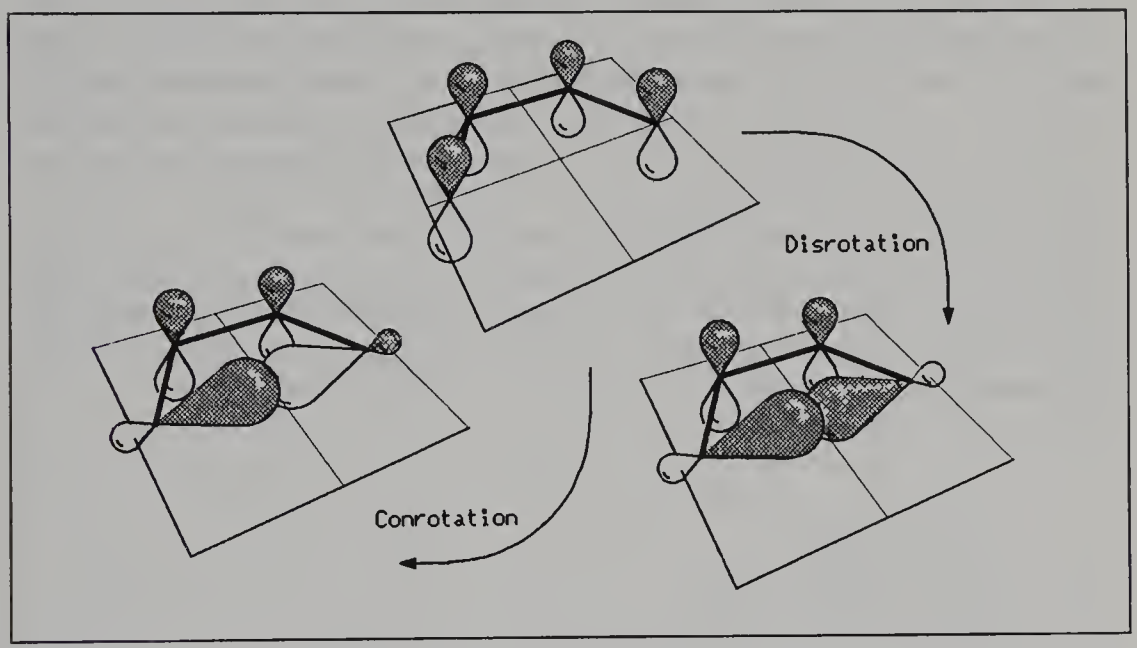
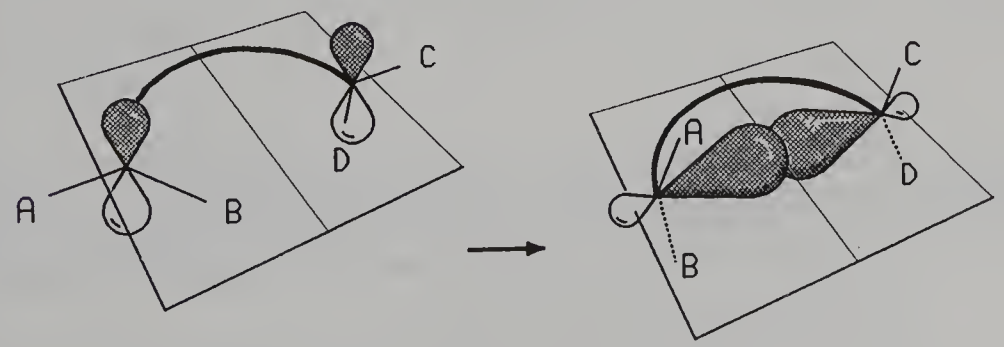


Figure 3.2: *Two modes of cyclization of butadiene.*

Problem 3.1:

A disrotatory ring closure of a conjugated polyene is shown below;



i) Predict the product of an alternate disrotatory process.

ii) How are the two products related to each other stereochemically?

It might be noted here that disrotation leads to a kind of upper-lobe-upper-lobe overlap (the other alternate for disrotation is a lower-lobe-lower-lobe overlap) while a conrotatory process involves an upper-lobe-lower-lobe overlap. However, during both these processes, the *p*-orbitals at the two terminal carbon atoms are involved; the *p*-orbitals on the other two carbon atoms remain unaffected. It should also be noted that the process of electrocyclization is accompanied by a change in hybridization at C1 and C4 from sp^2 in butadiene to sp^3 in cyclobutene.

3.1.2 Orbital Symmetry

As mentioned earlier, electrocyclization of butadiene is allowed only if the principle of conservation of orbital symmetry is observed. Therefore, the next step in the analysis of an electrocyclic reaction requires the identification of symmetry elements that are common to both the reactants and the products. The *symmetry elements* of a compound are the geometric elements in relation to which the symmetry operations are carried out. These elements may be a point, an axis or a plane. *However, a Proper Symmetry Element is defined as the one which bisects the bonds being formed, or broken, during the course of a reaction.* The symmetry elements which do not bisect the bonds involved in the process are, therefore, not considered. The following *proper symmetry elements* may be identified in both butadiene and cyclobutene.

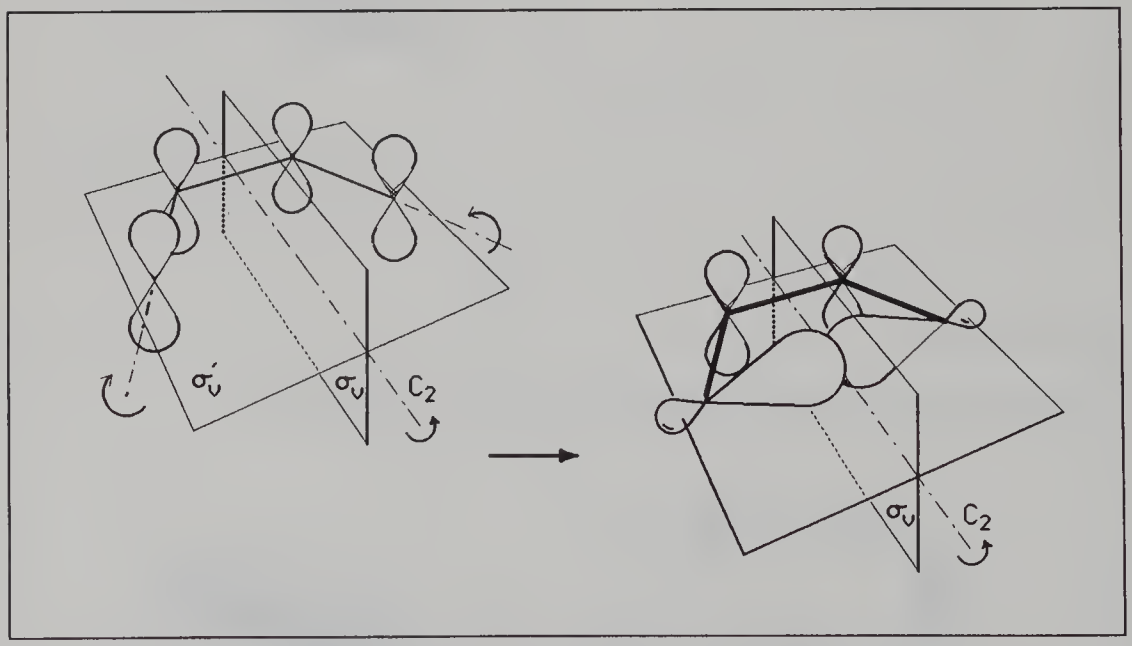


Figure 3.3: *Symmetry elements present in butadiene and cyclobutene.*

i) σ_v is the vertical plane in which lies the bond joining C2 and C3, and is perpendicular to the molecular plane σ'_v.

ii) C_2 -axis of symmetry is the two fold axis of symmetry which involves a 180° rotation about the *z*-axis.

***Problem 3.2*:**

Why can σ'_v not be regarded as a proper symmetry element?

The overall symmetry (*point group*) of both butadiene and cyclobutene is C_{2v}, each has a two-fold rotational axis (C_2) and a mirror plane σ_v both of which bisect the newly formed σ-bond (Appendix B). However, for this bond to be formed, the two methylene groups have to rotate out of the molecular plane σ'_v such that only one symmetry element can be retained along the reaction pathway. It would be seen later that the two-fold axis C_2 is retained during conrotation and the mirror plane σ_v is retained during disrotation. These symmetry characteristics of a molecule are also extendable to its molecular orbitals. Hence, the molecular orbital systems of both butadiene and cyclobutene share the same two proper symmetry elements, i.e. the σ_v plane and the C_2 axis of symmetry.

Therefore, while discussing the conversion of butadiene to cyclobutene, either through disrotation or through conrotation, the two symmetry elements σ_v and C_2 are taken into consideration. Having identified these proper symmetry elements in butadiene and cyclobutene, their molecular orbitals can now be classified on the basis of these symmetry elements. The molecular orbitals (MOs) of butadiene are formed by the interaction of four p_z atomic orbitals (AOs) present on the four carbon atoms. These degenerate AOs may interact in four different ways to give a set of four MOs of different energies. The molecular orbitals with energy lower than the starting atomic orbitals are called the bonding MOs while those with higher energy are called the antibonding MOs. The four molecular orbitals of butadiene are designated as ϕ_1, ϕ_2, ϕ_3 and ϕ_4 and are shown in Figure 3.4. The two lower energy MOs; ϕ_1 and ϕ_2 are termed as the bonding MOs while the two higher energy MOs ϕ_3 and ϕ_4 are described as antibonding MOs. The construction of these MOs is discussed in Appendix A. The four molecular orbitals of cyclobutene are also drawn in Figure 3.4. The pertinent orbitals corresponding to a σ- and a π-bond of cyclobutene are the σ- and the π-molecular orbitals; a σ-bond being formed by the interaction of two sp^3-hybrid orbitals on C1 and C4 while a π-molecular orbital is formed by the interaction of $2p_z$ atomic orbitals on C2 and C3. The σ- and the π-molecular orbitals are described as bonding while the corresponding σ^* and π^* as antibonding.

Since butadiene is a four-electron system, its electrons occupy the two lower energy bonding MOs. The ground state electronic configuration of butadiene is, therefore, written as $\phi_1^2 \phi_2^2$. On the same grounds, the ground state electronic configuration of cyclobutene is written as $\sigma^2 \pi^2$.

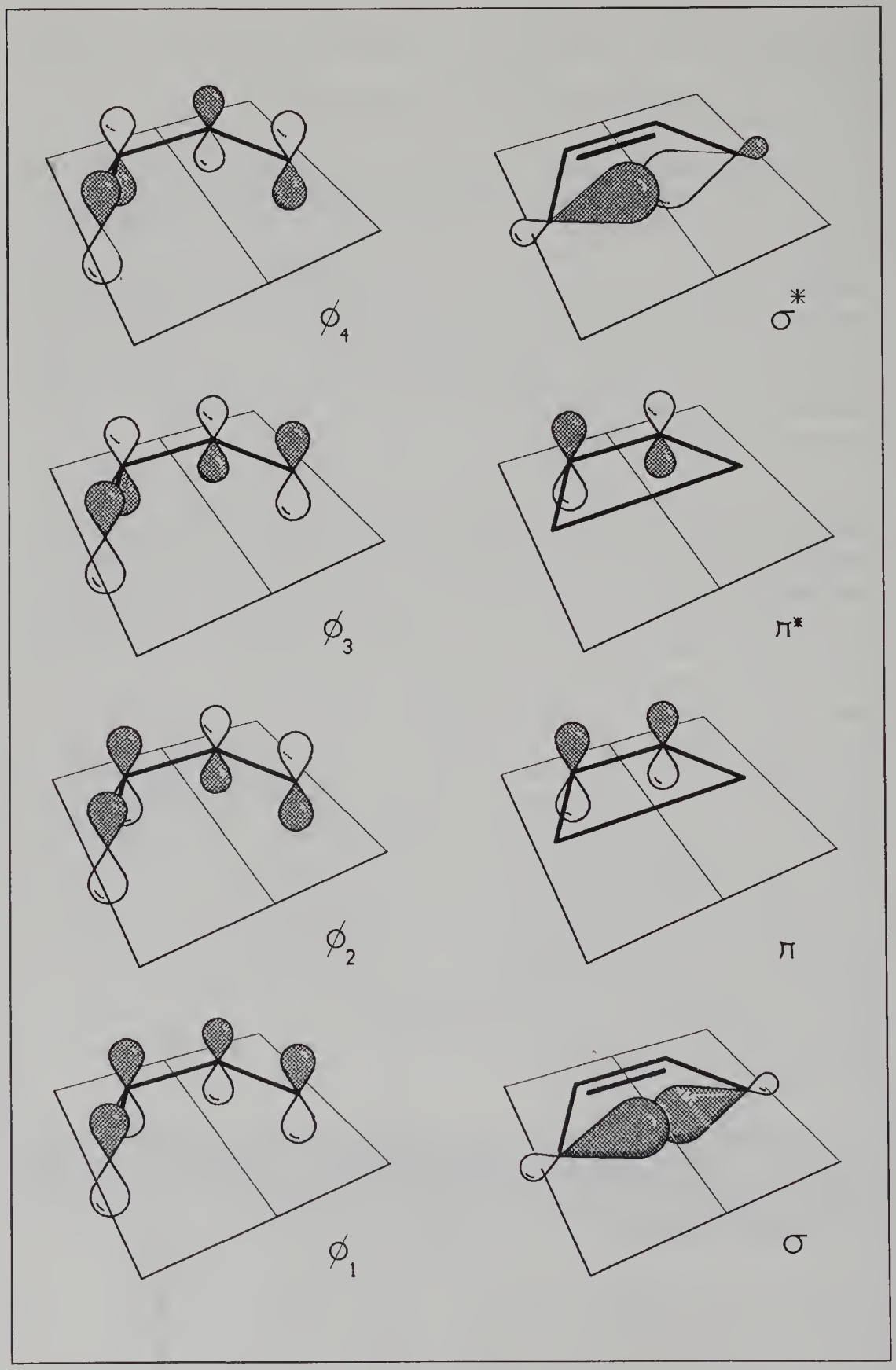


Figure 3.4: *Molecular orbitals of butadiene and cyclobutene.*

The molecular orbitals of both butadiene and cyclobutene can now be classified on the basis of the two proper symmetry elements, the σ_v plane and the C_2 axis, by doing *symmetry operations* on these orbital systems. A symmetry operation is a process which transforms the nuclear arrangement of any system into another which is indistinguishable from the initial. There are two important symmetry operations; a *reflection* in a plane and *rotation* about an axis. The reflection converts a right-handed coordinate system into a left-handed one (like a mirror image). In three dimensional space, a reflection is no more than reversing the direction of any one of the three coordinate axes. A 180° rotation (like a half turn spin) is equivalent to reversing the direction of any two of the three coordinate axes. A symmetry operation on any orbital system renders it either S (Symmetric) or A (Antisymmetric). See Appendix B for details of Symmetry Elements and Symmetry Operations.

A symmetry operation on molecular orbitals of butadiene and cyclobutene is preceded by symmetry operations on some simple molecular orbitals, e.g. the bonding σ- and π-orbitals are symmetric under reflection in σ_v while the corresponding antibonding σ^*- and π^* - orbitals are antisymmetric under the same operation (Figure 3.5).

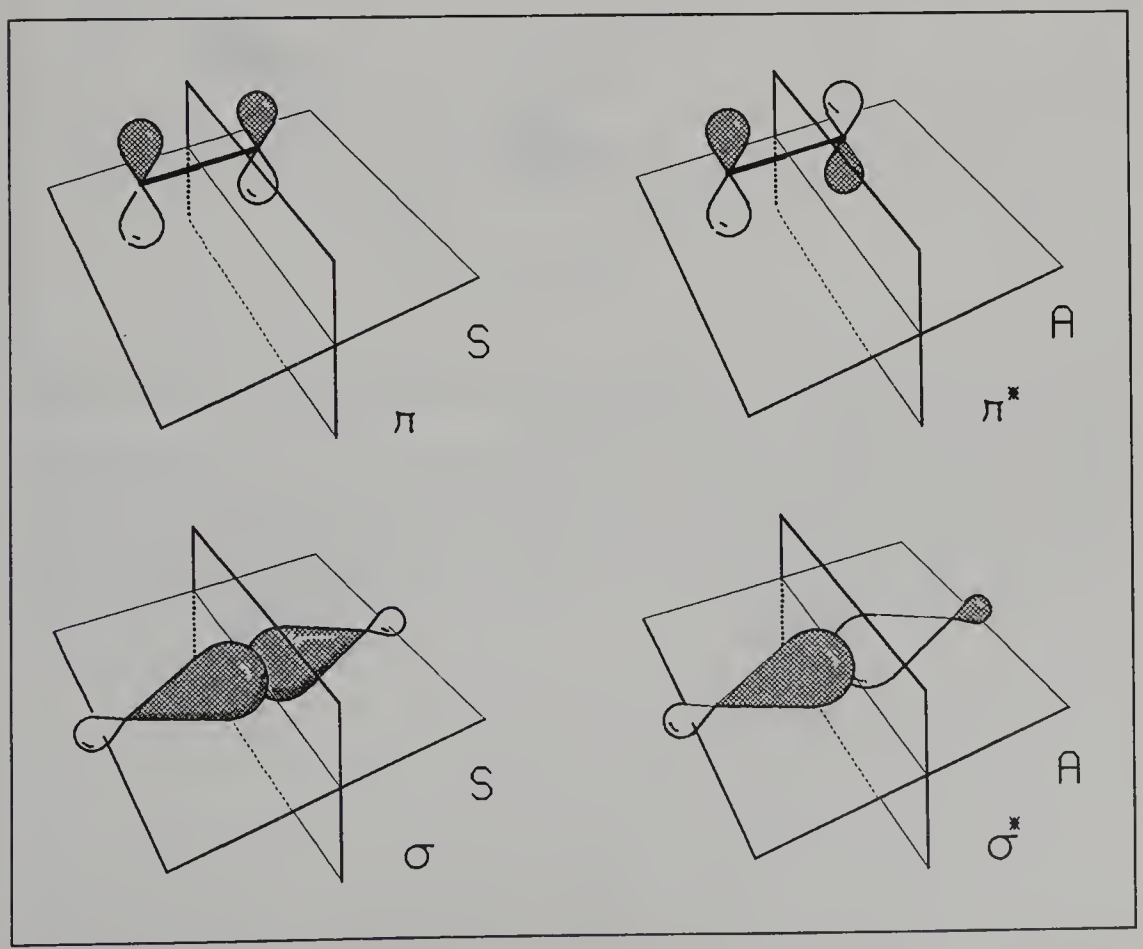


Figure 3.5: *Reflection in a mirror plane.*

Figure 3.6 shows a C_2 operation on σ and σ^* orbitals. It is evident that a 180° rotation about the *z*-axis does not change the symmetry of a σ orbital i.e. it remains symmetric however, σ^* becomes antisymmetric under the same operation.

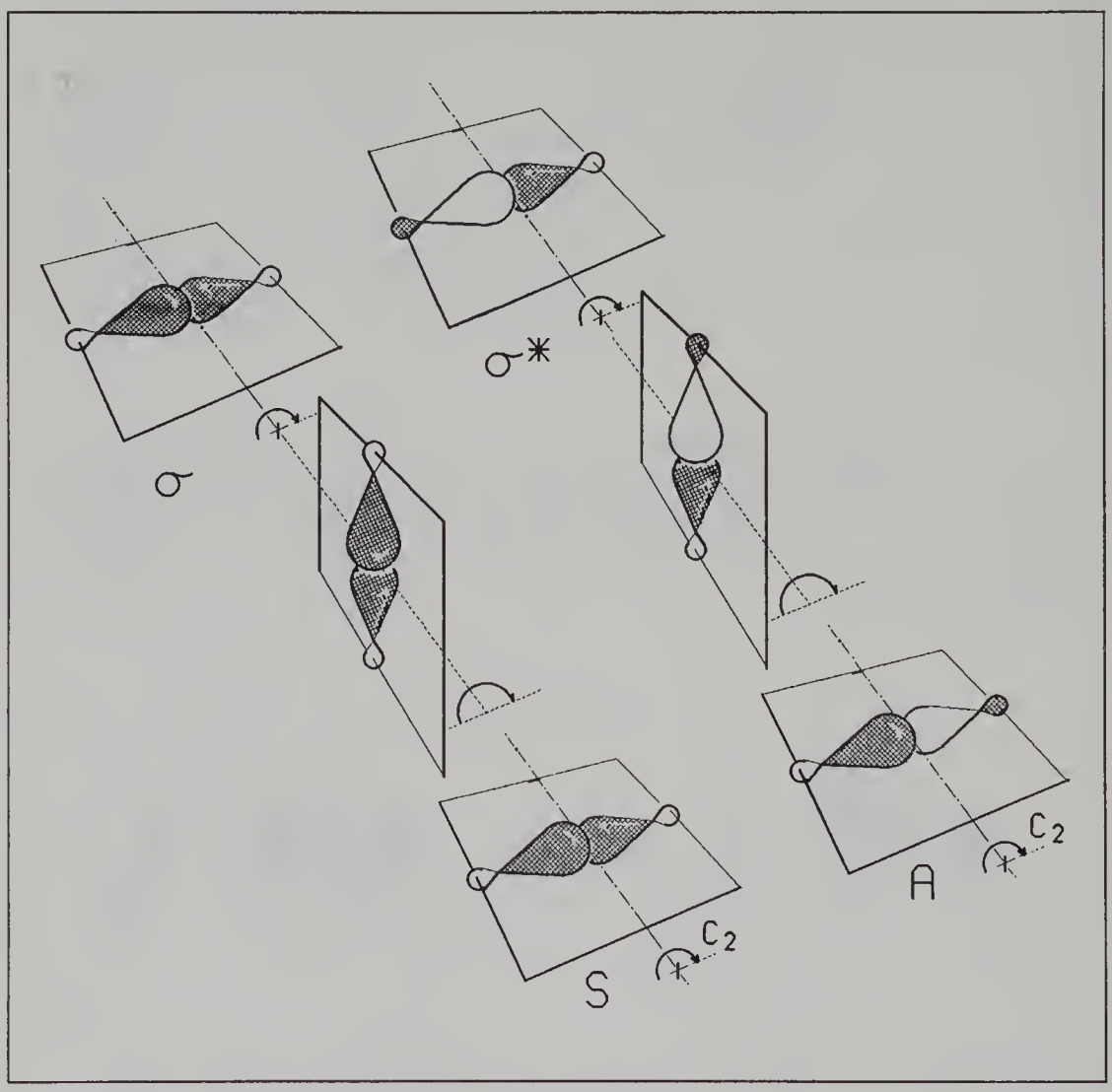


Figure 3.6: *C_2 operation on σ and σ^* orbitals.*

The same operation on π and π^* is shown in Figure 3.7. Obviously π is antisymmetric while π^* remains symmetric under this operation.

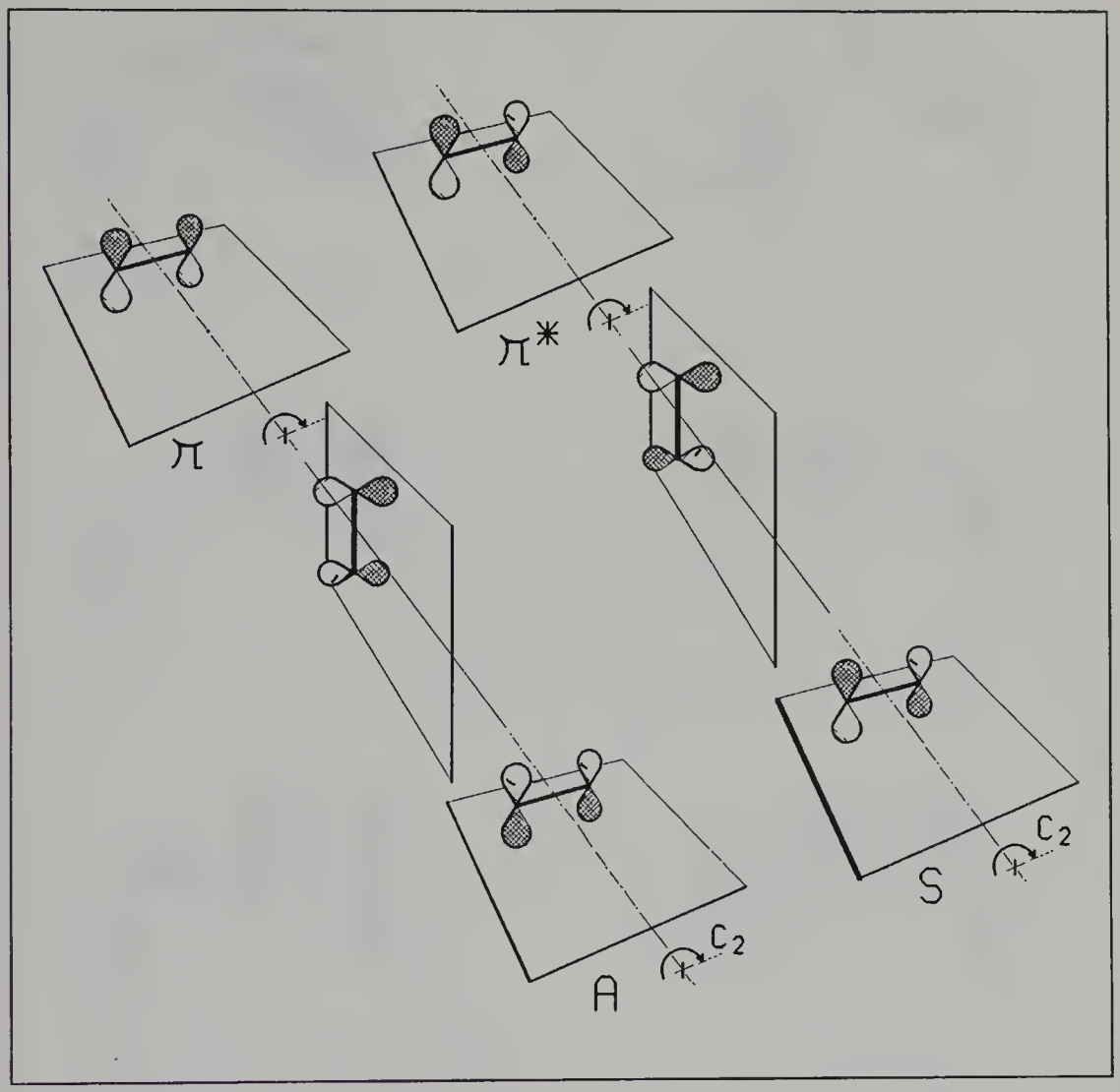


Figure 3.7: *C_2 operations on π and π^* orbitals.*

Symmetry properties of the molecular orbitals of butadiene and cyclobutene can be visualized the same way by doing the same two symmetry operations on these molecular orbitals. Figure 3.8 shows classification of molecular orbitals of butadiene and cyclobutene with respect to σ_v while Figure 3.9 illustrates their classification on the basis of C_2 axis.

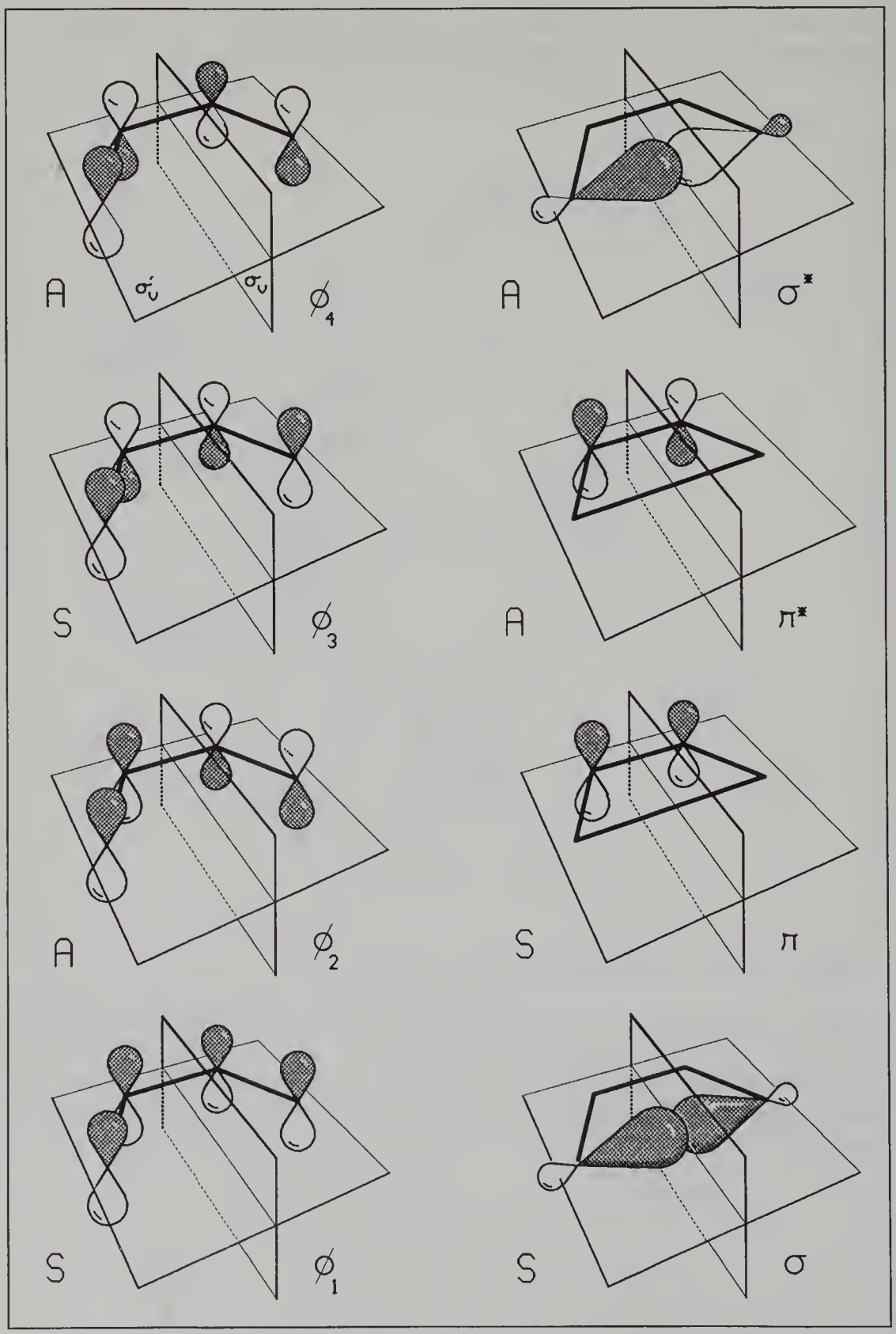


Figure 3.8: *Classification of molecular orbitals of butadiene and cyclobutene with respect to* σ_v.

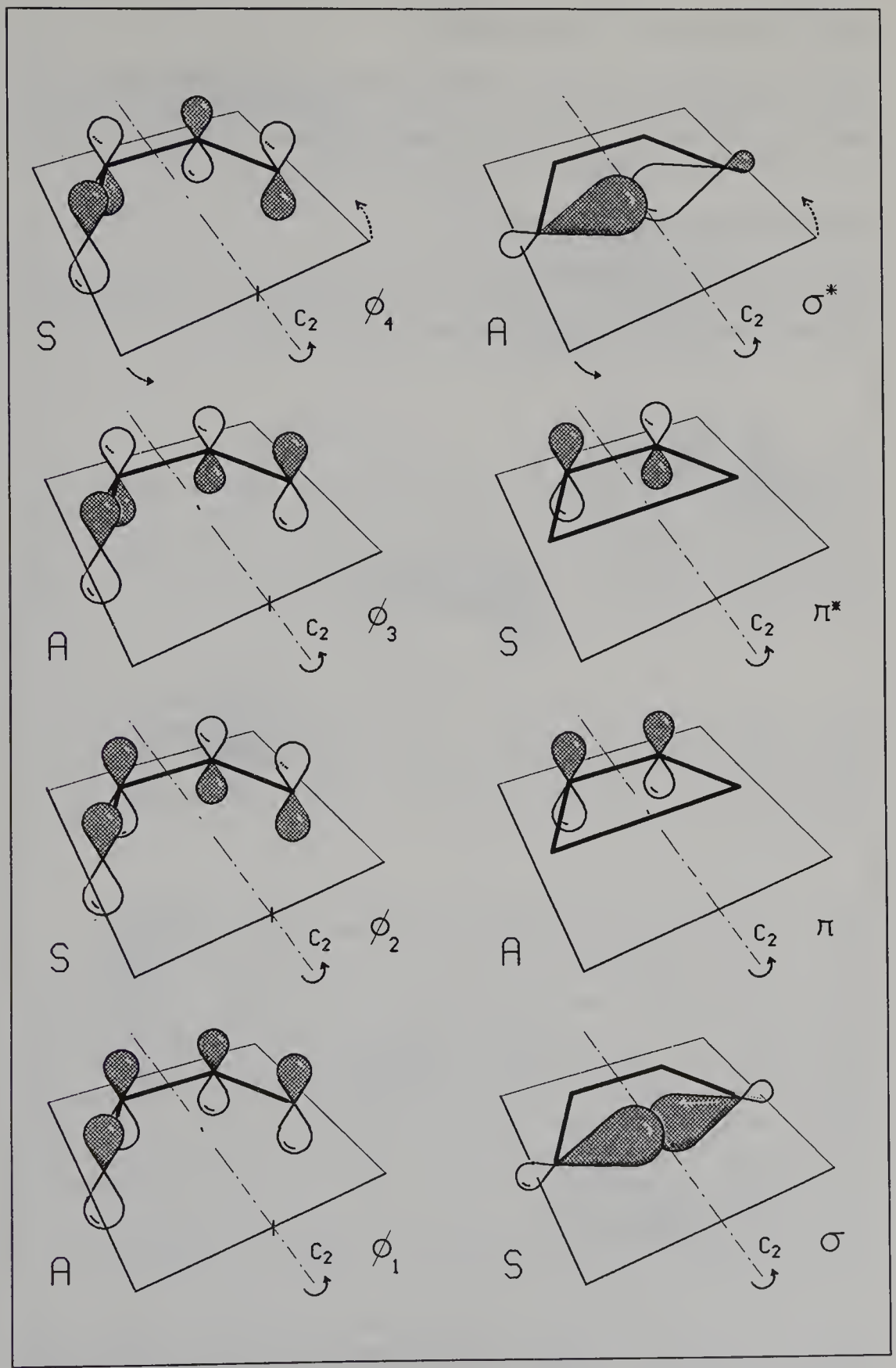


Figure 3.9: *Classification of molecular orbitals of butadiene and cyclobutene on the basis of C_2 axis.*

3.1.3 Symmetry Conservation

After having identified the proper symmetry elements of butadiene and cyclobutene and the classification of their MOs on the basis of these two symmetry elements, it should now be observed which of the symmetry elements are conserved during the two modes of interconversion of butadiene and cyclobutene.

3.1.3.1 Disrotatory Cyclization

It was mentioned earlier that disrotation involves a twist of the two termini of the diene in opposite directions. A diagrammatic representation of the cyclization of butadiene to cyclobutene through disrotation is shown in Figure 3.10.

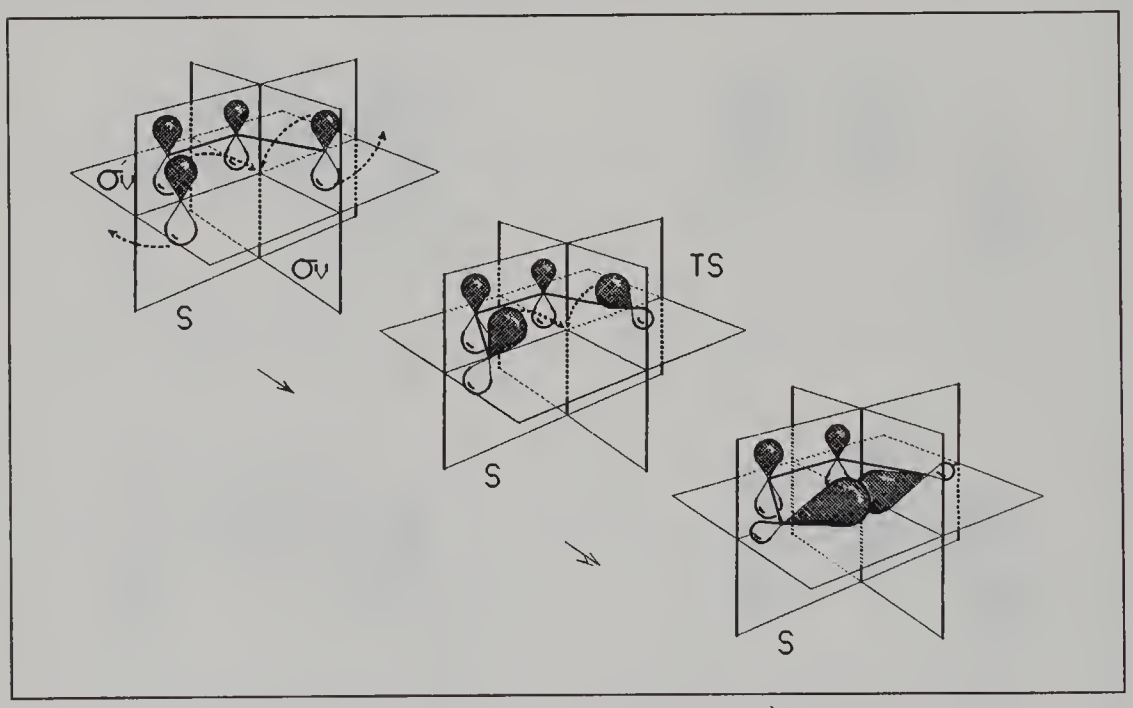
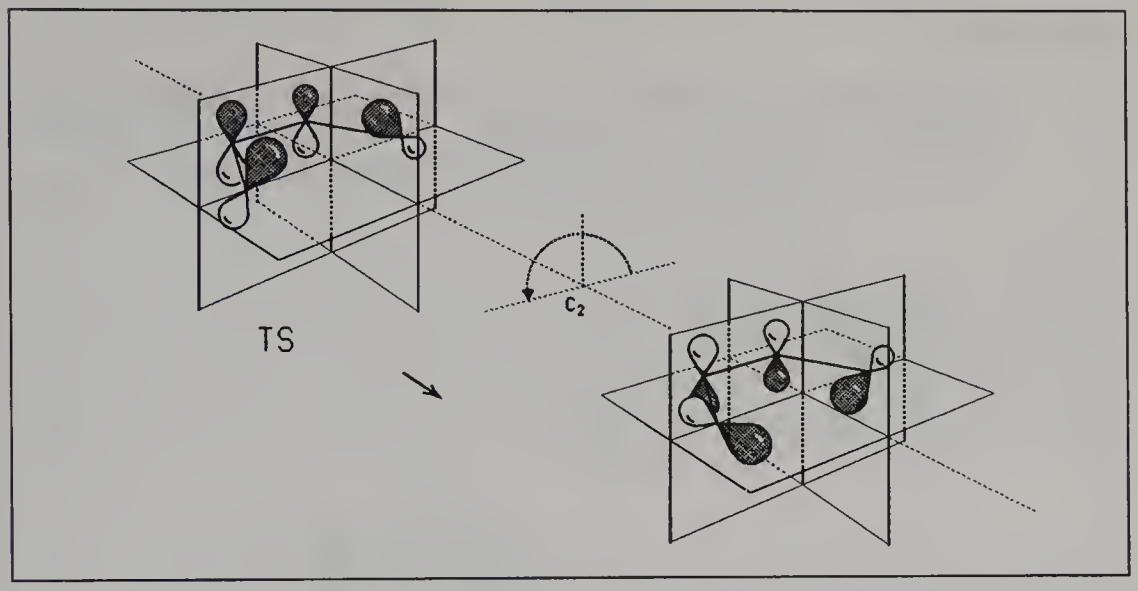


Figure 3.10: *Disrotatory cyclization of butadiene showing conservation of* σ_v.

The two interconverting species are placed in a common plane σ'_v. Figure 3.10 shows a gradual transformation of butadiene to cyclobutene via a transition state involving the rotation of the terminal *p*-orbitals in the opposite directions with a gradual change of hybridization from sp^2 to sp^3. It may be recalled here that the rotation of the terminal *p*-orbitals in the same, or in the opposite direction, does not affect the *p*-orbitals on the remaining two carbon atoms. A careful examination of all three species involved in the transformation reveals that they all share a common symmetry element σ_v with respect to which they are all symmetric. Therefore, σ_v can be considered as the symmetry element which is *conserved* during a disrotatory cyclization of butadiene. On the contrary, a C_2 operation on the orbital system of both butadiene and cyclobutene renders both these systems antisymmetric.

The transition state, however, may not be described as symmetric or antisymmetric during this C_2 operation because the orientation of the orbital system in space changes. Therefore, C_2 is not the symmetry element in a disrotatory transition state as shown in the following figure.



The same arguments apply to the reverse process in accordance with the principle of microscopic reversibility. Figure 3.10 portrays a disrotatory transformation of only one MO (ϕ_1) of butadiene, however, the choice of any other MO does not change the argument. Thus, while discussing the interconversion of butadiene and cyclobutene through a disrotatory process, their molecular orbitals are classified on the basis of σ_v.

3.1.3.2 Conrotatory Cyclization

A conrotatory transformation of butadiene to cyclobutene is shown in Figure 3.11. It is evident that all the three species are antisymmetric with respect to C_2 . Therefore, C_2 may be regarded as the symmetry element which is conserved during conrotation.

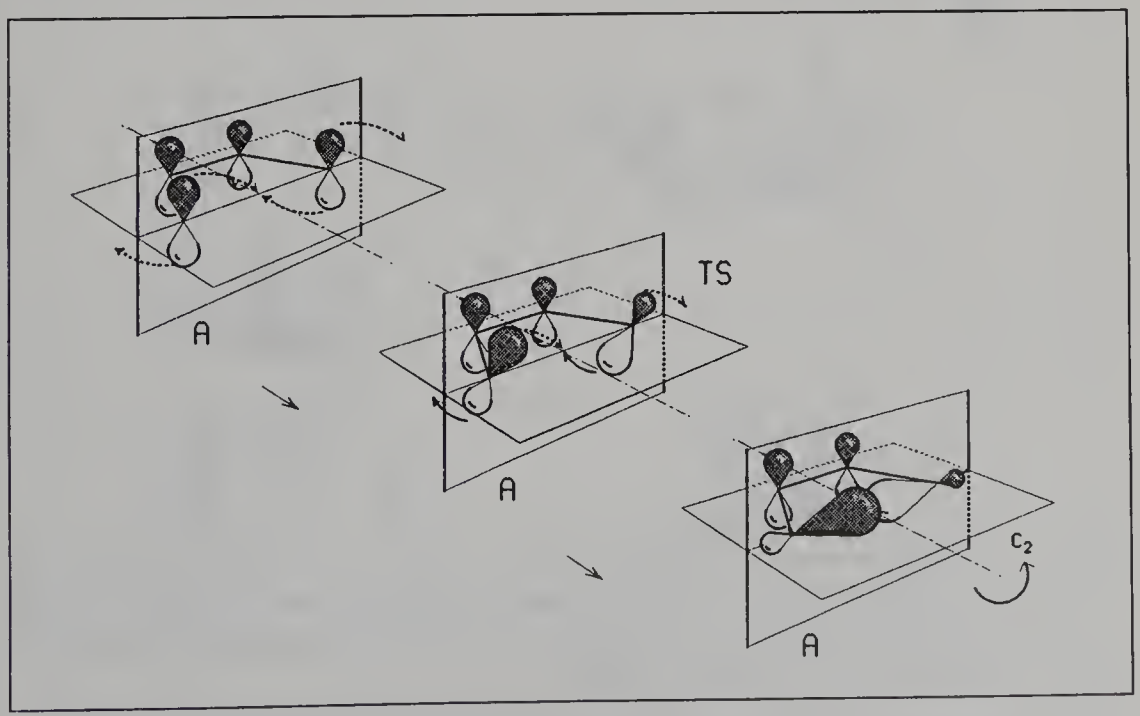
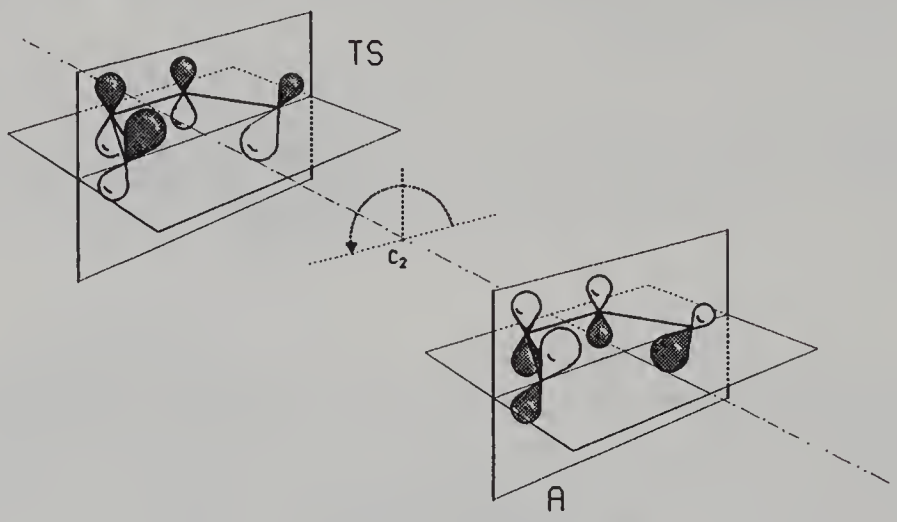


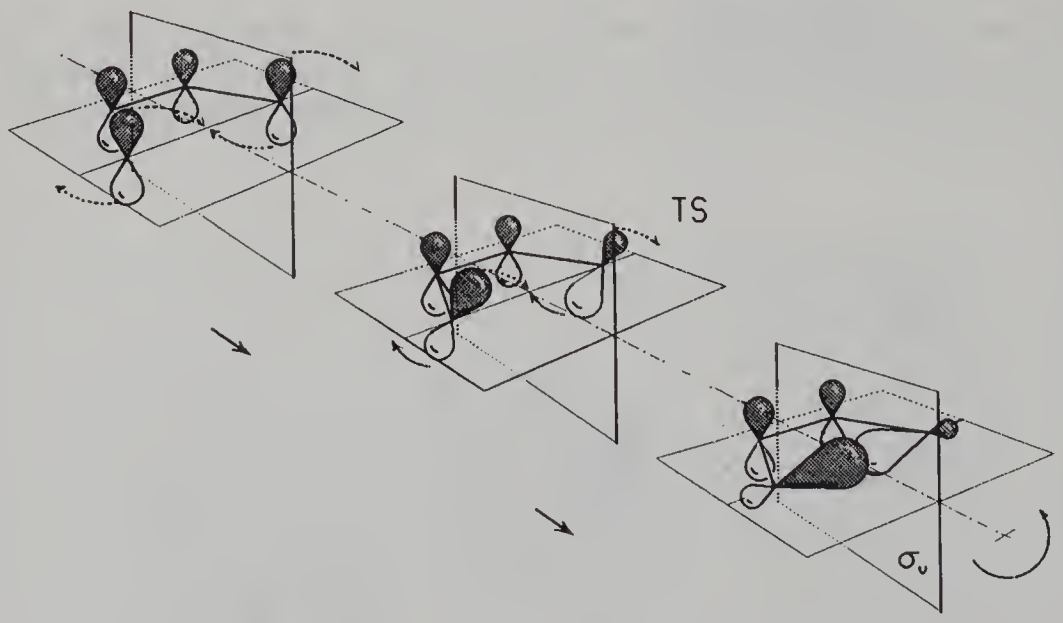
Figure 3.11:*Conrotatory cyclization of butadiene showing conservation of C_2 axis.*

Problem 3.3:

i) C_2 operation on the conrotatory transition state is shown. Perform the same operation on butadiene and cyclobutene and confirm that all the three species are antisymmetric with respect to this symmetry element.



ii) Take a look at the diagram below and confirm that σ_v is not conserved during a conrotatory process.



Thus, a conrotatory process does not have a plane of symmetry common to butadiene, cyclobutene and the transition state. Since the C_2 axis is conserved during conrotation, the classification of molecular orbitals of the interconverting species is done on the basis of this symmetry element.

A disrotatory mode conserves σ_v while a conrotatory mode conserves C_2 axis.

3.2 Applications

3.2.1 Energy Level Correlation Analysis

A pericyclic process is allowed only when the orbital symmetry is conserved during the course of a reaction in accordance with the principle of orbital symmetry conservation. Thus, the thermal interconversion of the ground state of butadiene and the ground state of cyclobutene would be allowed if the orbital symmetry is conserved. Below is an analysis of even-electron systems undergoing electrocyclic reactions.

3.2.1.1 Even-Electron Systems

The conjugated polyenes undergoing electrocyclic reactions may have an even-, or an odd number of electrons. The even-electron systems may be either neutral (even-numbered polyenes) or ionic (odd-numbered polyenes). These systems are discussed separately in the following section.

3.2.1.1.1 Even-Numbered Polyenes

- *(4n) Electron Systems*

The interconversion of butadiene and cyclobutene is an example of an even-numbered polyene with (4n) electrons. The MOs of the interconverting system have already been shown in Figure 3.4. A disrotatory transformation of the two bonding molecular orbitals of butadiene into those of cyclobutene is shown in Figure 3.12.

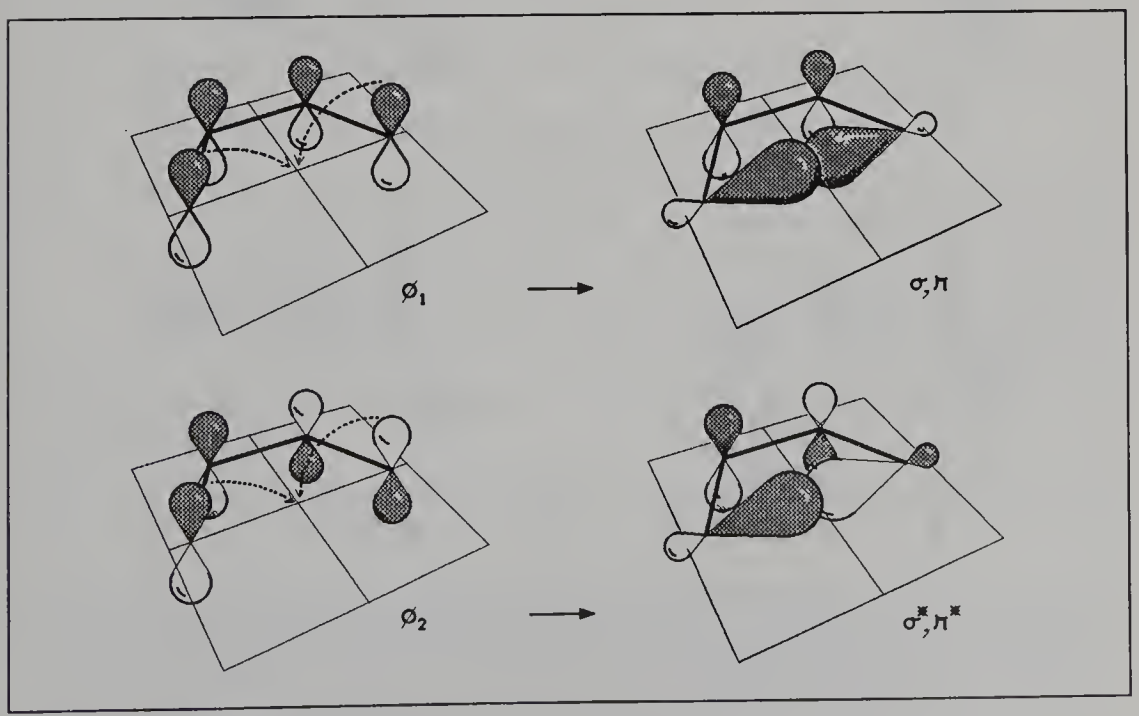


Figure 3.12: *Transformation of the bonding MOs of butadiene into those of cyclobutene during disrotation.*

The molecular orbital ϕ_1 may, on disrotation, transform either into σ or π of cyclobutene, while ϕ_2 on disrotation may transform either into σ^* or π^* (Figure 3.12). Likewise, the transformation of the antibonding molecular orbitals may be visualized. This picture of the interconversion of molecular orbitals of butadiene and cyclobutene is tabulated below.

Table 3.1: *Transformation of MOs of butadiene into those of cyclobutene during disrotation.*

MOs of butadiene	Disrotation	MOs of cyclobutene
ϕ_1	$\longleftrightarrow$	σ, π
ϕ_2	$\longleftrightarrow$	σ^*, π^*
ϕ_3	$\longleftrightarrow$	σ, π
ϕ_4	$\longleftrightarrow$	σ^*, π^*

Since a conrotatory process maintains a C_2 axis of symmetry, therefore, only this symmetry element is of interest. A conrotatory transformation of the bonding molecular orbitals of butadiene, ϕ_1 and ϕ_2 , into those of cyclobutene is shown in Figure 3.13.

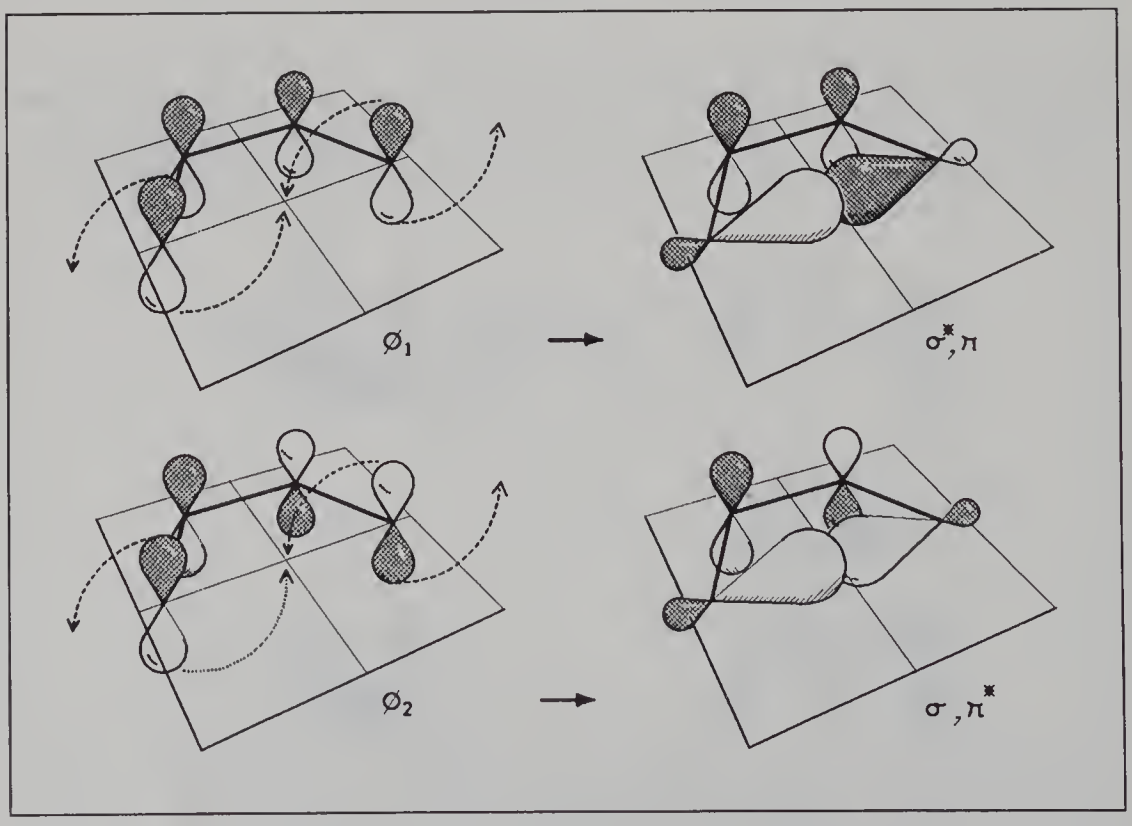


Figure 3.13: *Transformation of the bonding MOs of butadiene into those of cyclobutene during conrotation.*

Table 3.2: *Transformation of MOs of butadiene into those of cyclobutene during conrotation.*

MOs of butadiene	Conrotation	MOs of cyclobutene
ϕ_1	$\longleftrightarrow$	σ^*, π
ϕ_2	$\longleftrightarrow$	σ, π^*
ϕ_3	$\longleftrightarrow$	—, —
ϕ_4	$\longleftrightarrow$	—, —

Problem 3.4:

Show how the two antibonding MOs of butadiene transform into the MOs of cyclobutene during a conrotatory process and complete Table 3.2.

Since two important characteristics of a molecular orbital are its energy and symmetry, therefore, the conversion of molecular orbitals of the reactant into those of product should, in principle, depend on these two characteristics. This may be done by the construction of energy level correlation diagrams, an idea advanced by Longuett-Higgins-Abrahamson [2]. The steps involved during the construction of such a diagram are outlined below.

i) To begin with, a reaction coordinate is proposed.

ii) Bonds being formed or broken during a reaction are identified while ignoring the substituents and embedded heteroatoms.

iii) Proper symmetry elements are identified.

iv) Orbitals are classified on the basis of symmetry elements being conserved.

v) The orbitals of the product are treated the same way.

vi) The lowest energy molecular orbital of the reactant is correlated with the lowest energy molecular orbital of the product which has the same symmetry. The next higher energy molecular orbital of the reactant is similarly correlated with a product molecular orbital of the same symmetry, and so on, until the highest energy reactant molecular orbital is correlated.

vii) As a rule, the lines joining the orbitals of like symmetry should not cross each other.

viii) The number and the symmetry type of the reactant and the product orbitals must be the same so that all orbitals are correlated.

ix) If all ground state occupied orbitals of the reactant are correlated with the ground state occupied orbitals of the product with symmetry conservation, the reaction is thermally allowed by the proposed mechanism.

x) If one or more bonding MOs of the reactant correlate with antibonding MOs of the product, the reaction is forbidden.

By following these steps, an energy level correlation diagram for thermal disrotatory process is constructed below (Figure 3.14).

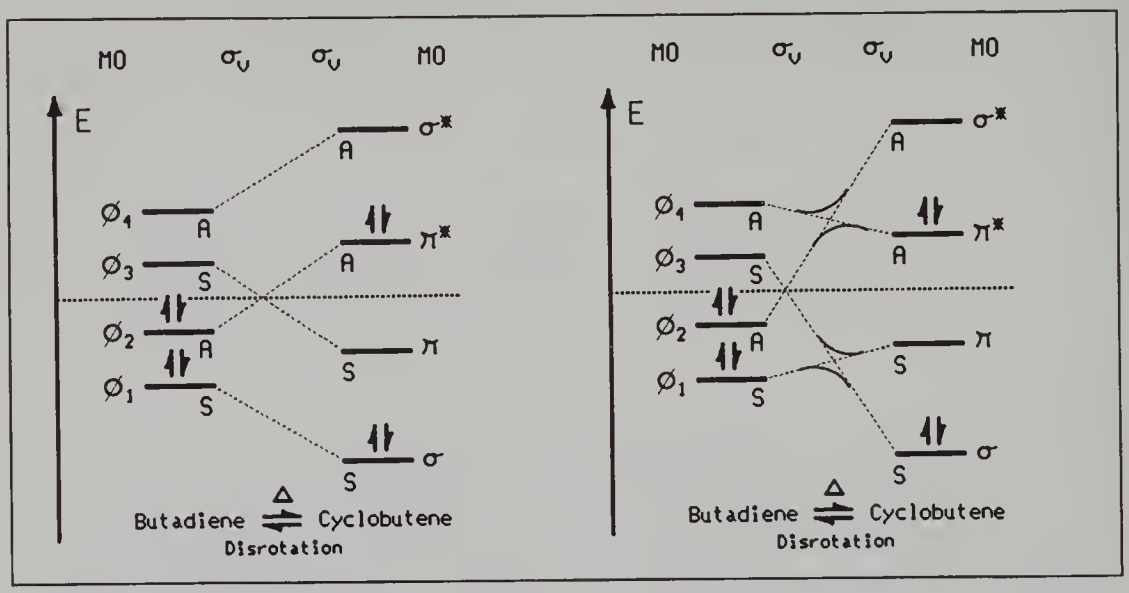


Figure 3.14: *Two alternate energy level correlations for a disrotatory interconversion of butadiene and cyclobutene.*

Since there are two orbitals of the same symmetry of both the reactant and the product, two correlations are possible (Figure 3.14). Of the two possibilities, the one on the left hand side is the only acceptable one. The other possibility is ruled out on the basis of a quantum mechanical principle of non-crossing of lines of the same symmetry, which states that *lines of the same symmetry do not cross.* A simple justification of this rule follows; a correlation of lines depicts a change in energy as it proceeds along the reaction coordinate. Since the energies of the two transitory orbitals are the same at the crossing point, they interact strongly because they have the same symmetry. This interaction causes a splitting (or pushing apart) of these two energy levels, thereby making two new energy levels; one of still lower energy and the other of still higher energy. The diffference of the energy levels tends to keep the transitory orbitals of the same symmetry apart, and thus prevent them from crossing. Hence, the lines of the same symmetry do not cross due to the symmetry imposed barrier.

The correlation showing an avoided crossing of the lines of the same symmetry, is drawn with solid curves in Figure 3.14. It should be emphasized here that this restriction of non-crossing of lines of the same symmetry does not apply to lines of opposite symmetry because orbitals of different symmetries do not interact at all. During a thermal reaction, only the bonding molecular orbitals of the reacting system are considered. The ground state electronic configurations of butadiene and cyclobutene, as mentioned earlier, are $\phi_1^2 \phi_2^2$ and $\sigma^2 \pi^2$ respectively. An inspection of the correlation diagram for a disrotatory process (Figure 3.14) reveals a correlation of the ground state of butadiene $\phi_1^2 \phi_2^2$ with the doubly excited state of cyclobutene $\sigma^2 \pi^{*2}$. This means that ϕ_1 , along with its electron pair, can be transformed smoothly into σ. However, the two electrons in ϕ_2 have to occupy the antibonding π^* if orbital symmetry is to be conserved. Thus, a correlation of the

bonding molecular orbitals of butadiene with the bonding molecular orbitals of cyclobutene is not possible. It can be concluded that, a *disrotatory mode forces a correlation of ground state butadiene with doubly excited state of cyclobutene i.e.*

$$\phi_1^2\phi_2^2 \longleftrightarrow \sigma^2\pi^{*2}$$

Likewise, an energy level correlation diagram for the conrotatory process may be drawn (Figure 3.15).

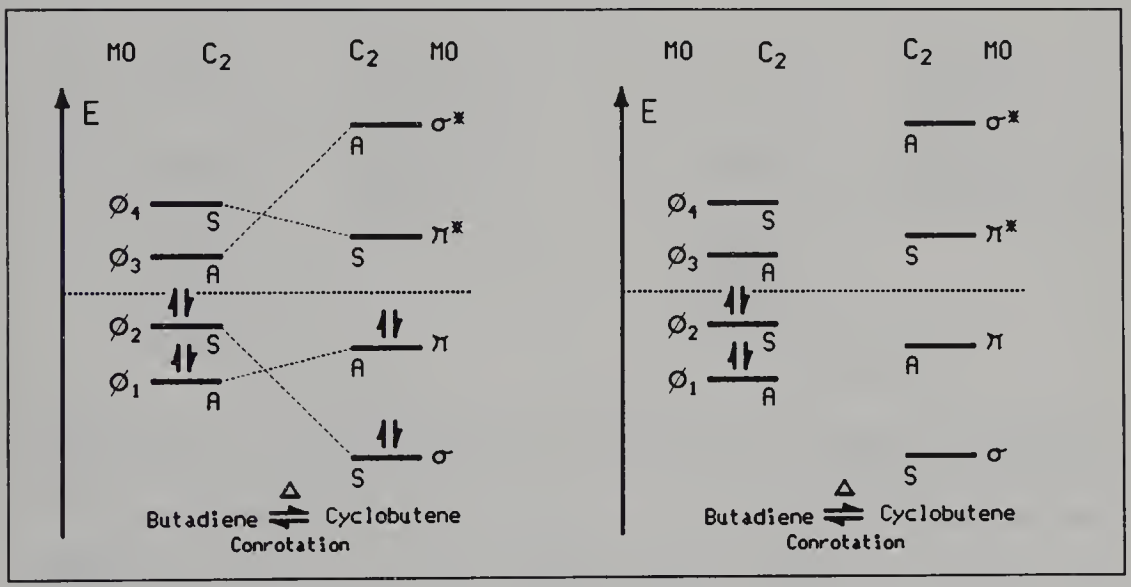


Figure 3.15: *. Energy level correlation diagram for a conrotatory interconversion of butadiene and cyclobutene.*

Problem 3.5:

Draw correlation lines in Figure 3.15 in order to make an alternate symmetry based correlation. Would you expect this correlation to be an unlikely one?

It is evident from Figure 3.15 that the ground state molecular orbitals of butadiene may transform smoothly into the ground state molecular orbitals of cyclobutene, with conservation of symmetry. Thus, *a conrotatory process leads to a correlation of ground state butadiene with ground state cyclobutene,* i.e.

$$\phi_1^2\phi_2^2 \longleftrightarrow \pi^2\sigma^2$$

Problem 3.6:

Confirm that the correlation shown in Figure 3.15 is also energy based.

One of the most important characteristic of a pericyclic reaction is the formation of a cyclic transition state, and hence its significance should not be overlooked. The approximate energy of any transition structure at any arbitrary position along the reaction coordinate may be found by looking at the correlation diagram. A vertical line is drawn at an arbitrary position on the correlation diagram and the intersection of this line with the lines emanating from ϕ_1 and ϕ_2 give an idea of the approximate energy of the transition structure at that particular point. If the two energy levels having energies E_1 and E_2 are doubly occupied then the total electronic energy

equals $2(E_1+E_2)$. It is evident from Figure 3.16 that the approximate total electronic energy of the transition structure at any point, along the reaction coordinate, for a conrotatory process is lower than that for a disrotatory process thereby making the former process energetically more feasible.

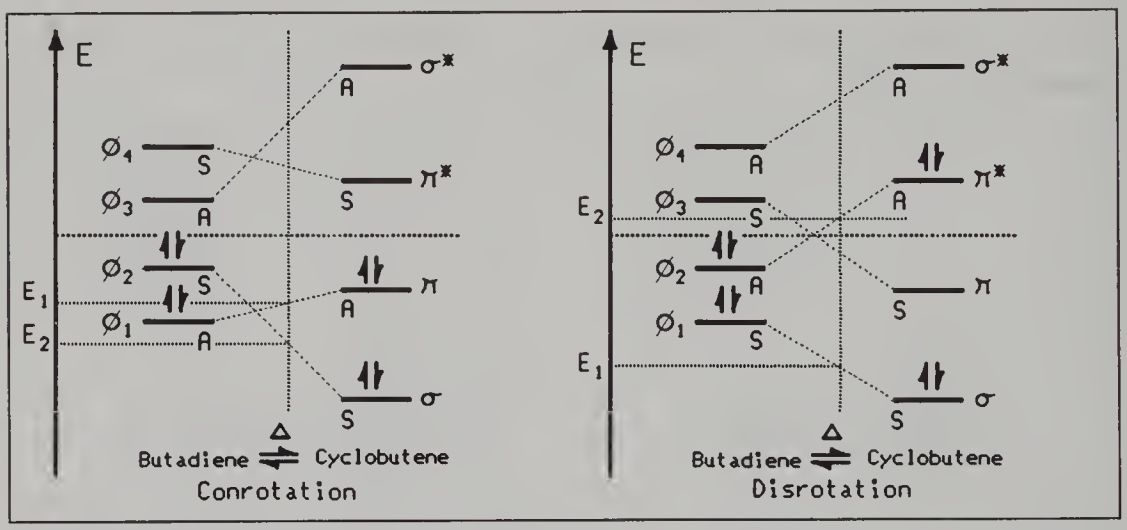


Figure 3.16: *A comparison of the energies of the transition structure along the reaction coordinate for a conrotatory and a disrotatory interconversion of butadiene and cyclobutene.*

The arguments developed for the thermal interconversion of butadiene and cyclobutene are extendable to other (4n) electron systems as well. It may, therefore, be generalized that *thermal electrocyclic reactions of polyenes with (4n)π electrons would proceed through conrotation.*

After having discussed the energy level correlation analysis of thermal reactions, the analysis of photochemical reactions is discussed. These reactions are caused by the absorption of visible and ultraviolet light. Light of these wavelengths cause excitation of electrons in the molecules from their ground state molecular orbitals to higher energy orbitals, thereby producing electronically excited states. As mentioned earlier in Chapter 2, the multiplicity of the excited species may either be singlet or triplet. In an excited singlet the two electrons have their spins paired, whether they are present in the same orbital or in different orbitals, while the electrons in an excited triplet occupy different orbitals with the same spin. So far, concerted photochemical reactions are known to take place from the excited singlets. Consider the simplest case of the photochemical interconversion of butadiene and cyclobutene. The photoexcited butadiene is shown as a singlet. The excited state electronic configuration of butadiene is written as $\phi_1^2\ \phi_2\ \phi_3$. An allowed photochemical process is the one which involves the transformation of an excited state of the reactant into the lowest excited state of the product. A correlation diagram for photocyclization of butadiene, in a disrotatory sense, can be constructed as before. However, this time by merely changing the electron occupancies by exciting one electron from ϕ_2 to ϕ_3 in butadiene.

From the correlation diagram shown in Figure 3.17 it can be seen that the *first singly excited state butadiene transforms into the first singly excited state of cyclobutene during disrotation.* Evidently the following correlation is energetically feasible:

$$\phi_1^2 \phi_2 \phi_3 \quad \longleftrightarrow \quad \sigma_2 \pi \pi^*$$

The correlation diagram for photoreaction with conrotation can be envisaged in an analogous manner.

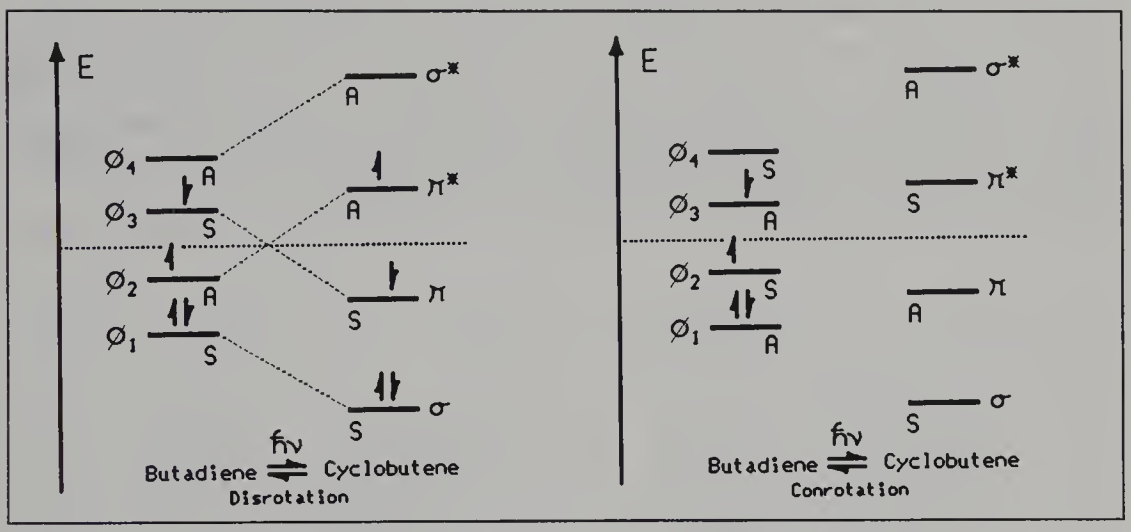


Figure 3.17: *Energy level correlations for the photochemical interconversion of butadiene and cyclobutene through disrotation and conrotation.*

Problem 3.7:

Energy levels along with their symmetries and electron occupancies are redrawn in Figure 3.17. Show a symmetry based correlation of these levels for a conrotatory interconversion of butadiene and cyclobutene and confirm that photoreaction would favour the disrotatory mechanism.

It may be seen from this correlation that the first excited state of butadiene $\phi_1^2 \phi_2 \phi_3$ is transforming into a still higher excited state $\pi^2 \sigma\sigma^*$ of cyclobutene. Evidently, such a correlation should not be preferred over the correlation shown for the disrotatory process. Moreover, the excited state reactants never give ground state products rather excited state products are formed first. These excited state products later on decay to ground state products. This point would be elaborated later.

Figure 3.18 summarizes the results of thermal and photochemical interconversion of butadiene and cyclobutene and the following conclusions may be drawn.

Conjugated polyenes with (4n) electrons undergo thermal electrocyclic changes through conrotation while photochemical reactions opt for the disrotatory path.

However, it does not appear reasonable, at first sight, why a photochemical process should be described as being allowed by disrotation and forbidden by conrotation, even though both these processes lead to a correlation of the excited states of the interconverting species. A disrotatory process leads to a correlation of the first excited states of both butadiene and cyclobutene, however, a conrotatory mode

forces a correlation of the first excited state of butadiene with a still higher excited state of cyclobutene. Obviously a correlation of the type

$$\phi_1^2 \phi_2 \phi_3 \longleftrightarrow \pi^2 \sigma \sigma^*$$

should not be preferred over the correlation

$$\phi_1^2 \phi_2 \phi_3 \longleftrightarrow \sigma^2 \pi \pi^*$$

Answers to these, and related queries, may be found by constructing symmetry state correlation diagrams which would be discussed in the following section. Since orbital symmetry considerations apply to reactions in both directions, these electrocyclic reactions may be described as reversible. It is also worth mentioning here that thermal reactions promote the formation of more stable butadienes while photoreactions lead to higher energy isomers, i.e., cyclobutenes.

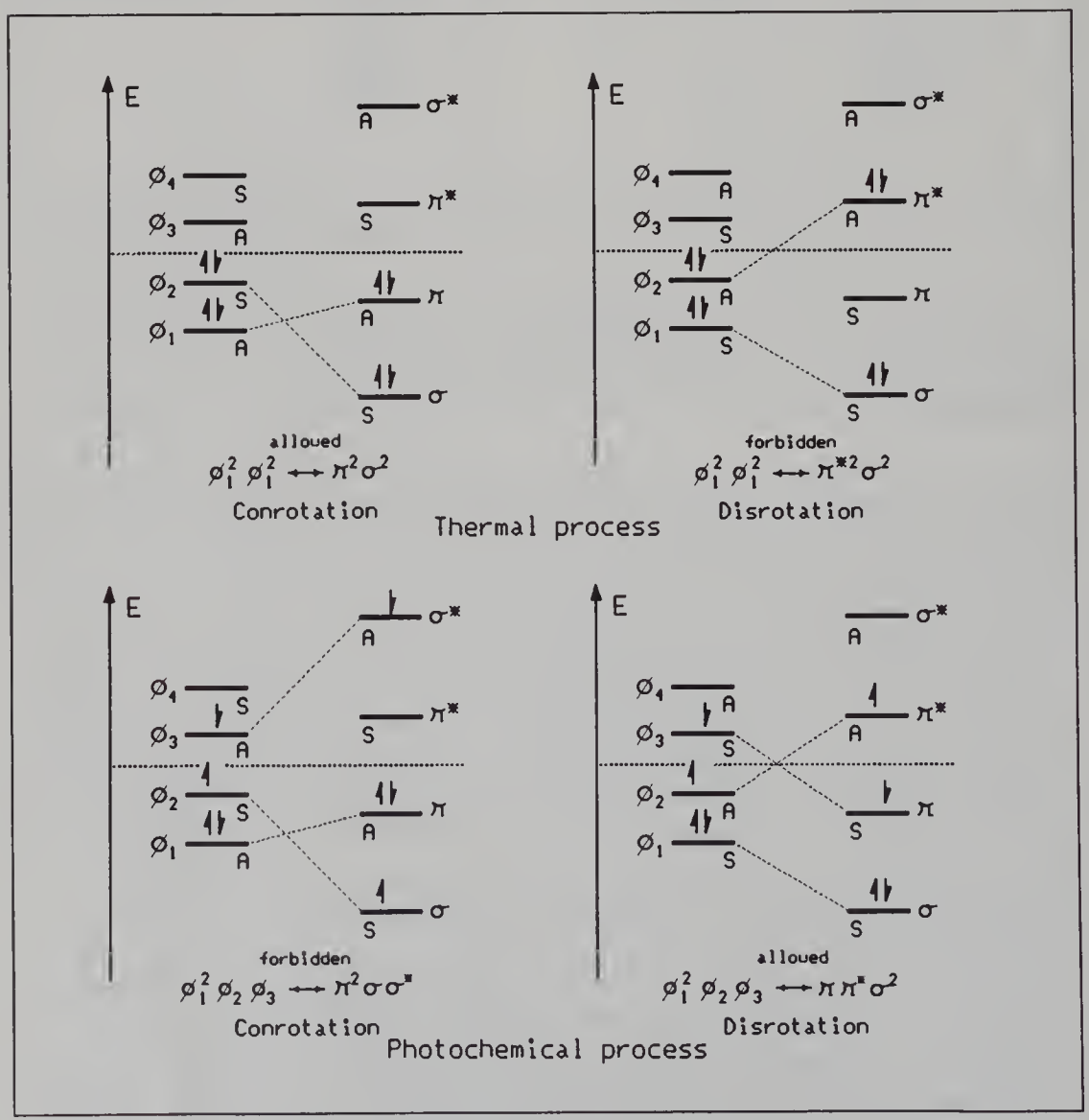


Figure 3.18: Comparison of thermal and photochemical processes through controtatory and disrotatory interconversion of butadiene and cyclobutene.

- ***(4n+2) Electron Systems***

Having discussed a (4n) electron system in detail, it is easier to study a (4n+2) electron system. The interconversion of 1,3,5–hexatriene and 1,3–cyclohexadiene is a prototype of such a system (Equation 3.2)

(3.2)

Problem 3.8:

Indicate the type of bonds and the number of electrons involved in the interconversion shown in Equation 3.2. How would the transition state of such a reaction look like?

The pertinent molecular orbitals of the interconverting species are shown in Figure 3.19. For hexatriene there are six molecular orbitals (ϕ_1 _ ϕ_6) formed by the interactions of six *p*-orbitals on six carbon atoms. The three lower energy orbitals are the bonding MOs and are occupied in the ground state while the three higher energy orbitals are the antibonding MOs. For the product cyclohexadiene, there is one σ- bonding and one σ^* antibonding MO. Moreover, the diene portion of the product has two π bonding MOs (π_1 and π_2) and two antibonding MOs (π_3 and π_4) similar to the MOs of butadiene. These molecular orbitals are also shown in Figure 3.19.

Problem 3.9:

Using molecular models identify the symmetry elements present in hexatriene and cyclohexadiene. Would you expect all these elements to be proper symmetry elements?

The classification of these MOs on the basis of proper symmetry elements is also shown in Figure 3.19. The transformation of hexatriene to cyclohexadiene can be affected again in a conrotatory, or in a disrotatory, manner remembering that the former process maintains the C_2 axis while the latter conserves the σ_v plane.

Problem 3.10:

With the help of a diagram, show a conrotatory transformation of the bonding MOs of hexatriene into those of cyclohexadiene and confirm that all the species involved in the process share a C_2 axis of symmetry. What would you expect for a disrotatory process ?

Refer to Figures 3.12, 3.13.

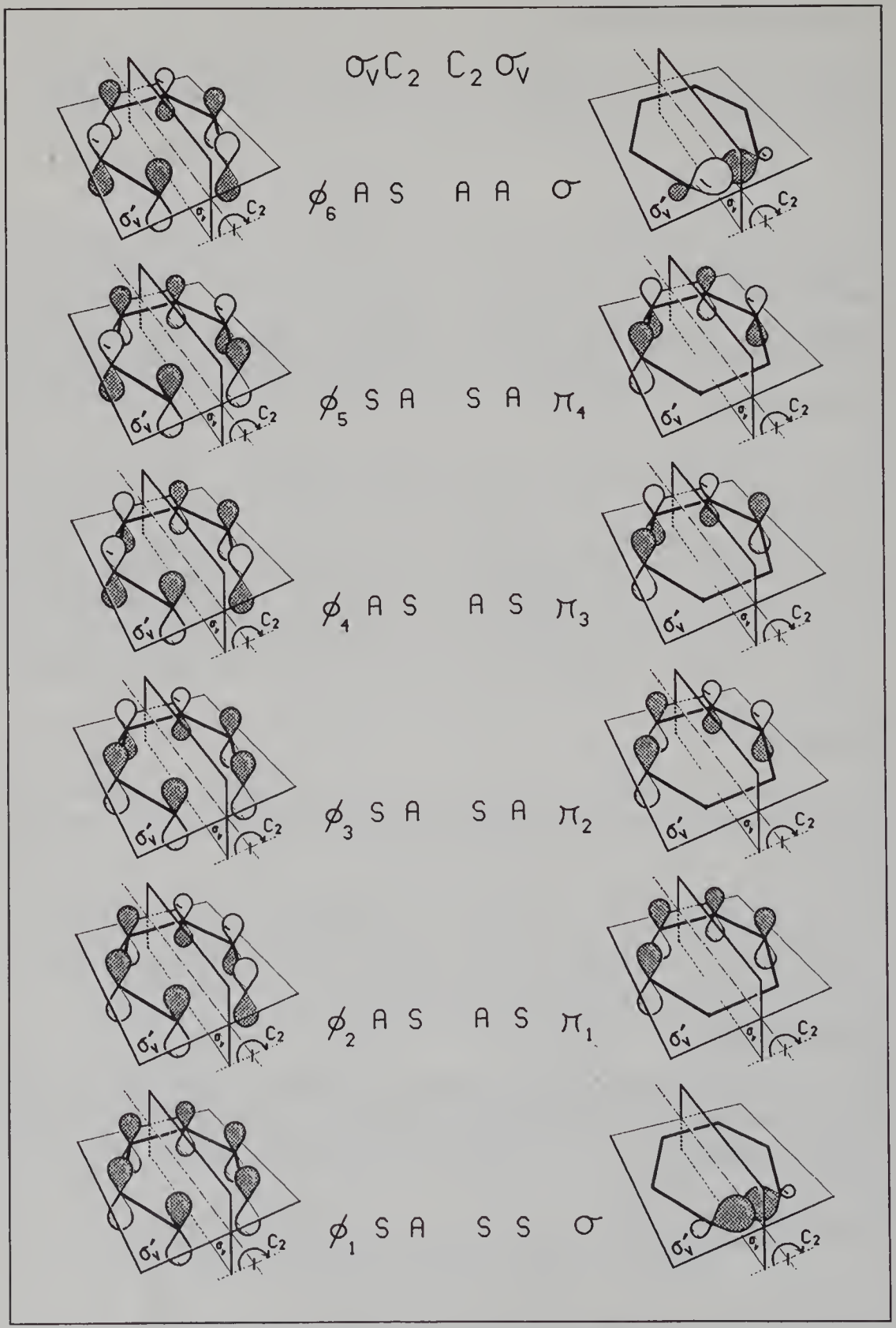


Figure 3.19: *Molecular orbitals of hexatriene and cyclohexadiene and their classification on the basis of* σ_v *and* C_2 *axis.*

Energy level correlation diagrams for the two modes of transformation can be constructed. Figure 3.20 shows a symmetry based correlation for a thermal conrotatory interconversion, which forces *a correlation of the ground state triene to an excited state cyclohexadiene, if orbital symmetry is to be conserved. i.e.*

$$\phi_1^2\phi_2^2\phi_3^2 \quad \longleftrightarrow \quad \sigma^2\pi_1^2\pi_3^2$$

Therefore, a thermal process would not be energetically feasible.

A correlation diagram for a disrotatory transformation may be drawn in an analogous way (Problem 3.11).

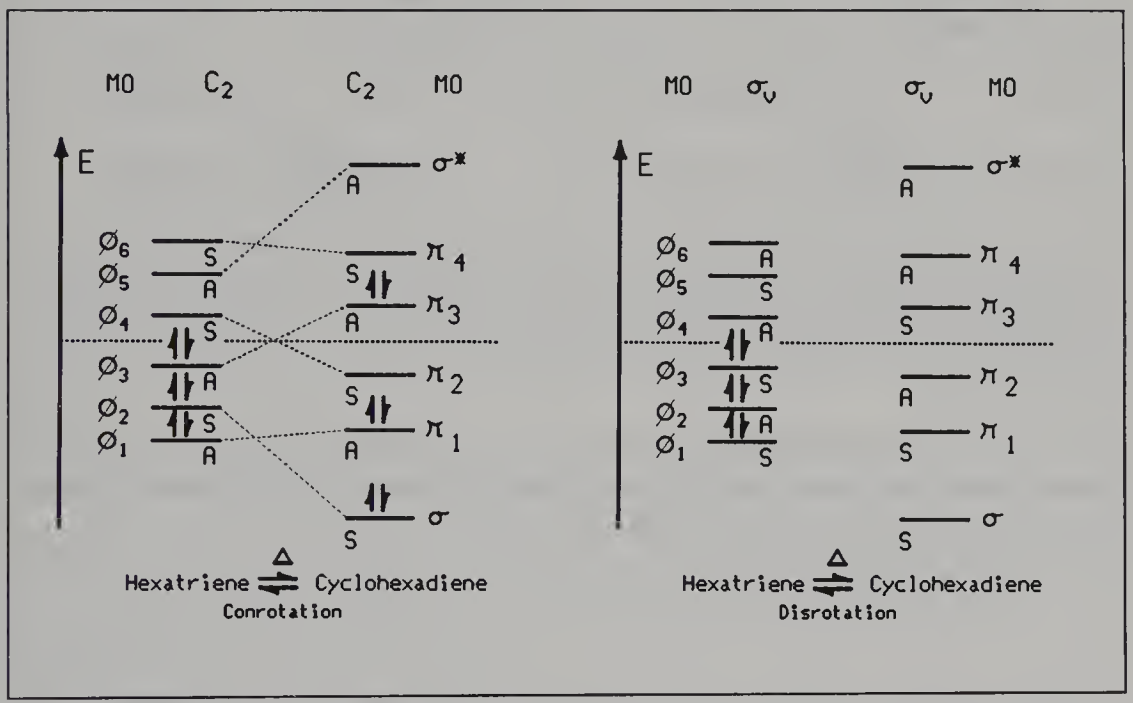


Figure 3.20: *Energy level correlations for thermal interconversion of hexatriene and cyclohexadiene. See Problem 3.11.*

Problem 3.11:

Energy levels along with their symmetry classification under σ_v are redrawn in Figure 3.20. Draw correlation lines showing a ground-state-ground-state correlation of the two species during a disrotatory process.

Obviously, *a thermal disrotatory process leads to a favoured correlation of the ground state reactant with the ground state product,* i.e.,

$$\phi_1^2\phi_2^2\phi_3^2 \quad \longleftrightarrow \quad \sigma^2\pi_1^2\pi_2^2$$

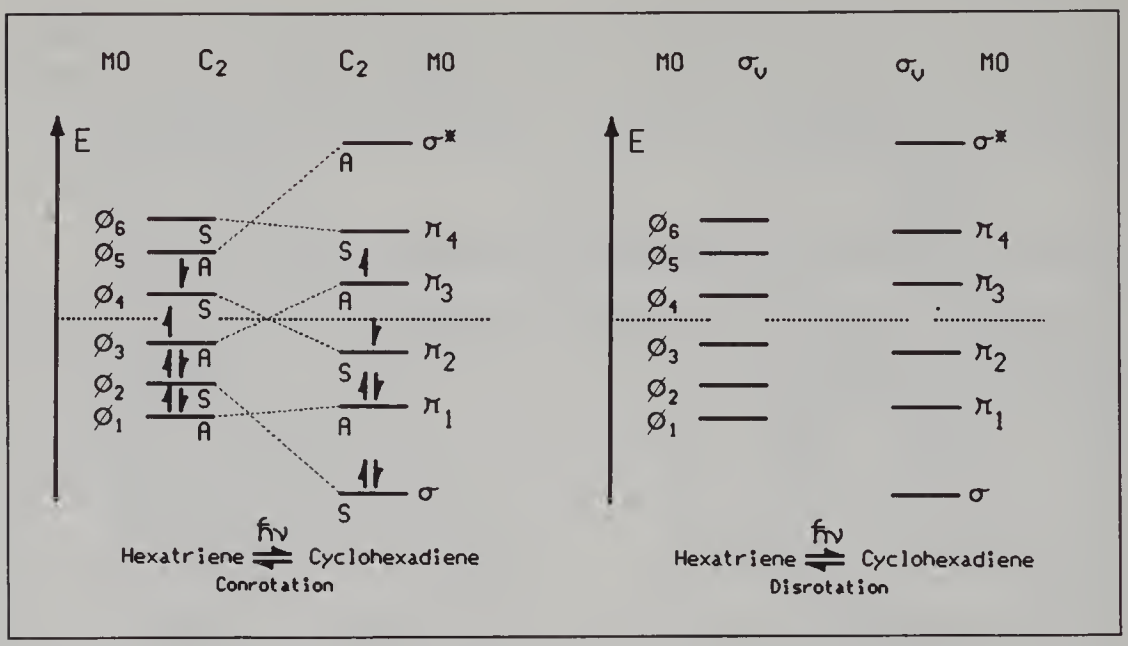


Figure 3.21: *Energy level correlations for photochemical interconversion of hexatriene and cyclohexadiene. See Problem 3.12.*

Problem 3.12:

Fill in the electrons in the MOs of hexatriene drawn in Figure 3.21 and complete an energy level correlation for disrotatory photocyclization of the reaction under discussion and confirm the following correlation:

$$\phi_1^2 \phi_2^2 \phi_3 \phi_4 \quad \longleftrightarrow \quad \sigma_2 \pi_1 \pi_2 \pi_4$$

In the preceding section the photochemical interconversion of butadiene and cyclobutene was discussed and it was observed that the photochemical processes showed a reversal of the rules developed for thermal reactions. A correlation diagram for photocyclization of hexatriene to cyclohexadiene in a conrotatory sense is shown in Figure 3.21. This diagram reveals that a conrotatory process which was found to be thermally forbidden now becomes allowed as the process involves an interconversion of the first excited states of both species.

It might, therefore, be concluded that *photochemical reactions of conjugated polyenes with (4n+2)π electrons would be allowed through conrotation.*

Problem 3.13:

i) Photochemical transformation of hexatriene to cyclohexadiene leads to a correlation of the excited states of the reacting species both by conrotation and disrotation. Why is the former process considered as allowed while the latter is termed forbidden?

ii) Compare the energies of the transition structures at any point along the reaction coordinate for thermal conrotatory and disrotatory processes.

Refer to Figure 3.16.

It can now be generalized that *thermal reactions of conjugated polyenes with (4n+2) electrons would proceed through disrotation while photochemical reactions would prefer conrotation.*

The results of both thermal and photochemical intramolecular electrocyclizations of even-numbered polyenes are tabulated below.

Table 3.3: *Selection rules for even-numbered polyenes undergoing electrocyclic reactions.*

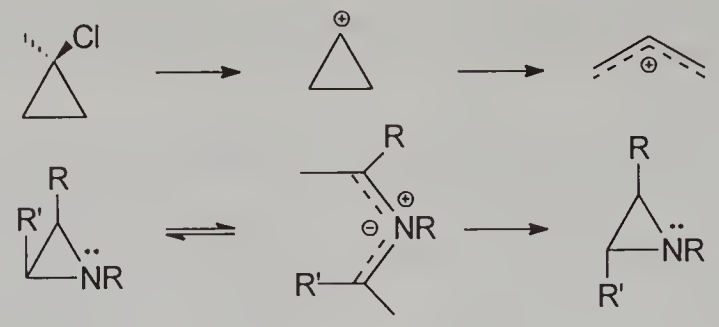
Number of electrons	Thermal		Photochemical	
	Conrotation	Disrotation	Conrotation	Disrotation
(4n)	allowed	forbidden	forbidden	allowed
(4n+2)	forbidden	allowed	allowed	forbidden

It is worth mentioning at this stage that the rules summarized in Table 3.3 do not exclude the possibility of the operation of the forbidden processes either under energetic conditions or through alternate non-concerted mechanisms. The Woodward Hoffmann rules are, therefore, only relative and cannot be considered absolute.

If correlation diagrams for higher systems are constructed then it would be found that the predicted selectivity reverses with every addition of two carbon atoms and an electron pair. It should also be kept in mind that the energies of the MOs of the reactant and product, as usually shown in the energy level correlation diagrams, are represented only schematically and one should not deduce from such diagrams the absolute thermochemistry of a reaction.

3.2.1.1.2 Odd-Numbered Polyenes

Besides studying the even-numbered polyenes, Woodward and Hoffmann also studied the odd-numbered systems and made predictions about the stereochemical course of their electrocyclic transformations [3]. These systems were also found to be amenable to their predictions. However, such systems cannot be experimentally studied because one has to deal with either cations or anions. As mentioned earlier in Chapter 2, cyclopropyl cations are produced by the solvolysis of cyclopropyl halides [4 a,b] (Equation 3.3) while the corresponding anions are obtained by the ring opening of three-membered heterocyclic systems, e.g. aziridines (Equation 3.4). These species interconvert via a zwitterion intermediate [5].



(3.3)

(3.4)

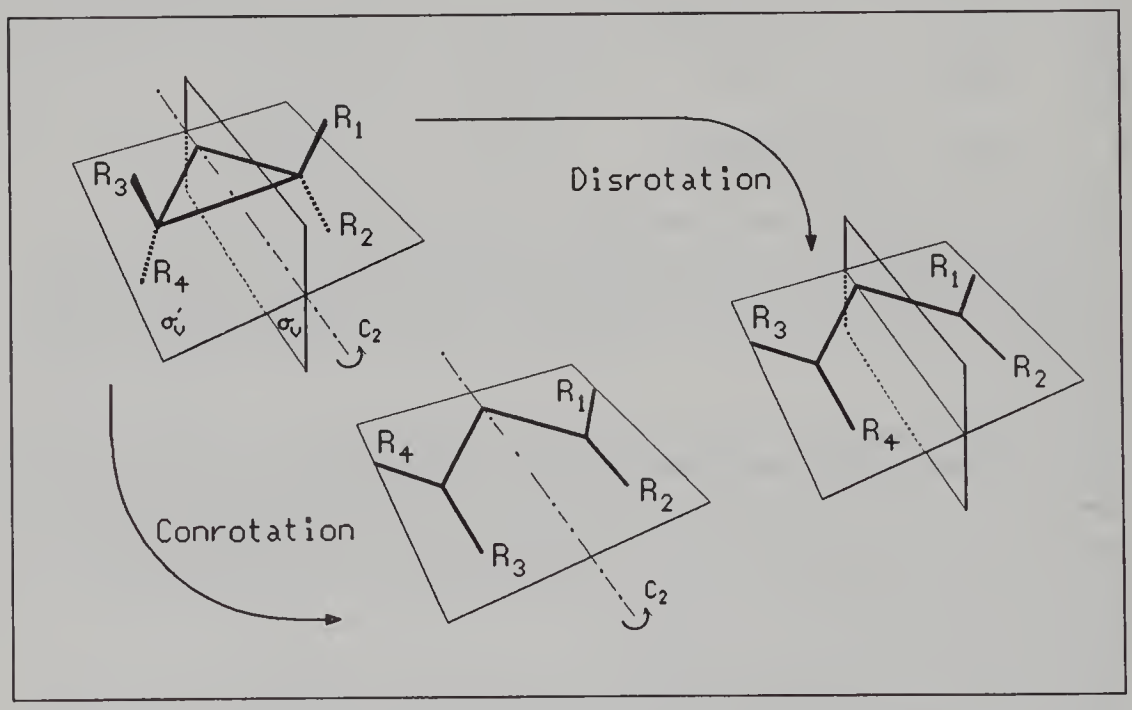


Figure 3.22: *Conrotatory and disrotatory ring opening of substituted cyclopropyl-allyl cation system.*

Figure 3.22 illustrates a disrotatory, and conrotatory, electrocyclic ring opening of a cyclopropyl cation (anion) to an allyl cation (anion). The three pertinent orbitals of the cyclopropyl system are the bonding σ-, the antibonding σ*- and the single *p*-orbital. The *p*-orbital, designated as ω, is vacant when the cation is involved and possesses a pair of electrons when the anion is involved. The molecular orbitals of the allyl system are ϕ_1, ϕ_2 and ϕ_3 and are shown in Figure 3.23 (Appendix A).

In the allyl cation ϕ_1 is occupied by two electrons while ϕ_2 and ϕ_3 are unoccupied. In the allyl anion ϕ_1 and ϕ_2 are occupied by two electrons while ϕ_3 is unoccupied. Therefore, the ground state electronic configuration of the allyl cation is ϕ_1^2 while that of the anion is $\phi_1^2\phi_2^2$. The ground state electronic configuration of the cyclopropyl cation is σ^2 while that of the anion is $\sigma^2\omega^2$. For a symmetry allowed reaction, the preferred mechanism is the one which leads to a correlation of the ground state MOs of the reactant with the ground state MOs of the product.

Since the interconversion of cyclopropyl-allyl cation involves 2 electrons (4n+2 electron system) and the favoured process, as predicted by the Woodward-Hoffmann

rules, would be disrotation while for the corresponding anion (4n electron system) the favoured process would be conrotation. These predictions are experimentally confirmed.

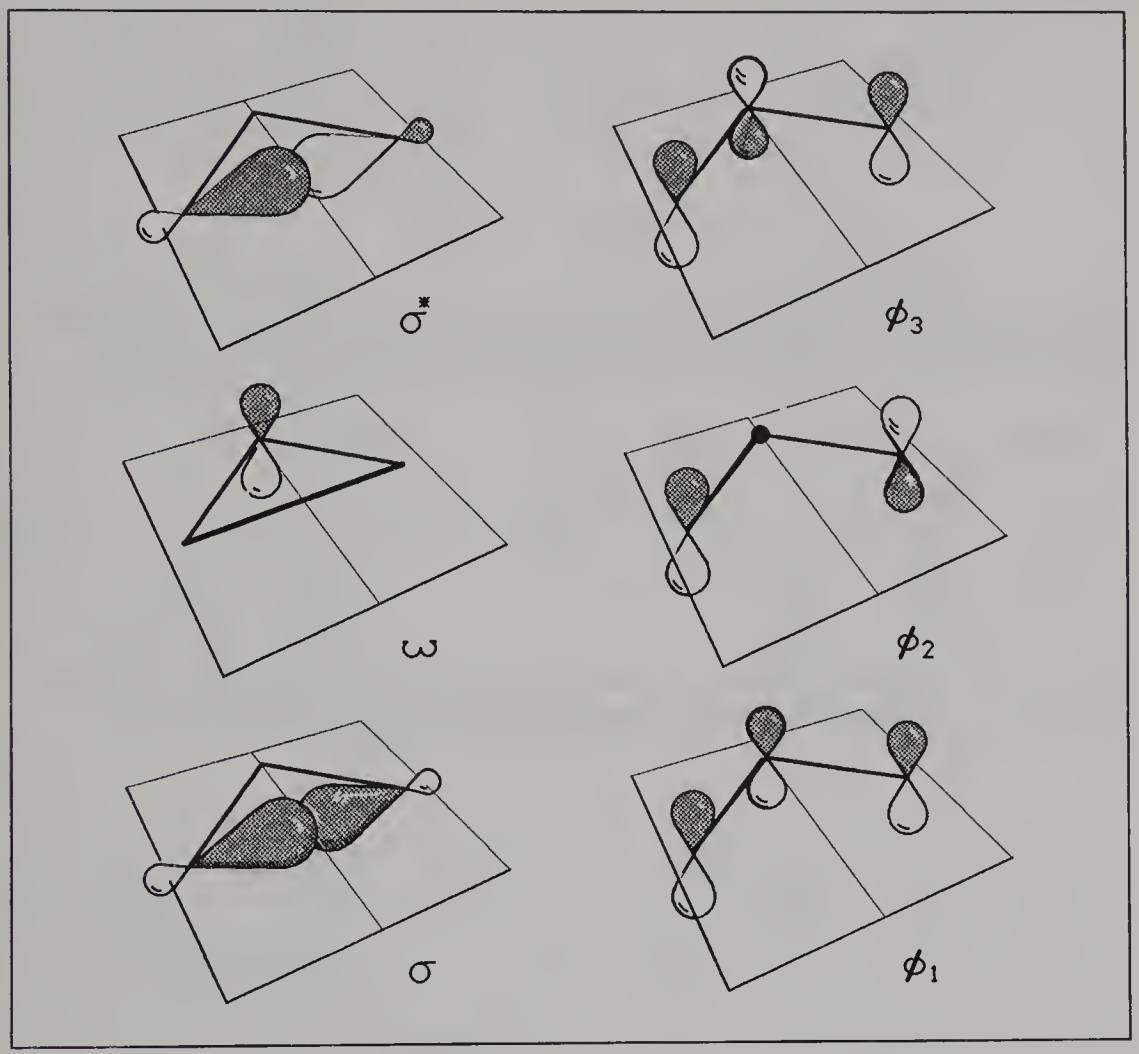


Figure 3.23: *Molecular orbitals of cyclopropyl-allyl system.*

Problem 3.14:

i) Given the molecular orbitals of the cyclopropyl-allyl system (Figure 3.23), draw energy level correlation diagrams for thermal disrotatory, conrotatory and electrocyclic transformations of the cation.

ii) Would the conrotatory process be energetically more feasible than the disrotatory?

iii) Show electron occupancies for the cyclopropyl-allyl anion system and draw correlations for the two modes of transformation. Also confirm that the anion behaves in a manner opposite to that of the cation.

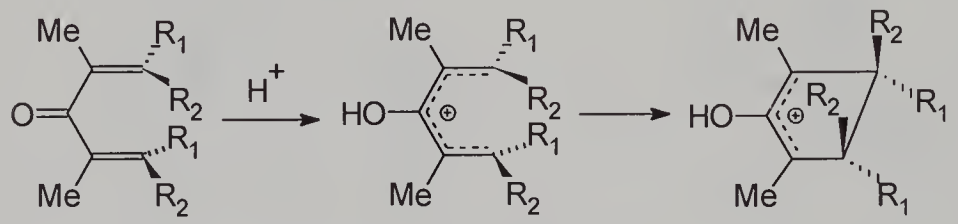
iv) Justify that the mode of photochemical transformations would be the reverse of the thermal processes of both the anion and the cation.

The orbital correlation analysis of electrocyclic reactions of higher odd-numbered polyenes e.g. the pentadienyl-cyclopentenyl system may likewise be carried out (Equation 3.5 and 3.6).

(3.5)

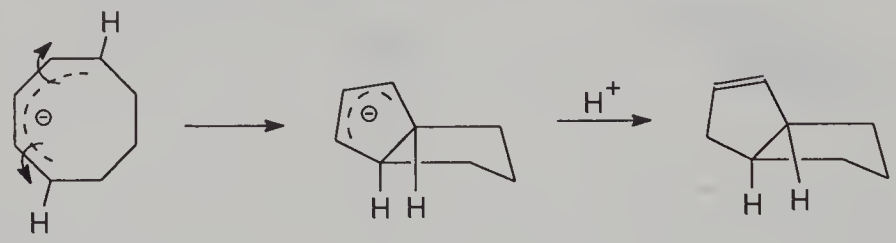
(3.6)

The cation (4-electron system) generated by the protonation of dienones undergo ring closure in the predicted conrotatory manner (Equation 3.7) [6].



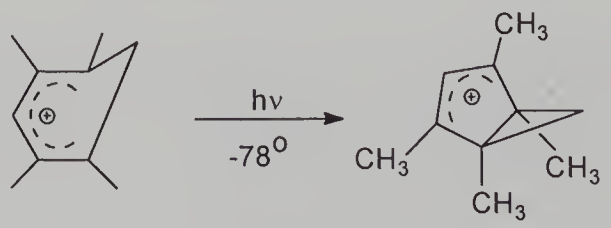
(3.7)

The pentadienyl anion (6-electron system) undergoes ring closure in a disrotatory manner. An example is the rapid isomerization illustrated in Equation 3.8 [7].



(3.8)

Equation 3.9 represents an example of the photochemical cyclization of a cyclic pentadienyl cation to a bicyclic system [8].



(3.9)

These examples reveal that the stereochemical outcome of these reactions is also in agreement with those predicted. Hence, the odd-numbered polyenes behave in a manner similar to the even-numbered polyenes

Problem 3.15:

Molecular orbitals of a pentadienyl-cyclopentenyl system are shown in Figure 3.24. Confirm the Equations 3.7 to 3.9 on the basis of orbital correlation analysis.

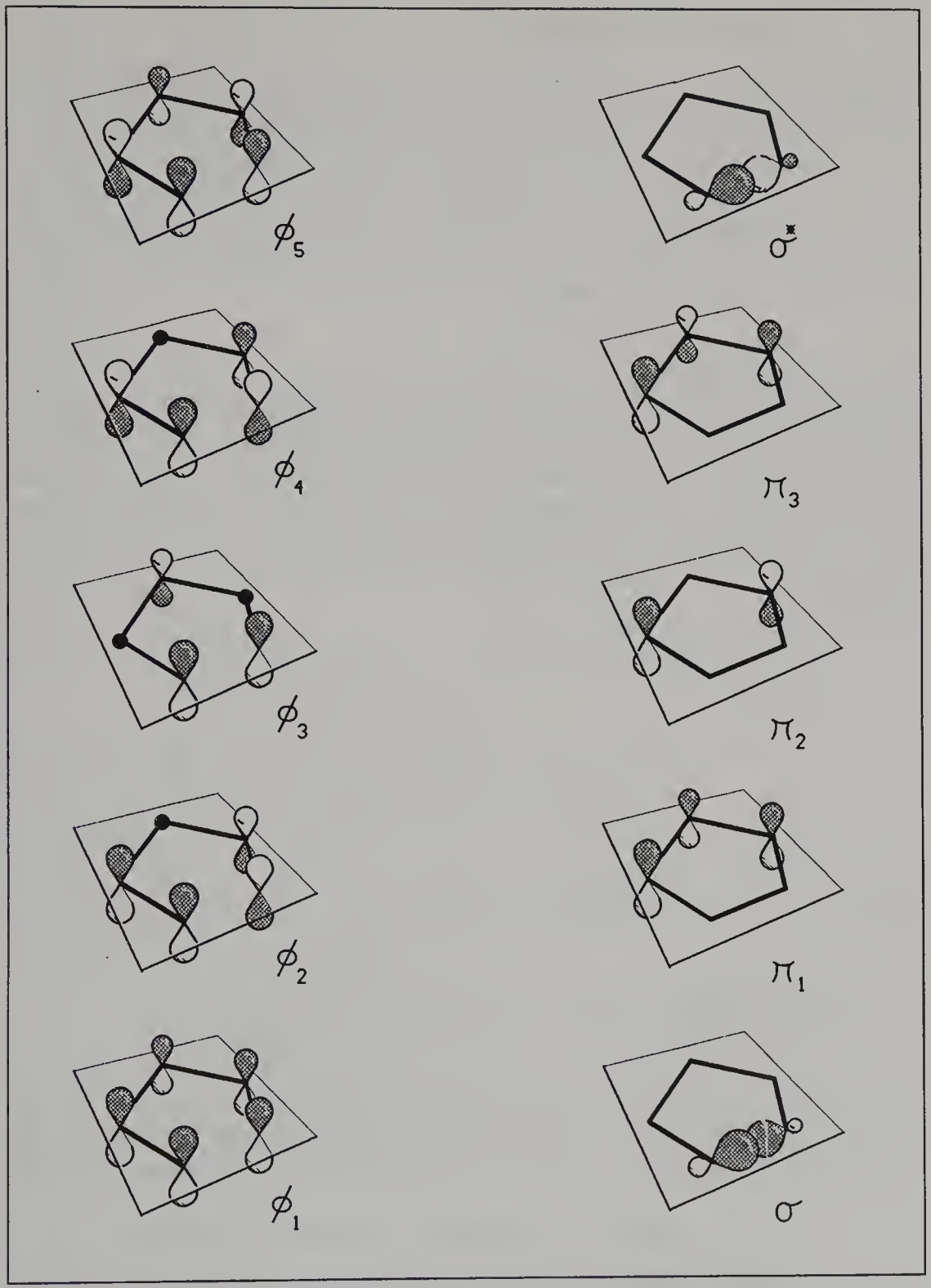


Figure 3.24: *Molecular orbitals of pentadienyl-cyclopentenyl system.*

Hence, *both even- and odd-numbered polyenes, with an even number of electrons, prefer a conrotatory process when (4n) electrons are involved and a disrotatory process for (4n+2) electrons. The photochemical processes show a reversal of the rules developed for thermal processes in both cases.*

3.2.1.2 Odd-Electron Systems

The prediction as to the mode and the stereochemical outcome of the electrocyclic reactions of odd-electron systems can also be made on the basis of orbital correlation analysis. The examples of odd-electron systems are organic radicals and radical ions. The ring opening of the cyclopropyl radical and the ring opening of the cyclobutene radical cation may be quoted as examples of odd-electron systems undergoing electrocyclic transformations. Such systems essentially possess a SOMO (Singly Occupied Molecular Orbital). These transformations may again be affected in either a disrotatory or a conrotatory manner.

3.2.1.2.1 Radicals

Energy level correlation diagrams for both the disrotatory and conrotatory mechanisms for the interconversion of cyclopropyl radical and the allyl radical are shown in Figure 3.25. It is evident from the figure that both the disrotatory and conrotatory modes of ring opening lead to a correlation of the ground state reactant with the excited state product. Therefore, it is not possible to arrive at a conclusion regarding the favoured path of the reaction. This problem would be discussed later in Chapter 6.

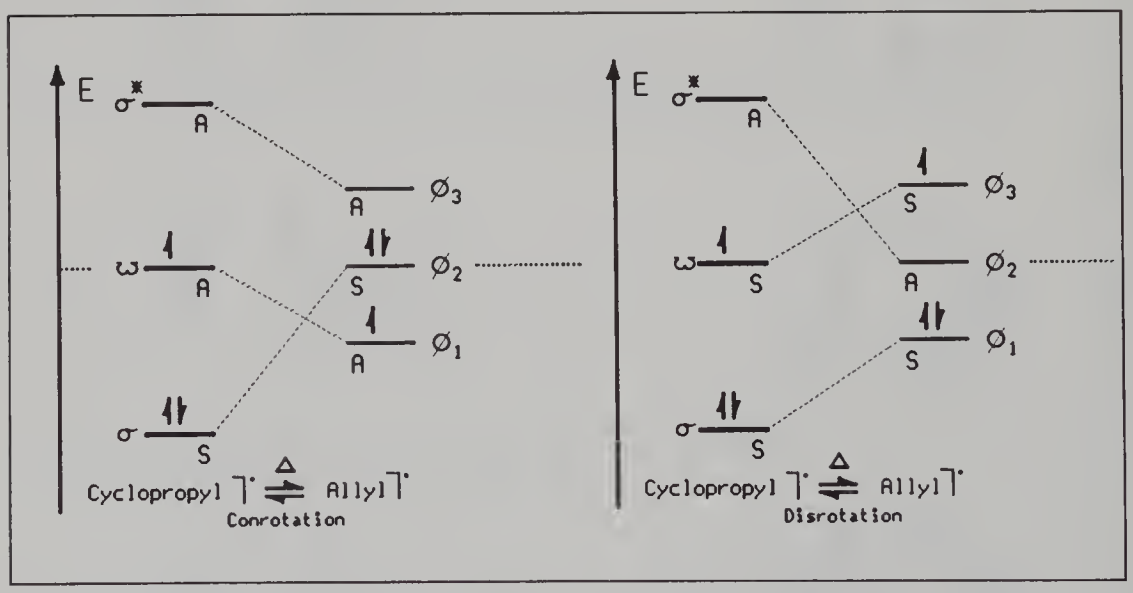
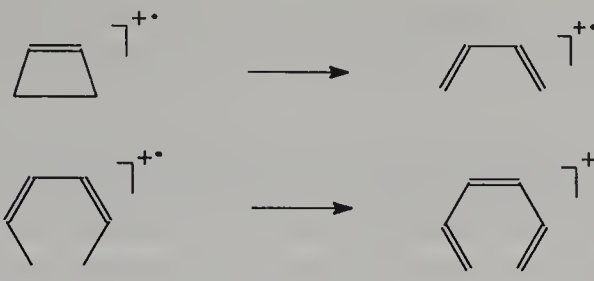


Figure 3.25: Energy level correlation diagram for the interconversion of the cyclopropyl radical and the allyl radical through conrotatory and disrotatory mechanisms.

3.2.1.2.2 Radical Ions

Radical ions undergo pericyclic transformations in the same manner as do the neutral, ionic and radical systems. Equations 3.10 and 3.11 show the ring openings of cyclobutene, and cyclohexadiene radical cations, to form the radical cations of their corresponding open chain isomers. The formation of these radical cations has already been discussed in Chapter 2. Energy level correlation diagrams are constructed for such systems (Figure 3.26).



(3.10)

(3.11)

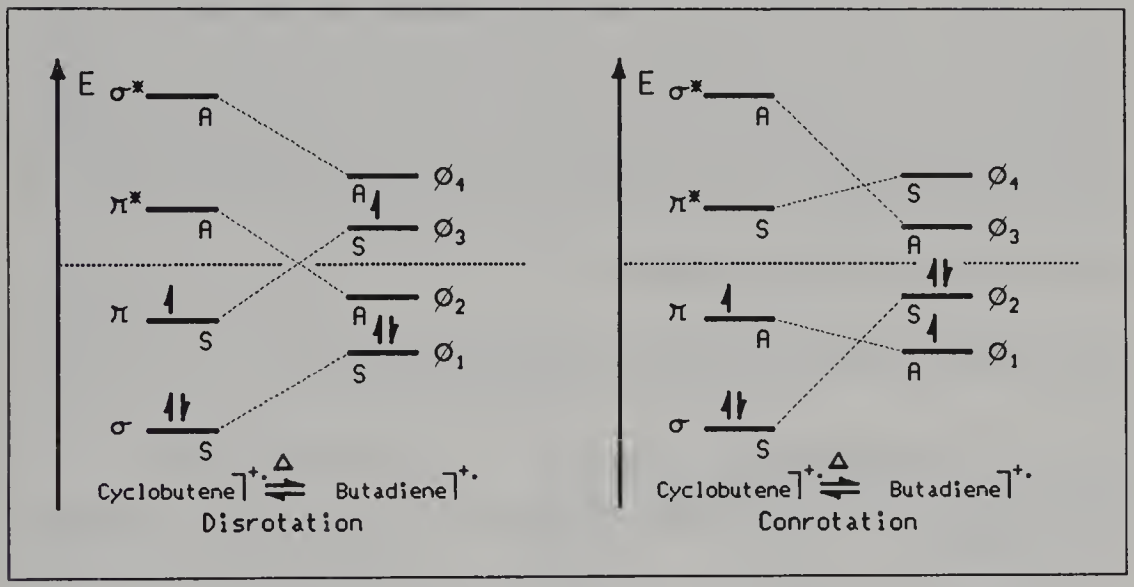


Figure 3.26: *Energy level correlation diagrams for the conrotatory, and disrotatory, interconversion of butadiene-cyclobutene radical cations.*

Problem 3.16:

Use Figure 3.26 and write down the electronic configurations of the interconverting species of both processes. Would it be possible to arrive at a conclusion regarding the energetically favoured process?

It is apparent from Figure 3.26 that none of the two possible mechanisms is associated with a ground-state-ground-state correlation corresponding to a favourable thermal reaction. Therefore, radical cations, just like radicals, do not appear to show any preference for the two alternate mechanisms. This problem would be discussed again in terms of symmetry state correlation analysis in the following section.

3.2.2 Symmetry State Correlation Analysis

Energy level correlation diagrams succeed in giving a good insight into the reason why certain thermal reactions are allowed. However, the course of photochemical reactions requires a careful analysis. A further limitation of these energy level correlation diagrams is that they are constructed on the assumption that both ground state and excited state molecules are in their ground state geometries. However, as mentioned earlier in Chapter 2, the geometry of a ground state molecule is different from its excited state geometry. Accordingly, on the basis of these energy diagrams,

any drastic deviation in the geometry of the excited state molecule, from the geometry of the ground state molecule, might create an uncertainty in the accuracy of any predicted mode.

Moreover, energy level correlations take into account pertinent molecular orbitals with special emphasis on the highest occupied molecular orbital. The symmetry state correlation analysis takes into account the effect of all the electrons in the pertinent molecular orbitals of both the reactants and products and provide a better insight into the behaviour of photochemical reactions. While making symmetry state correlation diagrams, the electronic configuration of the system is described in terms of the *symmetry of the orbitals* instead of describing it in terms of *the types of orbitals*. Classification of molecular orbitals is carried out as before on the basis of symmetry elements being conserved during a particular mode of transformation. Symmetry state correlation analysis is carried out for both even- and odd-electron systems.

3.2.2.1 Even-Electron Systems

Symmetry state correlation analysis is applied here to predict the mechanism of even-electron systems undergoing electrocyclic transformations.

3.2.2.1.1 Even-Numbered Polyenes

Even-numbered polyenes are discussed using the example of butadiene-cyclobutene interconversion.

- ***(4n) Electron Systems***

For a conrotatory process, the ground state electronic configuration of butadiene which is described as $\phi_1^2\,\phi_2^2$ may now be described as A^2S^2. This is because ϕ_1 is antisymmetric and ϕ_2 is symmetric on the basis of C_2 axis which is the symmetry element being conserved. Hence, A^2S^2 is the individual state symmetry of the ground state butadiene for a conrotatory process. The total state symmetry may be calculated by using the simple algebraic law of multiplication. Thus taking

$$S \times S = S; \qquad A \times S = A \qquad \text{and} \qquad A \times A = S$$

the ground state butadiene has an electronic configuration $\phi_1^2\phi_2^2$ which is also represented by A^2S^2 , and may be described as a totally symmetric state. The first excited state, having an electronic configuration $\phi_1^2\phi_2\phi_3$, may be represented as A^2SA which is a totally antisymmetric state. Similarly the individual, and total, state symmetries of the other excited states may be determined. Table 3.4 shows the electronic configurations of the ground state and various possible excited states of butadiene and cyclobutene along with the classification of pertinent molecular orbitals on the basis of the C_2 axis. However, before making connections between any of these states, the following points should be taken into account:

i) As with energy level correlation diagrams, states are correlated from the lowest to the next higher.

ii) Reactant states correlate with the product states only when they have the same symmetry and the same multiplicity.

iii) Lines joining the states of the same symmetry should not cross.

iv) While correlating the reactant and the product states, in addition to the total symmetry of any state, individual symmetries must also match. Thus, for example, two states having individual symmetries A^2SA and S^2AS cannot be correlated although both of them are totally antisymmetric i.e.;

$$A^2SA = A \qquad \text{and} \qquad S^2AS = A$$

However, two states such as A^2S^2 and S^2A^2 do correlate although the order of individual states is still different.

Different symmetry states corresponding to different electronic configurations of butadiene and cyclobutene are considered before constructing a new correlation diagram in state notation. The symmetry states to be considered are the ground state of each molecule and various reasonably accessible singly excited states (Table 3.4). For the sake of completion, doubly excited states are also included, although it is unlikely that such highly energetic states would be involved in most organic photochemical reactions.

Table 3.4: *Various possible electronic and symmetry states of butadiene and cyclobutene for a conrotatory process.*

Reacting species		Electronic configuration	Individual state symmetry	Total state symmetry
Butadiene	Ground state	$\phi_1^2\phi_2^2$	A^2S^2	S
	Singly excited state	$\phi_1^2\phi_2\phi_3$	A^2SA	A
	Singly excited state	$\phi_1^2\phi_2\phi_4$	A^2SS	S
	Singly excited state	$\phi_1\phi_2^2\phi_3$	AS^2A	S
	Singly excited state	$\phi_1\phi_2^2\phi_4$	AS^2S	A
	Doubly excited state	$\phi_1^2\phi_3^2$	A^2A^2	S
	Doubly excited state	$\phi_1^2\phi_4^2$	A^2S^2	S
Cyclobutene	Ground state	$\sigma^2\pi^2$	S^2A^2	S
	Singly excited state	$\sigma^2\pi\pi^*$	S^2AS	A
	Singly excited state	$\sigma^2\pi\sigma^*$	S^2AA	S
	Singly excited state	$\sigma\pi^2\pi^*$	SA^2S	S
	Singly excited state	$\sigma\pi^2\sigma^*$	SA^2A	A
	Doubly excited state	$\sigma^2\pi^{*2}$	S^2S^2	S
	Doubly excited state	$\sigma^2\sigma^{*2}$	S^2A^2	S

Symmetry classification on the basis of C_2 axis.

Various symmetry states are roughly arranged according to their energy. The ground state configuration is well separated from other configurations in this arrangement.

A correlation of the reactant states with the product states, on the basis of both their individual and total state symmetries is shown in Figure 3.27.

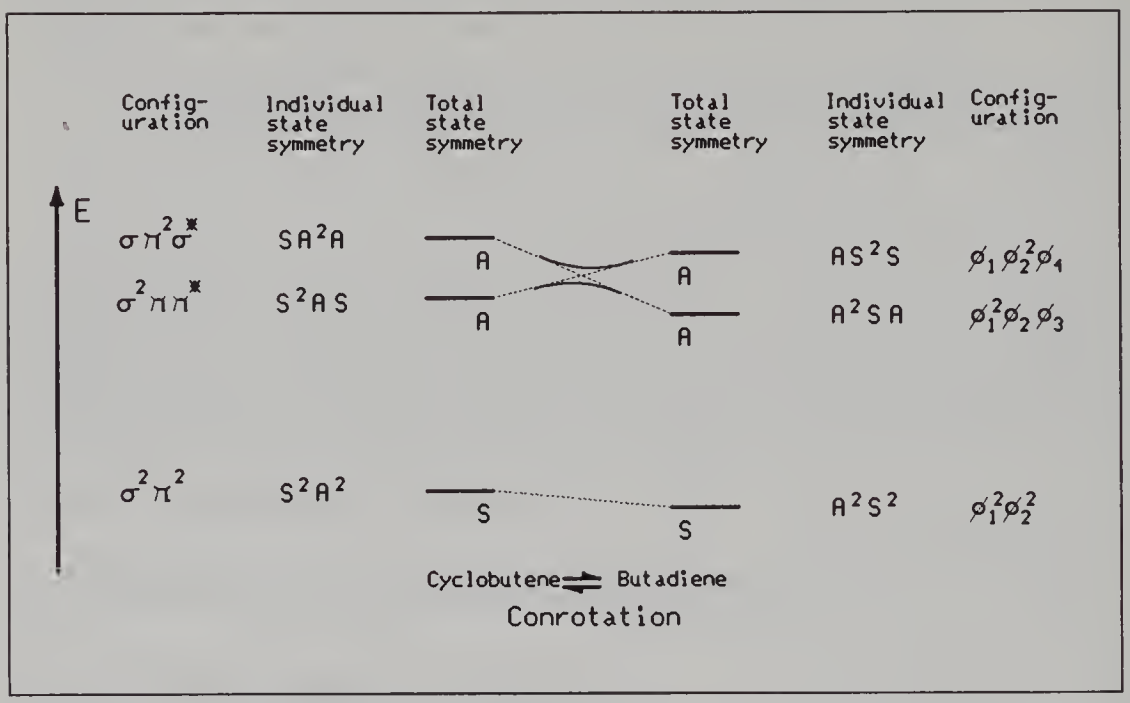


Figure 3.27: *Symmetry state correlation diagram for a conrotatory interconversion of butadiene and cyclobutene.*

A direct correlation of ground state of butadiene with the ground state of cyclobutene

$$A^2S^2 \longleftrightarrow S^2A^2$$

is evident from Figure 3.27 which allows the thermal process through conrotation.

The course of a photochemical conrotatory process can also be predicted from the same diagram. Such a process leads to an intended correlation of the first excited state of butadiene with a still higher excited state of cyclobutene, i.e.

$$A^2SA \longleftrightarrow SA^2A$$

if individual, as well as their total state symmetries, are to be matched. However, this intended correlation is avoided because of the restriction imposed by the rule of non-crossing of lines of the same symmetry. This intended, but avoided, correlation leads to a large symmetry imposed barrier which renders the photochemical process highly unfavourable. Thus, a thermal process is allowed while the photochemical is forbidden through a conrotatory mode of transformation. This conclusion is the same as was drawn earlier using the energy level correlation diagrams.

An analogous diagram may be constructed for a disrotatory process. Various electronic states, along with their symmetry characteristics on the basis of σ_v, are shown in Table 3.5. Figure 3.28 shows a symmetry state correlation diagram for a disrotatory process. Note that the selection of a set of different electronic states for a disrotatory process is made in order to match the individual symmetries of different

states of the reacting species. Other excited states of the reactant may possibly correlate with some other excited states of the product.

Table 3.5: *Various possible electronic and symmetry states of butadiene and cyclobutene for a disrotatory process.*

Reacting species		Electronic configuration	Individual state symmetry*	Total state symmetry
Butadiene	Ground state	$\phi_1^2\phi_2^2$	S^2A^2	S
	Singly excited state	$\phi_1^2\phi_2\phi_3$	S^2AS	A
	Singly excited state	$\phi_1\phi_2^2\phi_3$	SA^2S	S
	Singly excited state	$\phi_1^2\phi_2\phi_4$	S^2AA	S
	Singly excited state	$\phi_1\phi_2^2\phi_4$	SA^2A	A
	Doubly excited state	$\phi_1^2\phi_3^2$	S^2S^2	S
	Doubly excited state	$\phi_1^2\phi_4^2$	S^2A^2	S
Cyclobutene	Ground state	$\sigma^2\pi^2$	S^2S^2	S
	Singly excited state	$\sigma^2\pi\pi^*$	S^2SA	A
	Singly excited state	$\sigma^2\pi\sigma^*$	S^2SA	A
	Singly excited state	$\sigma\pi^2\pi^*$	SS^2A	A
	Singly excited state	$\sigma\pi^2\sigma^*$	SS^2A	A
	Doubly excited state	$\sigma^2\pi^{*2}$	S^2A^2	S
	Doubly excited state	$\sigma^2\sigma^{*2}$	S^2A^2	S

*Symmetry classification on the basis of σ_v.

A symmetry state correlation diagram for the disrotatory process can now be constructed (Figure 3.28). As is evident from the correlation shown, the ground state butadiene is now forced to correlate with the doubly excited state of cyclobutene.

$$S^2S^2 \quad \longleftrightarrow \quad S^2S^2$$

In this case a large symmetry imposed barrier would be involved.

During a photochemical reaction, the first excited state of butadiene correlates with the first excited state of cyclobutene, i.e.

$$S^2AS \quad \longleftrightarrow \quad S^2SA$$

without the imposition of a symmetry barrier.

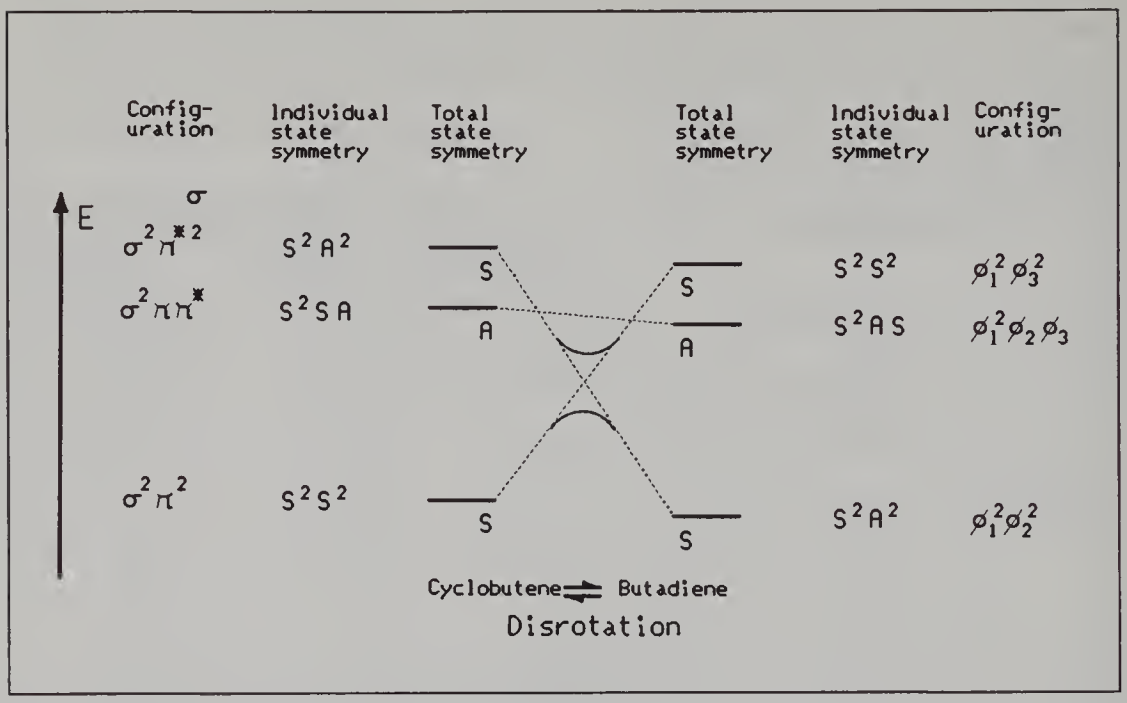


Figure 3.28: *Symmetry state correlation diagram for a disrotatory interconversion of butadiene and cyclobutene.*

It may be noted that the conclusions regarding the favoured mechanism of both thermal and photochemical reactions may be derived from a single symmetry state correlation diagram.

Problem 3.17:

i) Would you expect a thermal transformation through disrotation to be a forbidden process?

ii) Compare Figure 3.27 with Figure 3.28 and justify that the photochemical process would be allowed through disrotation .

The photocyclization of butadiene to cyclobutene was also investigated by Lugt [11] who observed that

i) Cyclobutene is ca. 20 Kcal $mole^{-1}$ higher in energy than butadiene.

ii) π-π^* excitation in conjugated butadiene requires ca. 30 Kcal $mole^{-1}$ less energy than π-π^* excitation of unconjugated cyclobutene.

iii) A high activation energy (ca. 50 Kcal $mole^{-1}$) is required for the conversion of the first excited singlet (S_1) of butadiene to the first excited singlet of cyclobutene (S_1 ′) which seems to be very unlikely because of the amount of energy required (Figure 3.29).

This is in conflict with the predictions made on the basis of the simple energy level correlation diagram (Figure 3.17) where a symmetry allowed correlation of the first excited states of both butadiene and cyclobutene is shown to be possible through disrotation. These diagrams also predict the formation of excited state products from

excited state reactants which is not the case. Such anomalies may be explained by a careful analysis of the energy changes involved during the photochemical processes.

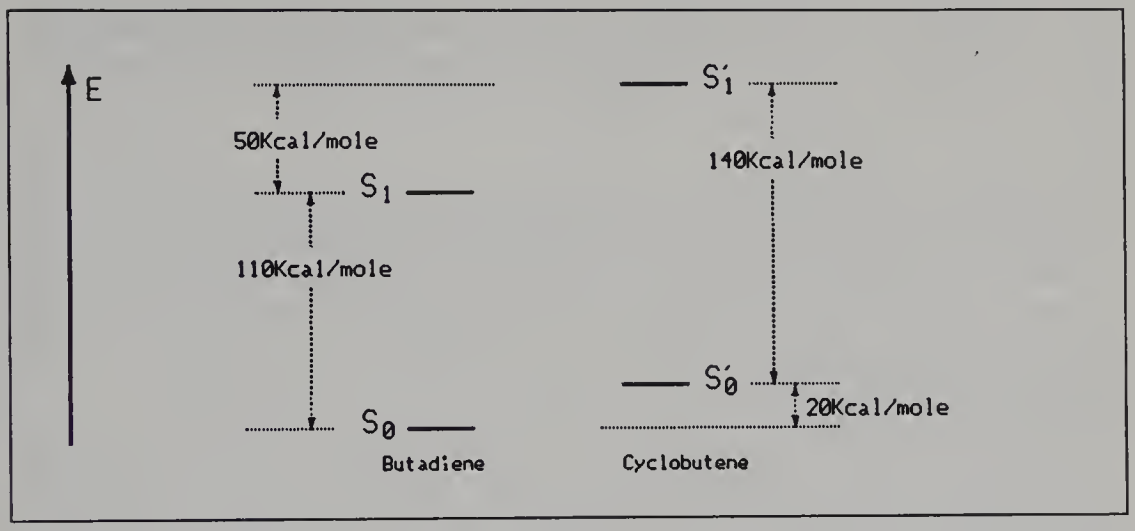


Figure 3.29: *Energy relationships between the ground states and the first excited states of butadiene and cyclobutene.*

Figure 3.30 shows a symmetry state correlation for the disrotatory interconversion of butadiene and cyclobutene. This figure differs from Figure 3.17 in that the multiplicity of different possible excited states is also included (Chapter 2).

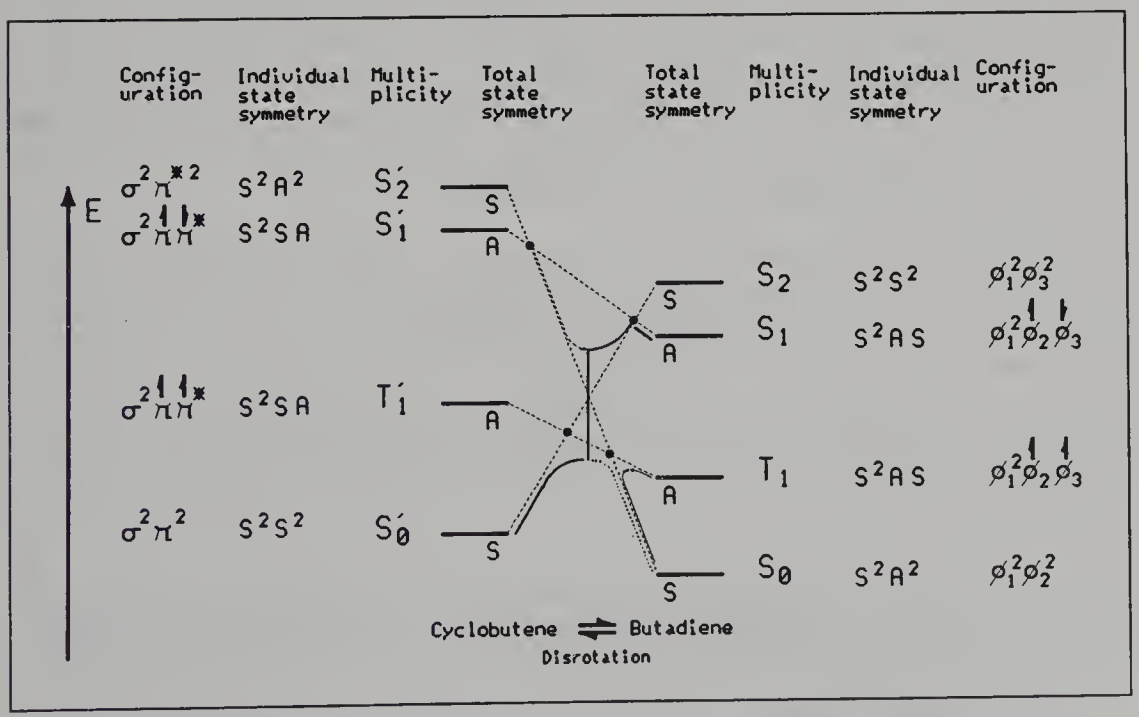


Figure 3.30: *Modified symmetry state correlation diagram for disrotatory interconversion of butadiene and cyclobutene showing triplet and singlet states.*

The energy levels corresponding to different states of butadiene are represented by the ground state singlet S_0, the first excited state triplet T_1 and the two excited state singlets S_1 and S_2. It should be noted that an excited state triplet is placed at a lower

level on the energy scale than an excited state singlet because a triplet state is of lower energy than a singlet state (Chapter 2).

The corresponding states of cyclobutene are represented by the same symbols except that a bar is placed on each state. The ground states are normally well separated from the excited states, however, the singly and doubly excited states are almost considered to be degenerate.

The symmetry classification of each state on the basis of the σ_v plane is also included in the above diagram. It is evident that the ground state of butadiene correlates with doubly excited state of cyclobutene if both individual and total state symmetries are to be matched. However, this crossing of the lines of the same symmetry is not allowed. A thermal reaction would, therefore, have a large symmetry imposed barrier.

The first excited state singlet of cyclobutene S_1, being higher in energy than the first excited state singlet of butadiene S_1, must initially climb an energy hill (5Kcal/mole). At the same time a second excited singlet S_2 of butadiene decreases in energy and soon encounters the first excited singlet S_1. After passing through an allowed crossing, it drops into a *potential energy well* of the second excited singlet S_2. A similar allowed crossing can be seen for the reverse reaction. These allowed crossings are shown by a dot on the diagram. The potential energy well (funnel) serves as a reservoir for the excited state species through which the excited singlet passes down and reaches the maximum energy point on the ground surface. Here it has two options, it may convert either to the product or to the starting material. The net result is that this first excited state singlet S_1 may convert back either to the ground state butadiene S_o or to the ground state cyclobutene S_o'. The actual path traversed is shown by solid lines in Figure 3.30. This path explains how ground state products are formed from the excited state reactants.

When the first excited state triplet of butadiene T_1 begins ring closure, it soon encounters the ground state energy surface. Since a triplet-singlet crossing is not allowed, therefore, it converts back to the ground state of butadiene (Figure 3.30). The result of this process is the conversion of the first excited state triplet T_1 of butadiene to its ground state S_o. The actual path traversed by the first excited state triplet T_1 is shown by a solid line [12]. These theoretical observations are confirmed experimentally. Thus butadiene, on direct excitation, closes to from cyclobutene in a disrotatory fashion.

From a discussion of the actual path traversed by the excited state singlets and triplets, it is clear why concerted reactions take place through the excited singlets and not through the excited triplets.

- ***(4n+2) Electron Systems***

Symmetry state correlation diagrams for a (4n+2) electron system may be constructed in a manner similar to that used for (4n) electron systems. Various symmetry states along with their individual symmetry characteristics for a conrotatory interconversion of 1,3,5-hexatriene and cyclohexadiene are shown in Figure 3.31.

Problem 3.18:

Tabulate the symmetries of the pertinent molecular orbitals of hexatriene and cyclohexadiene on the basis of the C_2 axis and the σ_v plane.

Problem 3.19:

i) Show various possible excited states and tabulate them in a pattern similar to that of Table°3.5.

ii) Select a set of symmetry states for a conrotatory and disrotatory process.

iii) Symmetry state correlation for a conrotatory interconversion of a (4n+2) electron system is shown in Figure 3.32. What conclusions may be drawn?

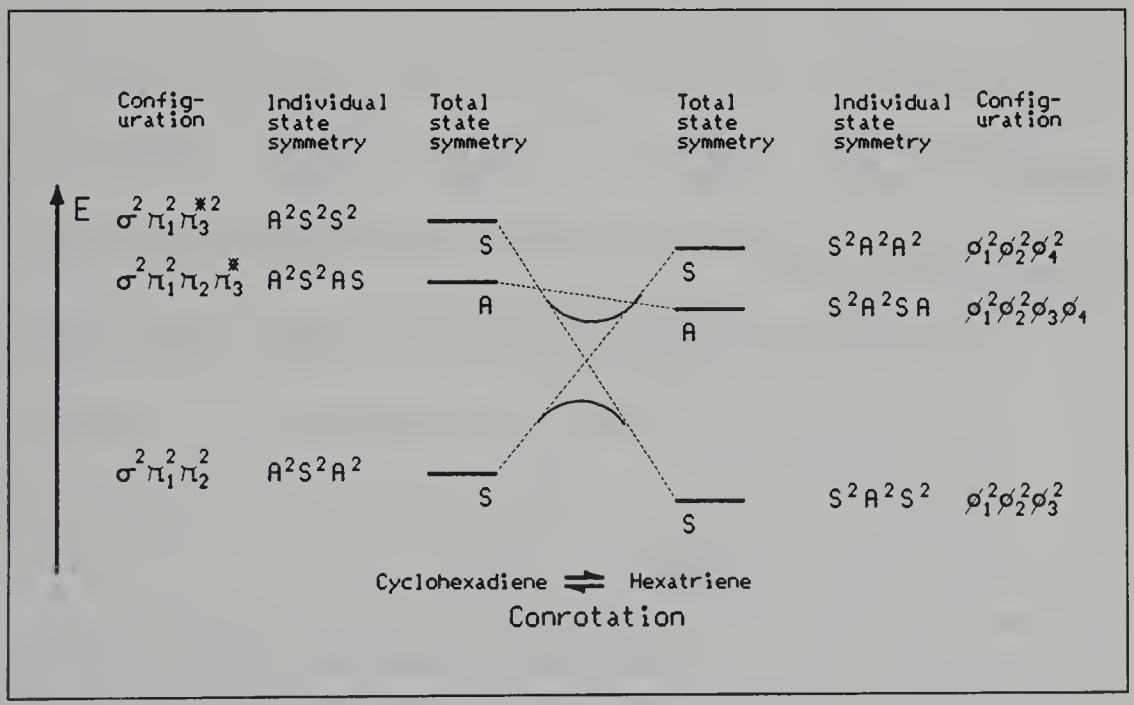


Figure 3.31: *Symmetry state diagram for a (4n+2) electron system (Conrotation).*

Evidently, a thermal conrotatory interconversion should not be possible due to the symmetry imposed barrier to a ground state reaction. However, a photochemical transformation which involves a direct correlation of the first excited state of the interconverting species would be an allowed process. A symmetry state correlation analysis of a disrotatory process may be accomplished the same way. A simplified energy level correlation for a disrotatory alternative reveals a ground-state-ground-state correlation of the two species (Figure 3.32).

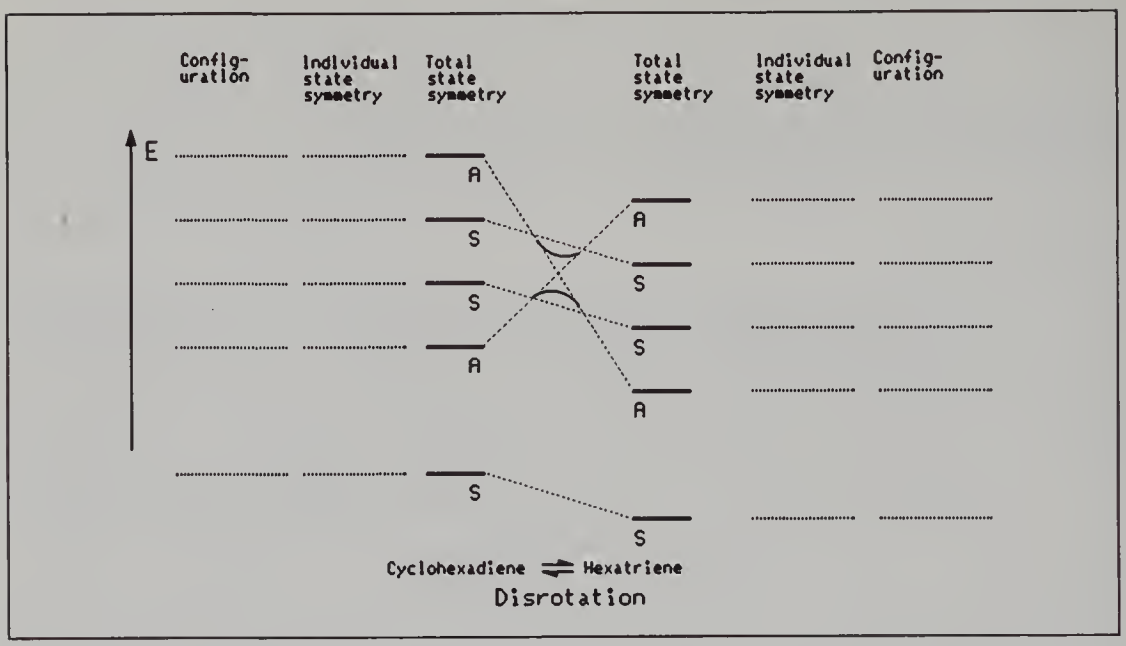


Figure 3.32: *Symmetry state diagram for a (4n+2) electron system (Disrotation).*

Problem 3.20:

Figure 3.32 illustrates a simplified diagram showing a correlation based on the total symmetry of different states.

i) Work out the corresponding individual state symmetries as well as their respective electronic configurations.

ii) Would this set of states differ from the set selected for a conrotatory process (Figure 3.31)?

iii) Verify that a disrotatory interconversion would be thermally allowed and photochemically forbidden.

From the symmetry state correlations constructed for the electrocyclization of butadiene and 1,3,5-hexatriene, it may be generalized that a thermal disrotatory process would have a large symmetry imposed barrier when (4n) electrons are involved (Figure 3.28). No such barrier is observed for the ground state process when (4n+2) electrons are involved (Figure 3.32). A comparison of conrotatory options for the two systems depicts that the thermal process is favoured for (4n)°electron systems (Figure 3.27) while the (4n+2) electron systems have to face a large symmetry imposed barrier (Figure 3.31). Thus, (4n) electron systems follow a conrotatory mechanism while those with (4n+2) electrons prefer disrotation in the ground state. The observations for photochemical processes are again opposite to those for thermal processes. These conclusions are the same as those derived from their energy level correlation analysis.

3.2.2.1.2 Odd-Numbered Polyenes

Symmetry state correlation analysis of odd-numbered polyenes may likewise be carried out.

Problem 3.21:

i) Electronic configurations of some possible electronic states of cyclopropyl cation are σ^2, $\sigma\omega$ and ω^2, while those of allyl systems are ϕ_1^2, $\phi_1\phi_2$ and ϕ_3^2. Work out the symmetries of these states and predict whether a disrotatory transformation would be thermally, or photochemically, feasible.

ii) Do the same exercise for a conrotatory process.

iii) Write ground state electronic configuration of the cyclopropyl-allyl anion system and show a symmetry state correlation for the corresponding anion.

3.2.2.2 Odd-Electron Systems

3.2.2.2.1 Radicals

Figures 3.33 and 3.34 show symmetry state correlations of two possible mechanisms for the interconversion of cyclopropyl-allyl radical system (an odd-electron system).

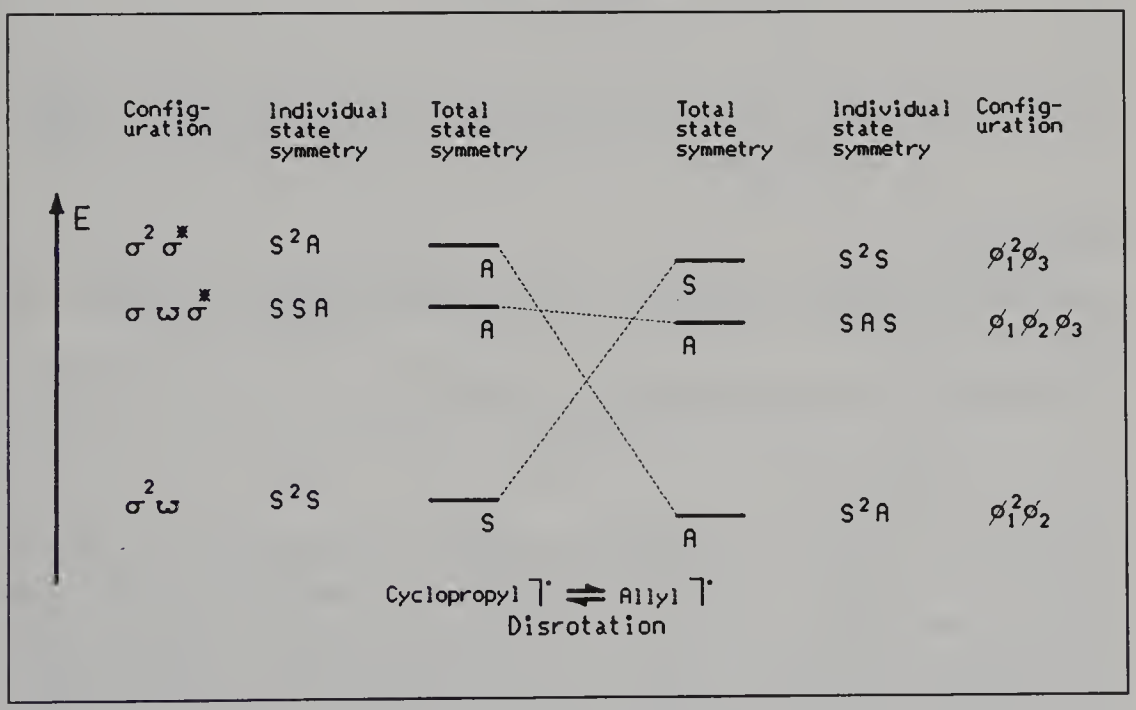


Figure 3.33: *Symmetry state correlation diagram for cyclopropyl-allyl radical system through disrotation.*

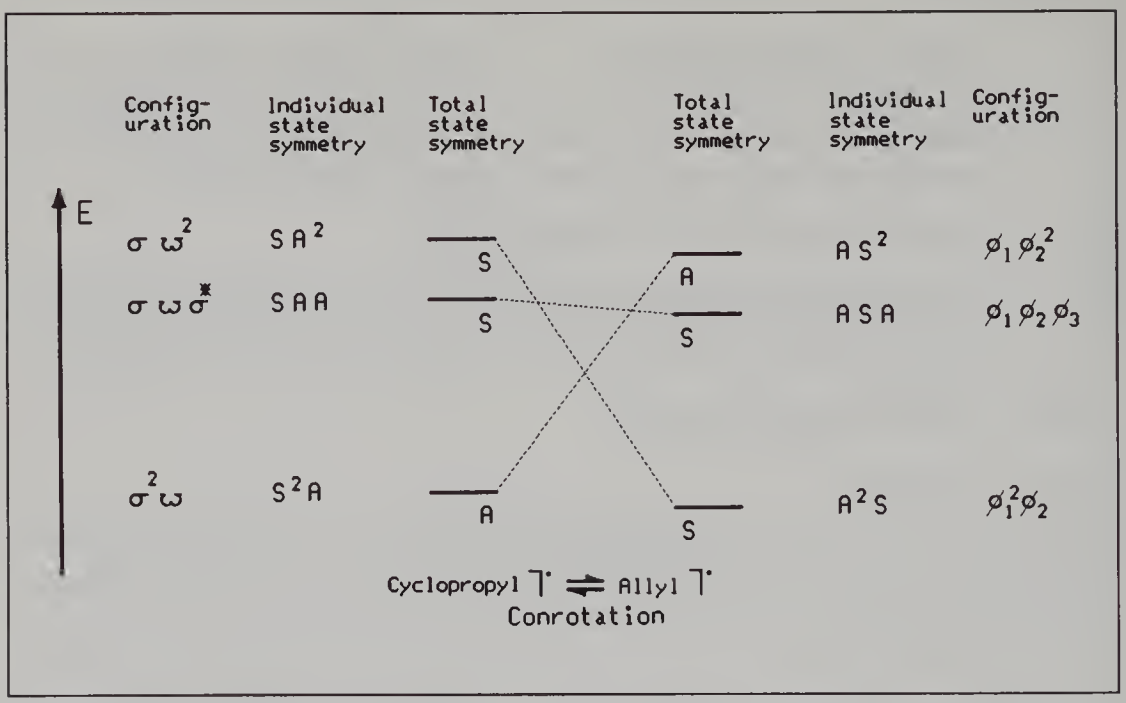


Figure 3.34: *Symmetry state correlation for cyclopropyl-allyl radical system through conrotation.*

Problem 3.22:

From Figure 3.33 and Figure 3.34, is it possible to determine the favourable path of ring opening [9]?

Compare your results with those discussed in Chapter 6.

3.2.2.2.2 Radical Ions

Symmetry state diagrams for cyclobutene-butadiene radical cations are constructed below. It is evident from Figures 3.35 and 3.36 that both the conrotatory and disrotatory mechanisms involve the conversion of the ground state of cyclobutene to the excited state of butadiene. However, the conrotatory process is preferred since it involves the conversion of a ground state cyclobutene radical cation to an excited state butadiene radical cation without passing over a symmetry imposed barrier. It is also interesting to note that only the ring opening process proceeds through conrotation as the cyclization process has to pass over a symmetry barrier. As for the photochemical process, the disrotatory mechanism is the favoured one because it involves a direct transformation of the first excited state cyclobutene radical cation to the ground state butadiene radical cation without the imposition of a symmetry barrier.

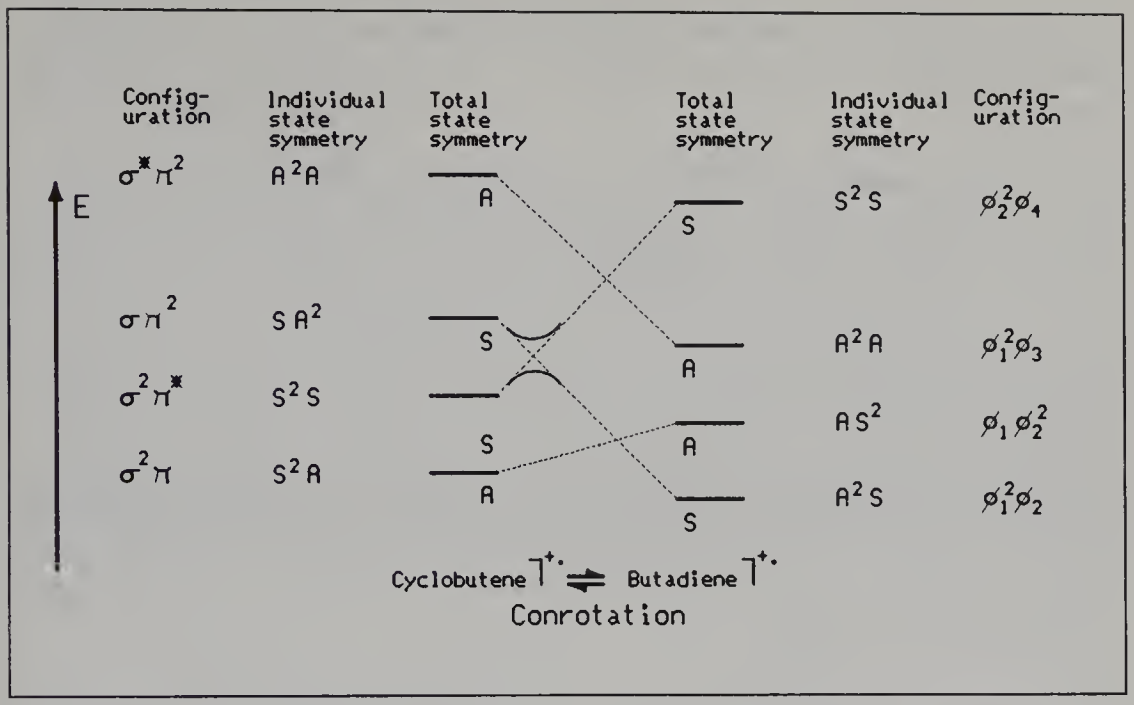


Figure 3.35: *Symmetry state correlation analysis of the interconversion of butadiene-cyclobutene radical cations through conrotation.*

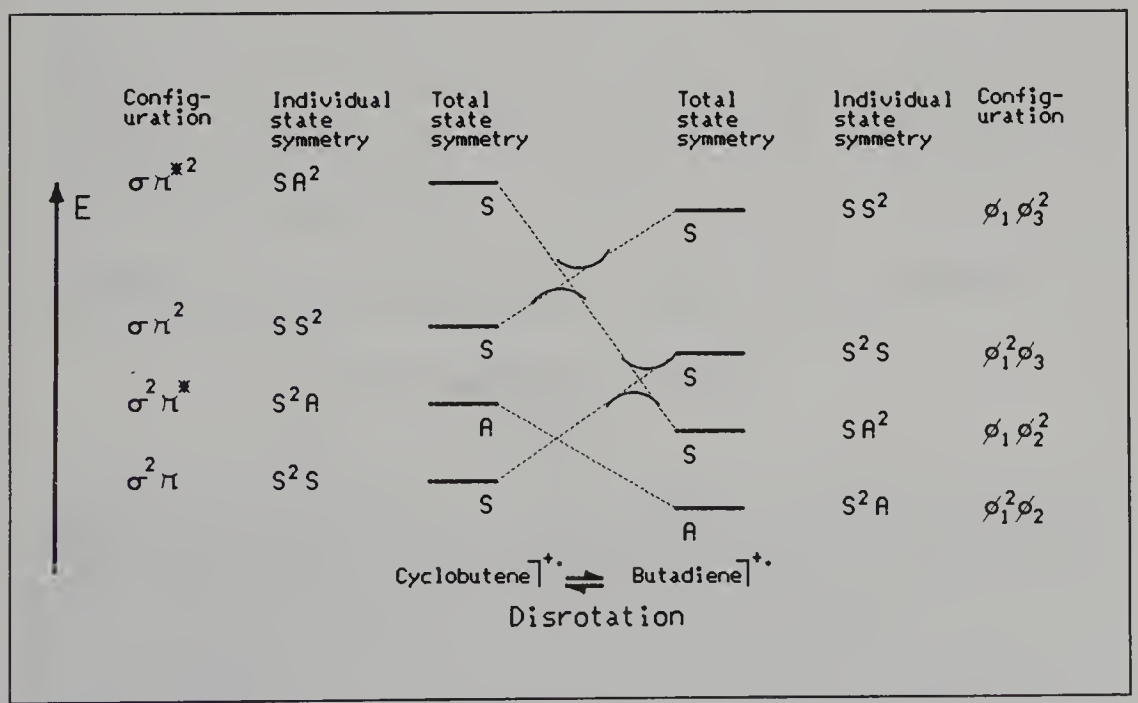


Figure 3.36: *Symmetry state correlation analysis of the interconversion of butadiene-cyclobutene radical cations through disrotation.*

Problem 3.23:

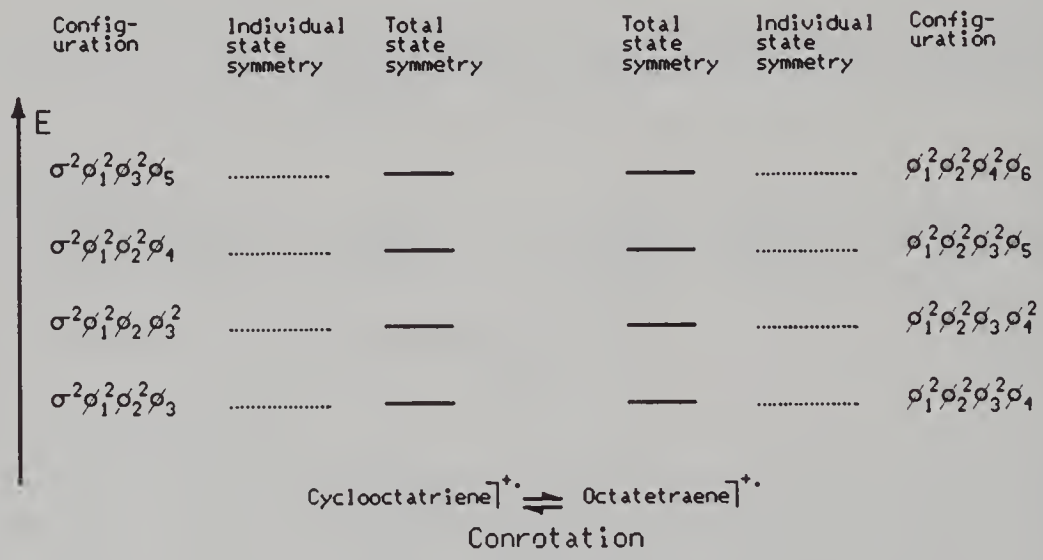
Following the sequence of steps given in Section 3.2.2.1.1, perform a symmetry state correlation analysis of a 5-electron system, e.g. interconversion of hexatriene-cyclohexadiene radical cations [13].

An electrocyclic interconversion of 1,3,5-cyclooctatriene and 1,3,5,7-octatetraene radical cations, a 7-electron system, i.e. (4n+3) electrons, is shown in Equation 3.12.

(3.12)

Problem 3.24:

Different electronic configurations for conrotatory interconversion of cyclooctatriene-octatetraene radical cations as given by Dunkin [10] are shown below. Determine individual and total state symmetries and complete state correlation diagram for the reaction. Do the same for a disrotatory process. What conclusions may be drawn?



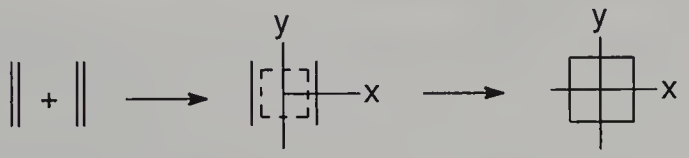
Dunkin [10] reported a very thorough state correlation analysis of the ring opening of radical cations of cyclobutene (3-electron system), cyclohexadiene (5-electron system) and cyclooctatriene (7-electron system) and observed that both 3-electron and 7-electron systems undergo thermal ring opening through conrotation while the 5-electron system opts for the disrotatory path in the ground state. However, for photochemical reactions, it is difficult to arrive at a conclusion since the preferred pathway also depends on the particular excited state undergoing an electrocyclic change.

Problem 3.25:

Make a set of selection rules for odd-electron systems and compare them with those for the even-electron systems.

3.3 Limitations

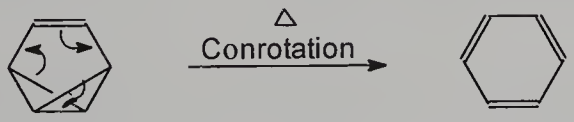
Although both energy level diagrams and symmetry state correlation diagrams often give a reliable indication of the course of a reaction, it is not possible to follow a reaction in any quantitative way even if highly accurate molecular orbital energies are available at all points along a reaction coordinate. Another difficulty in making these diagrams is the identification of the symmetry of the reacting system, and that of the transition state, which is required to be conserved during the entire course of a reaction. It becomes even more difficult to identify a symmetry element in substituted compounds. Organic molecules generally do not possess any symmetry, and the few that do possess, might lose it during the course of a reaction. Consider the dimerization of ethylene as an example (Equation 3.13).



(3.13)

If the reacting system retains two planes of symmetry throughout, it can be shown that the reaction leads to a highly excited form of cyclobutane if symmetry is to be retained. The transition state, where new bonds are equally formed, is shown symmetric in Equation 3.13 even though it need not be symmetric, i.e. the structure might become trapezoidal if one bond is formed to a greater extent than the other, hence, losing one of the planes of symmetry. Thus, the concept of symmetry conservation is inapplicable here.

In some cases, the energy level diagrams are even known to yield incorrect results. Consider the rearrangement of benzvalene to benzene (Equation 3.14).



(3.14)

Benzvalene is thermodynamically much less stable than benzene. On the contrary it is remarkably resistant to thermal isomerization and experimentally a high energy barrier is observed for this reaction. The molecule may be viewed as a bicyclobutane moiety fused onto ethylene. Anh [14] has analyzed this reaction on the prior assumption that the role of the double bond between C3 and C4 is negligible and that the reaction may be viewed as a valence isomerization of bicyclobutane and butadiene. Bicyclobutane has 70 Kcal $mole^{-1}$ of strain energy, and yet an additional 40 Kcal $mole^{-1}$ of activation energy must be supplied before isomerization of bicyclobutane to butadiene results. Offhand this looks like a typical forbidden reaction. The process involves a double electrocyclic ring opening due to the simultaneous breaking of two σ-bonds (marked with asterisks in Equation 3.15).

(3.15)

Empirically there is no doubt that the energetic demands of the simultaneous rupture of both σ-bonds are too high. Extensive theoretical and computational studies [15] reveal that the two σ-bonds are lengthened unequally in the transition state for thermal isomerization. However, only one transition state is formed along the reaction pathway. Thus, the bond breaking process has to be characterized as concerted and not synchronous. A synchronous process is a concerted process in which bond rupture and bond formation have progressed to the same extent at the transition state. Closs [16] has come to a very curious conclusion regarding the ring opening of bicyclobutane. According to his studies, one of the σ-bonds of bicyclobutane breaks in a conrotatory manner while the other in a disrotatory manner. This was experimentally confirmed.

The same arguments may be extended to benzvalene-benzene isomerization if it is assumed that the double bond of benzvalene does not shift its position in the transition state. Accordingly, one of the two σ-bonds of benzvalene should break in a conrotatory manner, while the other in a disrotatory manner. As predicted by the Woodward-Hoffmann rules the reaction should be allowed in the ground state by disrotation as it contains (4n+2) electrons. On the contrary, the correlation analysis shown in Figure 3.37 predicts a conrotatory mechanism for this valence isomerization. These anomalies cannot be explained on the basis of orbital symmetry conservation or orbital correlation analysis.

Based on the Woodward and Hoffmann rules, the direct thermal conversion of cyclooctatetraene to cubane would be considered forbidden. However, recent experimental results reveal that cubane may be rearranged to cyclooctatetraene with a relatively low activation barrier. The rearrangement is thought to involve a number of intermediates which were not observed [17].

This problem and many other related problems may be approached by carrying out the *Correspondence Analysis*, i.e. the OCAMS view (Orbital Correspondence Analysis in Maximum Symmetry), a method developed by Halevi [18]. This is a rigorous method to determine whether a chemical reaction is allowed or forbidden, since it considers both the electronic and vibrational changes in the molecule. Moreover, all the symmetry elements retained along a reaction pathway are explored and none is ignored. In this approach the correlation diagrams are called *correspondence diagrams* in order to distinguish them from the Woodward-Hoffmann energy level *correlation diagrams*. This method gives the same results as the Woodward-Hoffmann procedure if a given reaction is predicted to be forbidden. However, some reactions which are allowed by the Woodward-Hoffmann rules are shown to be forbidden.

The method of correspondence analysis is much more complicated when compared with the methods which focus only upon changes in the electronic structure. Therefore, the approach introduced by Woodward and Hoffmann, based on orbital symmetry conservation, has received widespread acceptance and utilization.

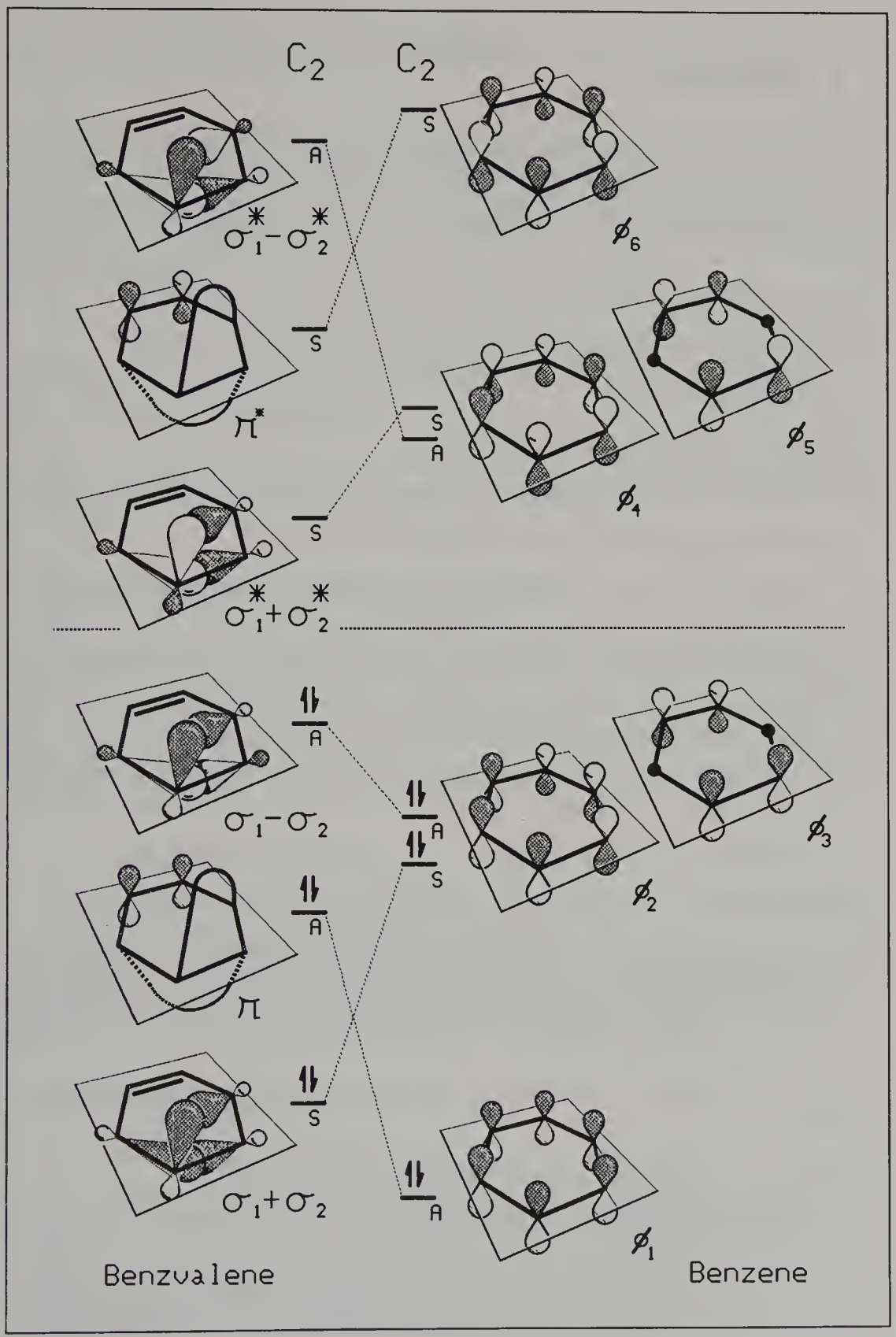


Figure 3.37: *Orbital correlation diagram for a conrotatory interconversion of benzvalene and benzene.*

3.4 References

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4. Frontier Orbitals Approach

The selection rules developed for electrocyclic reactions on the basis of orbital symmetry conservation, as discussed in Chapter 3 may also be rationalized by analyzing interactions of frontier orbitals. This was the method Woodward and Hoffmann developed in their first paper on pericyclic reactions [1] and subsequently used by Fukui and others [2 a-c].

4.1 Basic Concepts

Before proceeding to the analysis of pericyclic reactions on the basis of the *frontier orbitals approach*, it is worth discussing some fundamental concepts related to this approach.

4.1.1 Interactions between Orbitals

During a chemical reaction, the formation of a bond between two atoms takes place as a result of interactions between the orbitals present on these atoms. These orbital interactions help in examining the structures of molecules, as well as their kinetic and thermodynamic stabilities, moreover, they also aid in understanding the fundamental processes in chemistry [3 a,b]. A discussion of a variety of possible orbital interactions follows.

4.1.1.1 Atomic Orbitals

Chemical processes take place as a result of electronic interactions between atomic or molecular orbitals. Moreover, hybrid orbitals also undergo the same type of interactions as do the atomic or molecular orbitals. These interactions lead to the formation of a bond which may be described as a homonuclear bond (between two like atoms) or a heteronuclear bond (between two different atoms).

4.1.1.1.1 Degenerate Interactions

- ***s orbitals***

The formation of a molecule of hydrogen from two hydrogen atoms exemplifies a case of the interactions of two degenerate *s* orbitals resulting in the formation of a homonuclear bond. As two hydrogen atoms (each having an electron in its 1*s* orbital) approach from infinity to within bonding distance, two possible combinations of the atomic orbitals may be thought of:

The first is a bonding combination which is the result of an interaction between orbitals of the same sign. The electronic cloud on each atom is attracted by the positively charged nucleus of the other atom. These attractive forces lead to an overall energy lowering of the system. The result is the formation of a lower energy orbital which is called a *bonding* molecular orbital and is designated as σ.

The second way of combining the two orbitals is called *antibonding*. The point where the function changes its sign is called a node, and all the nodes of a molecule lie in a plane called the nodal plane The sign of the function (which describes the electron distribution) on one nucleus is opposite to that of the other nucleus. Also if there were any electrons in this orbital then the electron density would be low in the region between the two nuclei. The low electron density in the nodal region leads to a strong repulsion between the two nuclei and thus results in an increase in the energy of the system.

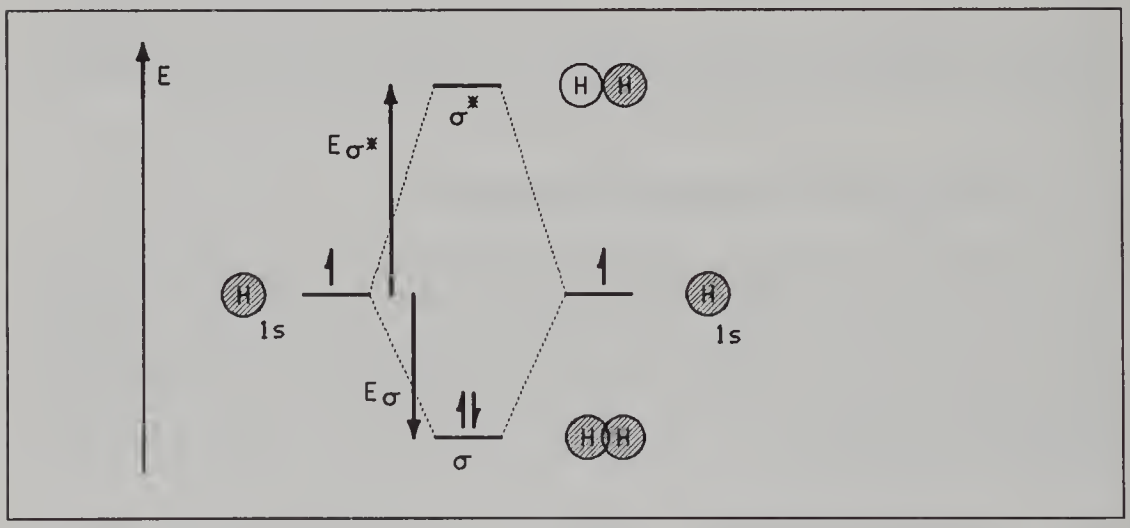


Figure 4.1: *Interactions between two s orbitals.*

The result of this interaction is a high energy antibonding molecular orbital designated as σ*. The two electrons, initially in two degenerate 1*s* atomic orbitals, now occupy the lower energy bonding molecular orbital σ with their spins paired in accordance with Pauli's Exclusion principle. The energy changes involved during the formation of a bond between the two hydrogen atoms are illustrated in Figure 4.1.

Problem 4.1:

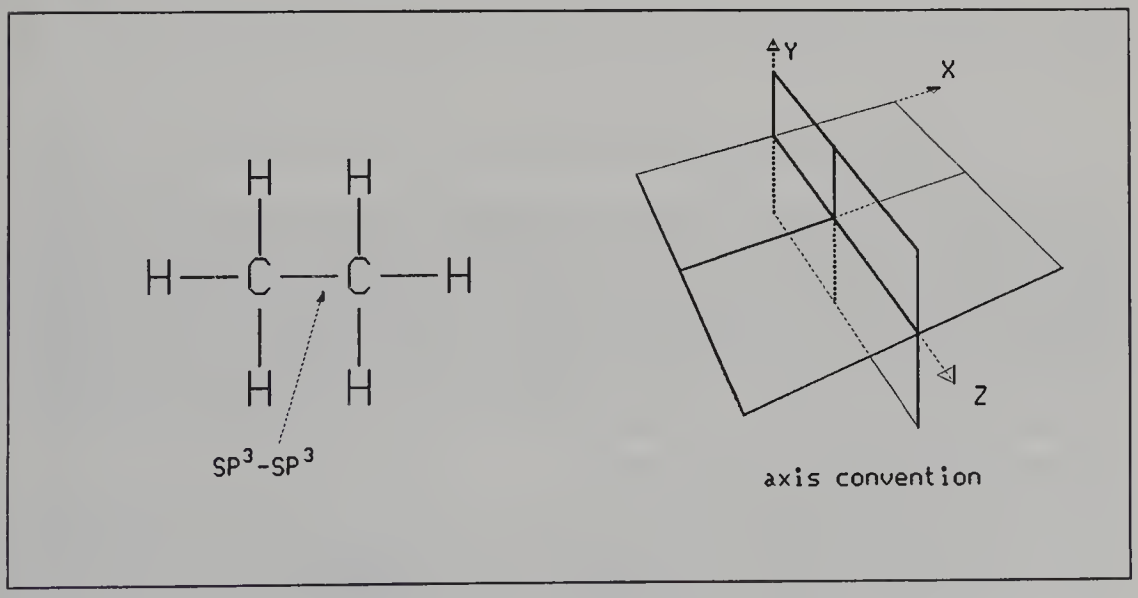
i) The formation of a molecule of H_2 is an example of a two-electron stabilization whereby 103 Kcal $mole^{-1}$ energy is released. Calculate the value of E_σ for this reaction. Predict whether the energy released during the formation of H_2^+, He_2^+ and He_2 would be smaller, or greater, than 103 Kcal $mole^{-1}$.

ii) The bond length in a situation of two-electron stabilization is found to be 0.74Å. Would the bond length during one-electron and a three-electron stabilization be smaller than 0.74 Å ?

The energy lowering as a result of bonding combination is labeled as E_σ while a corresponding increase in energy, as a result of antibonding interactions, is represented by $E_{\sigma*}$. The magnitude of energy lowering, as a result of bond formation E_σ , should be equal to a corresponding energy increase as a result of antibonding interactions. However, more precise calculations indicate that the energy lowering is smaller than the energy rise, i.e. $E_\sigma < E_{\sigma*}$. Moreover, a net lowering in energy on bond formation should be $2E_\sigma$ because two electrons are involved in bond formation. However, placing two electrons in a bonding orbital does not achieve twice the energy-lowering as the placing of one electron does. Two electrons can be placed in an orbital if they have opposite spins but they still repel each other because they have to share the same space. Consequently, by forcing a second electron into a σ orbital, some of the bonding character is lost that it might otherwise have gained, had a single electron been placed. It is for this reason that the value E_σ is smaller than that of E_σ*. It should be noted that the formation of a bonding combination is an exothermic process while that of an antibonding combination is an endothermic process.

- ***sp^3 Hybrid Orbitals***

The interactions between two sp^3 orbitals, just like the interactions between two *s* orbitals, also lead to the formation of a homonuclear bond. As an example, ethane has six 1*s* orbitals on its hydrogen atoms and four sp^3 hybrid orbitals on its carbon atoms. Emphasis is placed on orbitals which hold the two carbon atoms together by making a σ_{C-C} bond. This bond is formed by the interactions of two sp^3 hybrid orbitals on two carbon atoms as shown.



An interaction of two degenerate sp^3 orbitals on two carbon atoms is illustrated in Figure 4.2. The two approaching orbitals, each having an electron, undergo a head-on overlap. Two possible combinations lead to the formation of a lower energy σ bonding molecular orbital and a higher energy σ* antibonding molecular orbital. Electron density is concentrated in the region between the two nuclei in a σ bond

while it is away from the internuclear region in a σ* bond. The two electrons obviously occupy the lower energy σ bonding molecular orbital.

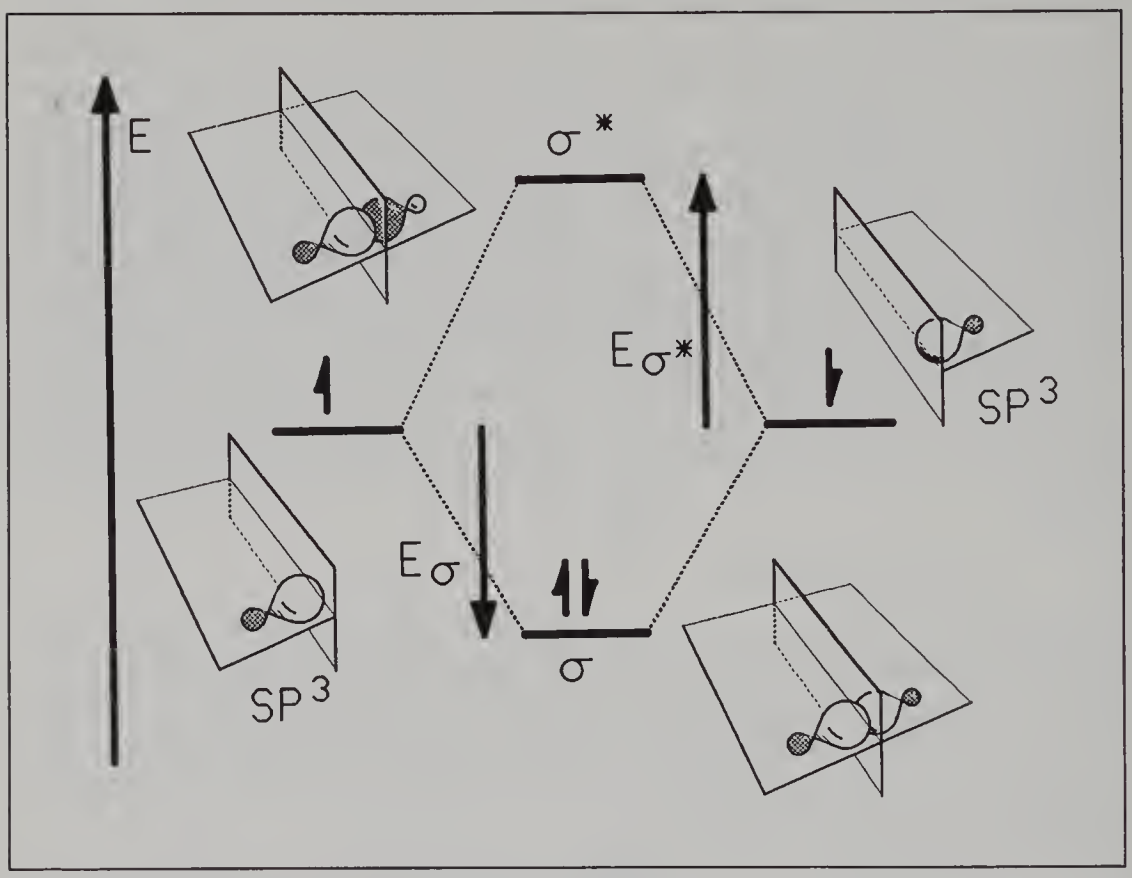
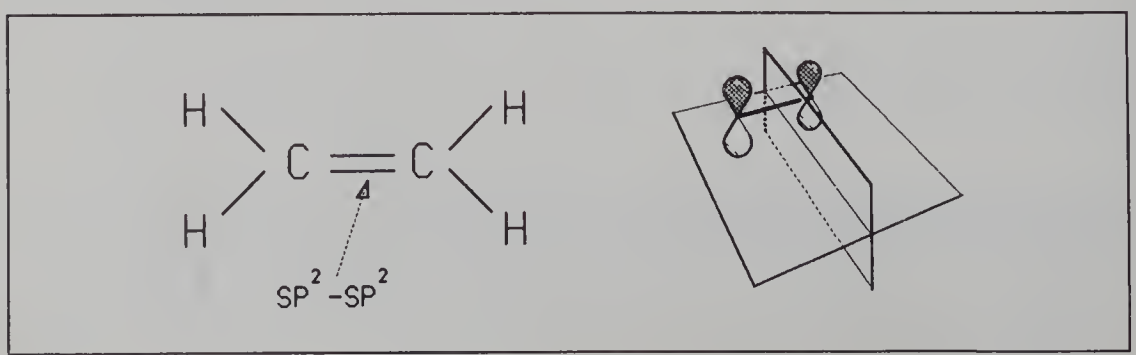


Figure 4.2: *Interactions between two sp^3 hybrid orbitals (coaxial approach).*

- ***p Orbitals***

The formation of a σ bond by the coaxial approach leading to a head-on overlap of two *s* orbitals, or between two sp^3 hybrid orbitals, is discussed. The formation of a σ bond between two carbon atoms is also possible by an interaction of two sp^2 hybrid orbitals. For example, in an ethylene molecule, there are three sp^2 hybrid orbitals; two of them are involved in a σ bond formation with two hydrogen atoms while the third sp^2 hybrid orbital forms a σ bond with the other ethylene carbon, by a coaxial approach of these two sp^2 hybrid orbitals.



However, there remains a $2p_z$ orbital on each carbon atom which is perpendicular to the plane of the molecule and may overlap sideways to form a new type of bond called a π bond. Interactions between two *p* orbitals on two carbon atoms, each having an electron, are shown in Figure 4.3. Two possible combinations of these orbitals give rise to a π-bonding and a π*-antibonding molecular orbital.

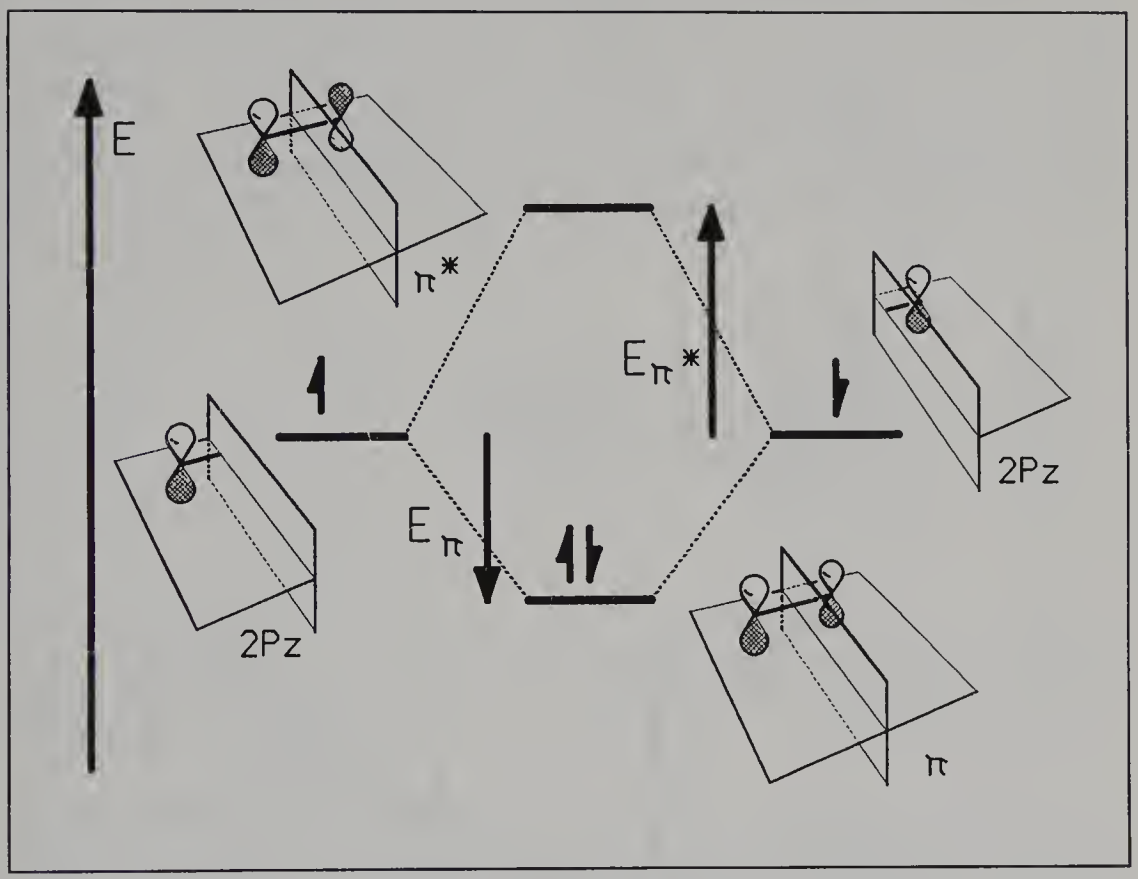


Figure 4.3: *Interactions between two p orbitals (parallel approach).*

It is noteworthy that the energy-drop during a π bond formation is smaller than the energy drop during a σ bond formation, i.e. $E_\pi < E_\sigma$, as the electron density is not concentrated in the region between the two nuclei but is spread above and below the plane of the σ_{C-C} bond. Therefore, the interaction between two orbitals approaching each other, in a parallel manner, is not very strong.

4.1.1.1.2 Non-Degenerate

After having discussed the interactions between two degenerate orbitals present on two similar atoms, the energy changes during the interactions between orbitals present on different kinds of atoms is observed. This leads to the formation of a heteronuclear bond.

The orbitals may approach coaxially, or in a parallel manner, resulting in the formation of a σ- or a π-bond, respectively. The C—O bond in a molecule such as methanol, just like the C—C bond in ethane, has several orbitals contributing to the force which keeps the two atoms bonded to each other. However, by abstracting one

of the important orbitals, such as the orbital making a σ_{C-O} bond, an orbital interaction diagram can be constructed.

- ***sp^2 Hybrid Orbitals***

To begin with, the sp^2 orbital of an oxygen atom is of a lower energy than the sp^2 orbital of a carbon atom. However, in the bonding combination σ_{C-O}, the oxygen atom, being more electronegative than the carbon atom, keeps a greater share of electrons while the situation reverses in the antibonding combination; i.e. the carbon atom keeps a larger share in σ^*_{C-O}. Since the two interacting orbitals are initially of different energies, they do not interact strongly, hence, the energy drop E_σ as shown in Figure 4.4 is smaller than the energy drop E_σ shown in Figure 4.2.

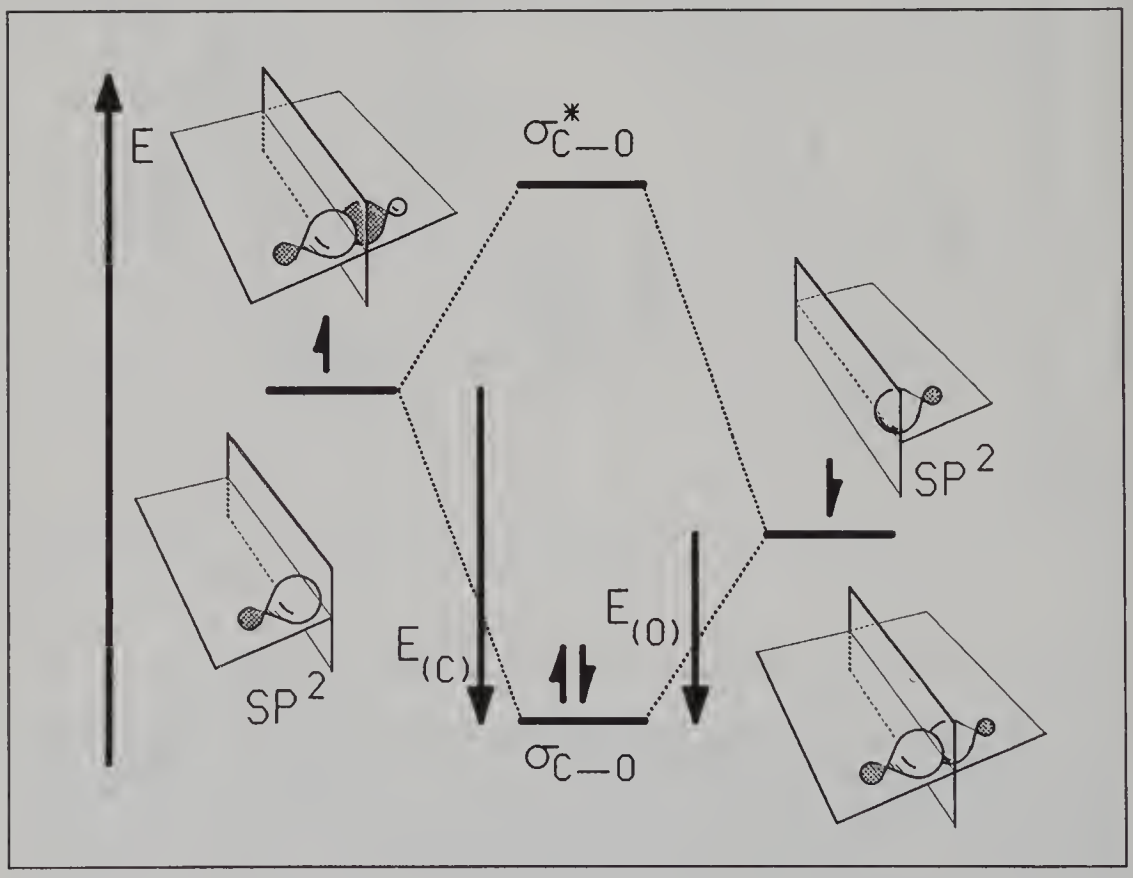


Figure 4.4: *Interactions between two sp^2 hybrid orbitals of different energies (coaxial approach).*

- ***p Orbitals***

A parallel approach of *2p* orbitals on two different atoms is a case of interactions between two atomic orbitals of different energies leading to a π_{C-O} bond. It occurs in much the same way as a π-bond of ethylene, except that the raising, and lowering, of the energy of the interacting orbitals is less than that for the corresponding σ_{C-O} bond. Figure 4.5 depicts the energy changes involved during the interactions between two 2*p* orbitals present on carbon and oxygen atoms.

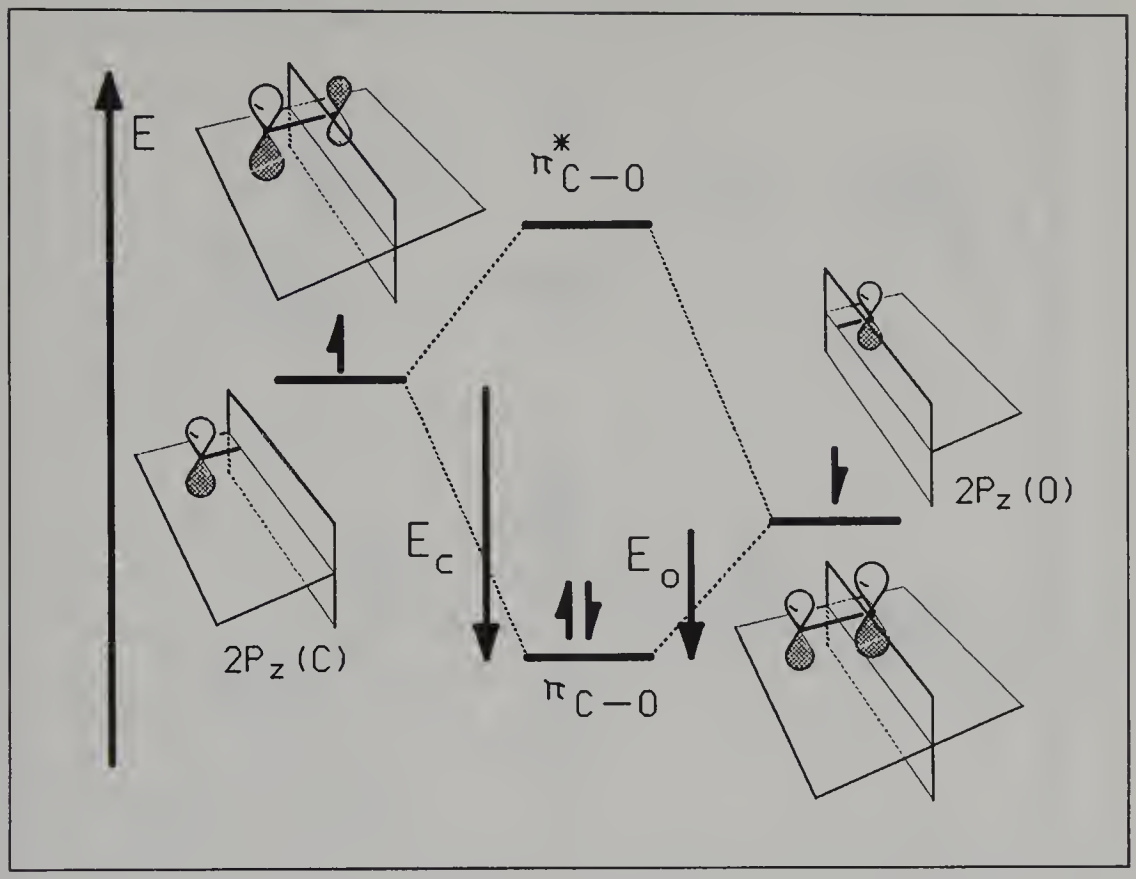
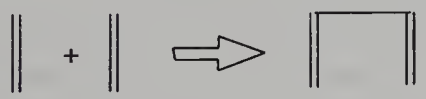


Figure 4.5: *Interactions between two p orbitals of different energies (parallel approach).*

4.1.1.2 Molecular Orbitals

Interactions between molecular orbitals are just like the interactions between atomic orbitals. A hypothetical interaction between the molecular orbitals of two ethylene molecules to form the molecular orbitals of 1,3-butadiene is shown in Equation 4.1.



(4.1)

Imagine a coaxial approach of two ethylene molecules approaching each other from an infinite distance down to bonding distance.

An ethylene molecule is made up of a set of one bonding molecular orbital π, and one antibonding molecular orbital π*. Each bonding molecular orbital has an electron pair as shown in Figure 4.6.

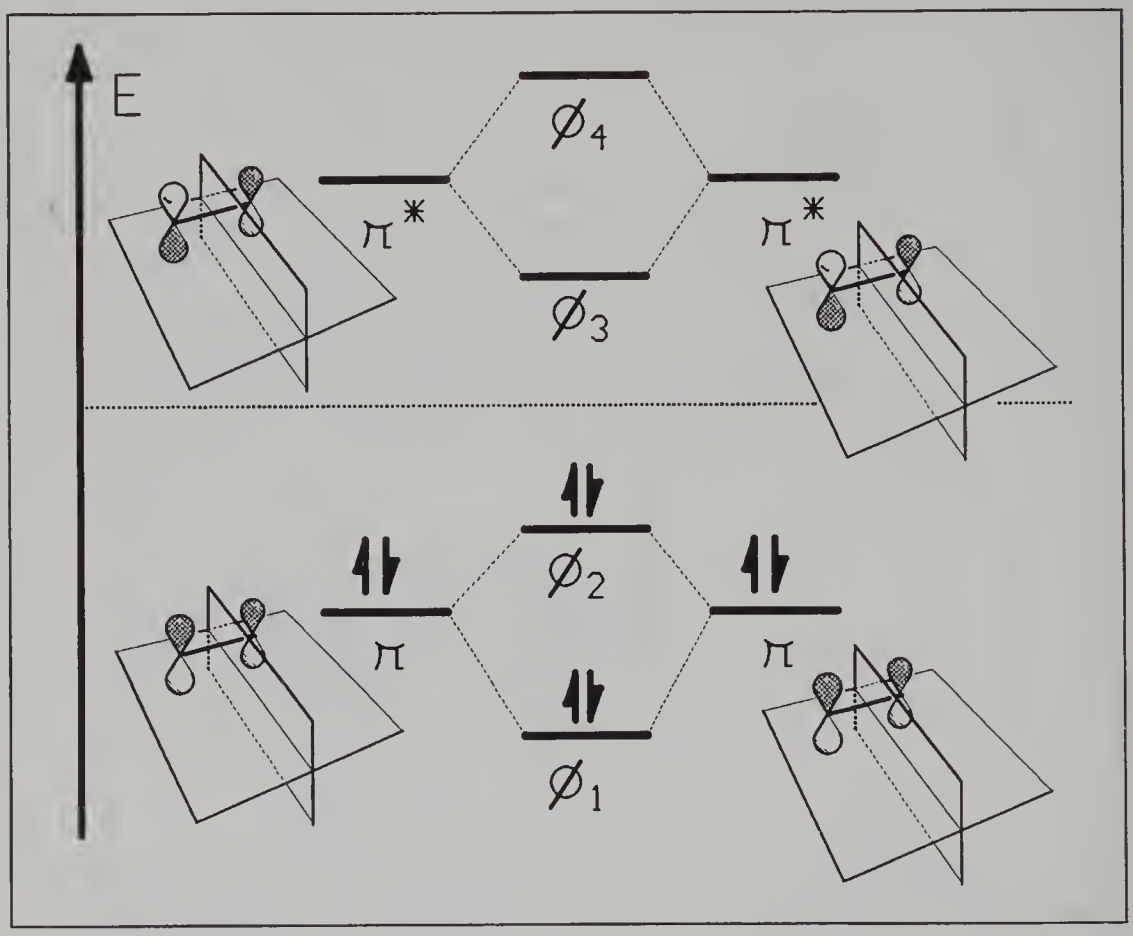


Figure 4.6: *Interactions between molecular orbitals of two ethylene molecules.*

The interactions between two MOs of ethylene gives rise to a lower energy combination ϕ_1 and a higher energy combination ϕ_2. This situation is very much like the interactions between two degenerate atomic orbitals. Likewise the interactions between two antibonding MOs, i.e. π^*, would lead to two possible combinations ϕ_3 and ϕ_4. These MOs were illustrated earlier in Figure 3.4.

The four electrons of butadiene occupy the lower energy bonding molecular orbitals ϕ_1 and ϕ_2. The ground state electronic configuration of butadiene, $\phi_1^2\,\phi_2^2$, indicates that there are more than one pair of filled and unfilled orbitals. There are still more filled orbitals lying lower in energy (σ framework) than either ϕ_1 or ϕ_2 . However, these orbitals do not draw any attention because they are very low in energy and are quite unreactive. Hence, for butadiene, ϕ_2 is the HOMO (Highest Occupied Molecular Orbital) while ϕ_1 is the NHOMO (Next to the Highest Occupied Molecular Orbital). In addition to filled orbitals, there are unfilled orbitals ϕ_3 and ϕ_4. Here ϕ_3 is described as LUMO (Lowest Unoccupied Molecular Orbital) while ϕ_4 is the NLUMO (Next to the Lowest Unoccupied Molecular Orbital). The HOMO-LUMO pair is described as *frontier orbitals* and the electrons therein as *frontier electrons*. The NHOMO-NLUMO pair of orbitals, also abbreviated as NHO-NLU pair, is known as *superjacent-subjacent* orbitals. All these orbitals, along with their symbols, are shown in Figure 4.7.

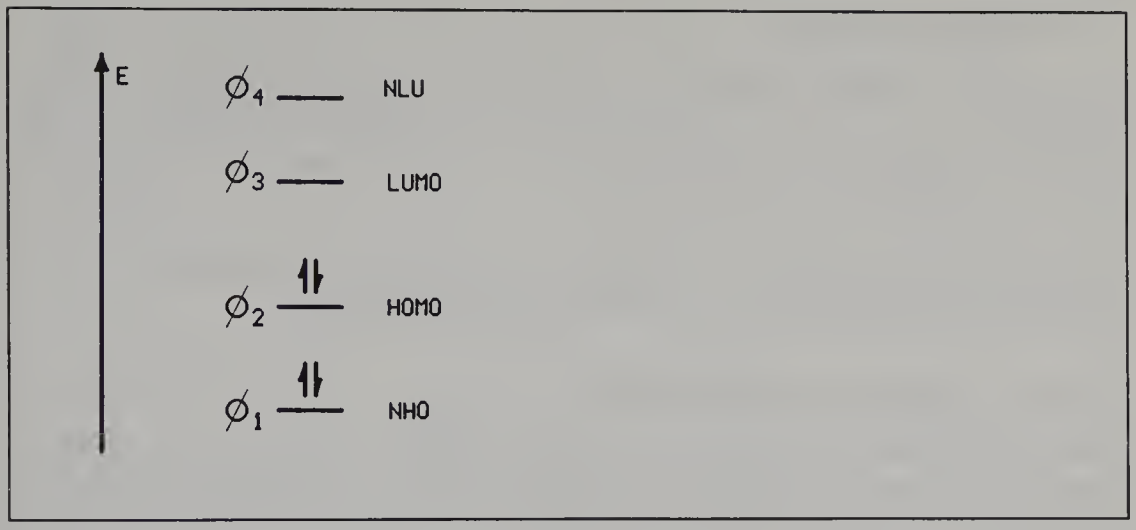


Figure 4.7: *Symbols used to label MOs of butadiene.*

If two molecules of butadiene labeled A and B approach each other from infinity, all of their four orbitals undergo mutual interactions in a variety of ways. Some possible interactions are described below:

4.1.1.2.1 Filled Orbitals

As mentioned earlier, ϕ_1 and ϕ_2 are the filled orbitals of butadiene; the former is the NHOMO, and the latter is the HOMO. The following two possibilities of their interactions may be envisaged.

- ***HOMO-HOMO***

The interactions between two HOMO's result in a lower energy bonding and a higher energy antibonding combination. Since this situation resembles the case of interactions between two filled degenerate orbitals, there is no net stabilization (Figure 4.8).

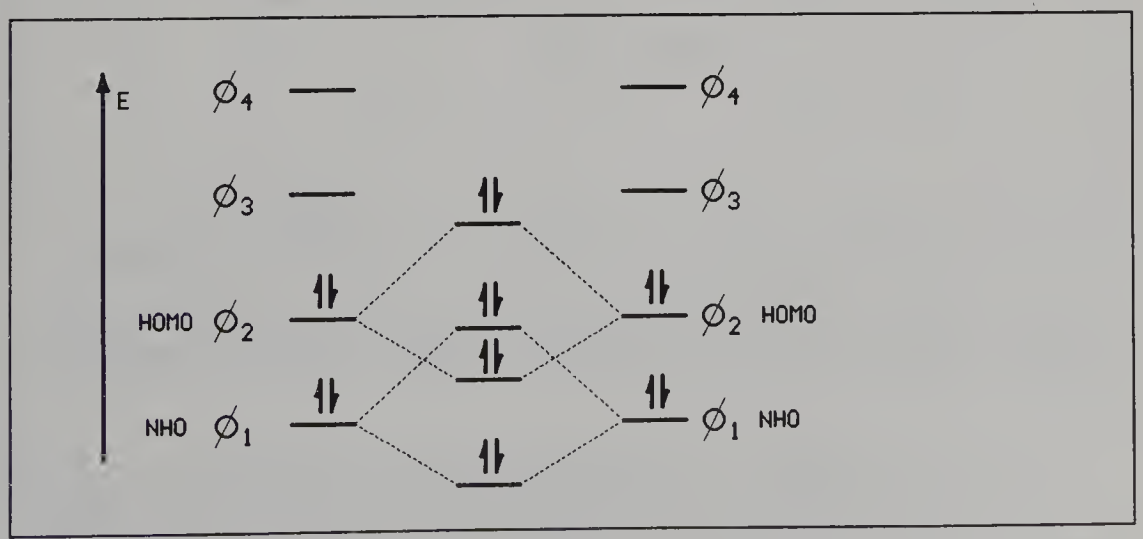


Figure 4.8: *Interactions between filled orbitals of butadiene.*

- ***NHOMO-NHOMO***

The result of NHOMO-NHOMO interactions is the same as between HOMO-HOMO interactions. The only difference being that the NHOMO-NHOMO pair lies deeper in energy than the HOMO-HOMO pair and thus the electrons therein are less easily accessible for reactions (Figure 4.8).

Interactions between unfilled and unfilled orbitals are obviously of no use because without electrons there is no way of losing, or gaining, energy.

4.1.1.2.2 Filled and Unfilled Orbitals

These interactions are the most significant since there are large attractive forces between the occupied orbitals of one molecule with the unoccupied orbitals of the other and thus lead to a net decrease in the energy of the system. Moreover, the closer the two interacting orbitals are in energy the greater is the energy drop. Two orbital interactions, HOMO-LUMO and NHOMO-NLUMO, are possible.

- ***HOMO-LUMO***

Of the HOMO-LUMO interactions, two pairs of frontier orbitals are possible: the $HOMO_A$-$LUMO_B$ or the $HOMO_B$-$LUMO_A$. Since the HOMO of two molecules are of the same energy (as in the case of two LUMO's), whichever HOMO-LUMO pair is chosen, the energy-drop would be found to be the same (Figure 4.9).

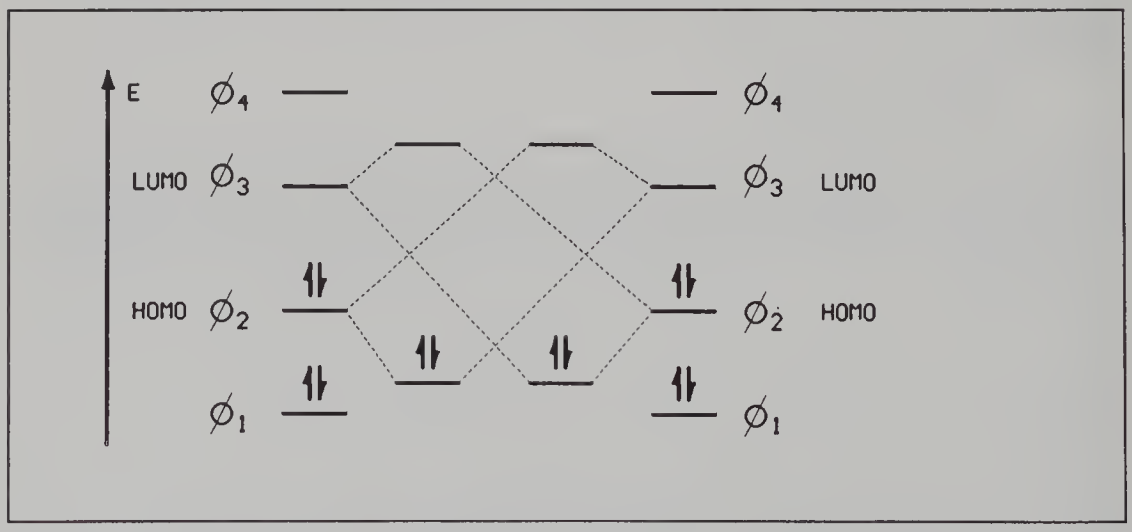
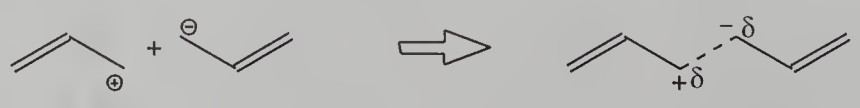


Figure 4.9: *Interactions between two sets of frontier orbitals of the same energy.*

However, a situation might arise where two pairs of orbitals lead to different energy changes. Interactions between the MOs of allyl cation and allyl anion portray such a situation.



(4.2)

The two interacting systems, allyl cation and allyl anion, have the same set of MOs. However, the difference in their ground state electron occupancies leads to two

different sets of orbitals i.e. $HOMO_{cation}$-$LUMO_{anion}$ and $HOMO_{anion}$-$LUMO_{cation}$ These two sets of orbitals differ significantly in their energies (Figure 4.10).

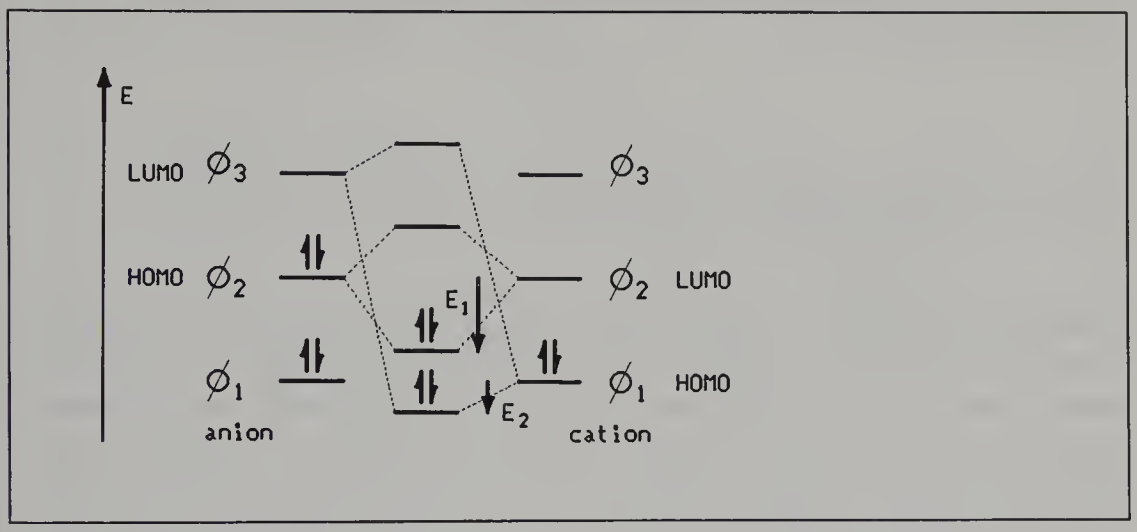


Figure 4.10: *Interactions between two sets of frontier orbitals of different energies.*

Obviously the latter pair of the orbitals is the *frontier orbitals pair*, since the energy lowering is more significant in this case, i.e., $E_1 > E_2$

- ***NHOMO-NLUMO***

A look at the energy changes between a lower-filled and a higher-unfilled orbital of butadiene shows that the energy of the system evidently decreases as a result of this interaction. This energy-drop is very insignificant, because the two interacting orbitals are far apart on the energy scale and thus do not interact strongly (Figure 4.11). These interactions are less significant than those shown in Figure 4.9.

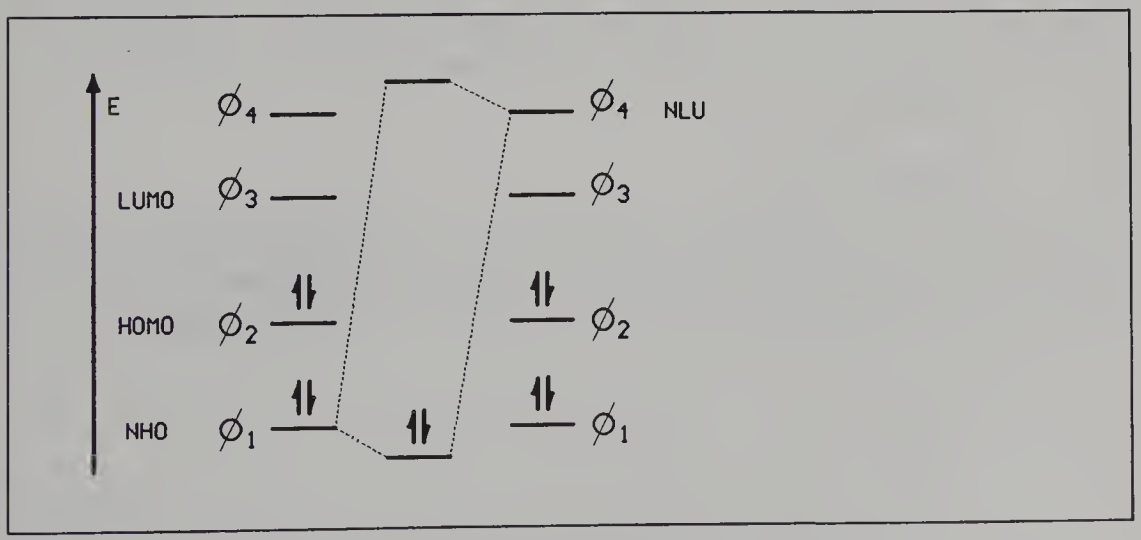


Figure 4.11: *Interactions between NHOMO-NLUMO of butadiene.*

Problem 4.2:

Arrange ΔE in three different situations as shown in Figures 4.9 to Figure 4.11 in an increasing order of energy.

From a comparison of the energy-drop, as shown in different situations, it can be concluded that *the energy lowering is maximum when the interacting orbitals are a pair of HOMO-LUMO*, i.e. the frontier orbitals.

The significance of these orbitals becomes apparent since the interactions between non-degenerate orbitals is inversely proportional to the energy gap between the orbitals. Indeed, the dominant role these orbitals often play has led to the development of the FMO (Frontier Molecular Orbital) theory, where chemical arguments are based on the energy and symmetry properties of just these orbitals. The FMO theory is widely applicable and is used successfully to rationalize an enormous range of chemical phenomena. Some areas of chemistry where FMO arguments are commonly considered include molecular structures and conformations, reactivity and stereochemistry, solvation and charge-transfer complexes as well as allowed and forbidden pericyclic reactions.

Before applying the FMO theory to electrocyclic reactions, the concept of the geometric approach of reactants is discussed.

4.1.2 Suprafacial and Antarafacial Geometries

The transition state of a pericyclic reaction may be envisaged as being made up of different fragments which may also be designated as components. Thus, the orbital systems making up a σ- or a π-bond may well be described as σ- or π-components. Likewise the isolated *s*-, *p*- or *d*- AOs may also be described as *s*-, *p*- or *d*- components, respectively. These components approach, or interact, in the following two distinct geometrical manners and the component is described accordingly.

i) Suprafacial approach

ii) Antarafacial approach

A component is said to interact suprafacially if the interaction (overlap) occurs at two lobes located at the same side of the nodal plane (molecular plane). Figure 4.12 illustrates interactions of *s*-, *p*- and *d*- atomic orbitals in a suprafacial fashion.

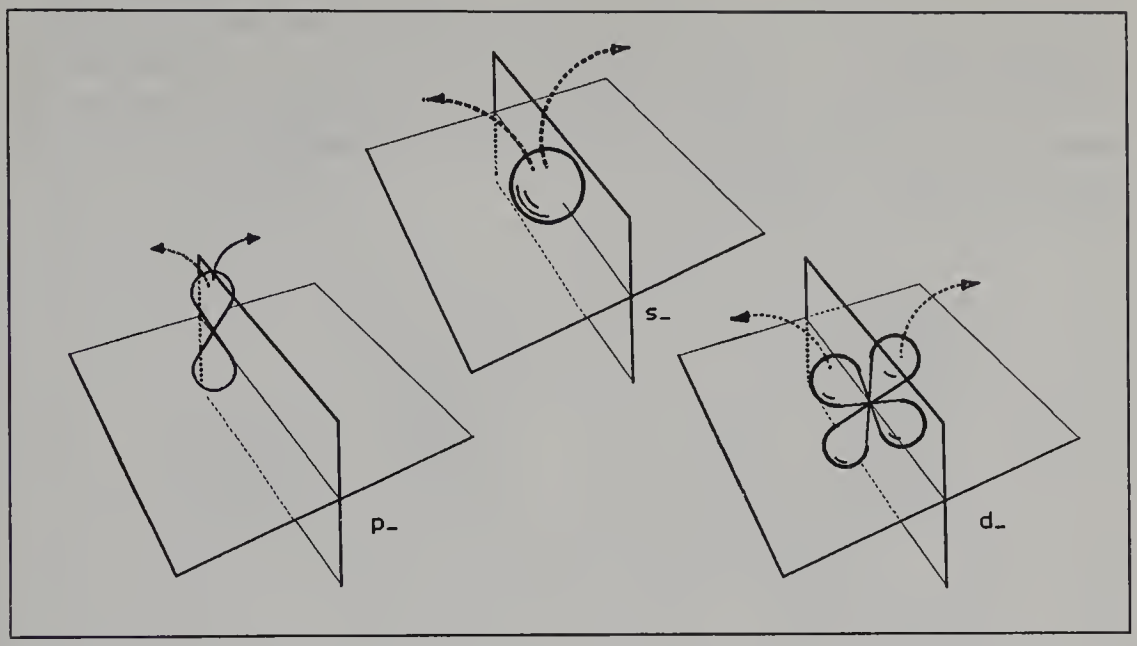


Figure 4.12: *Atomic orbitals (components) which make up the transition state of a reaction are shown interacting suprafacially.*

Likewise σ- and π-molecular orbitals (components) may interact suprafacially in two different ways which may, or may not, be distinguishable (Figure 4.13).

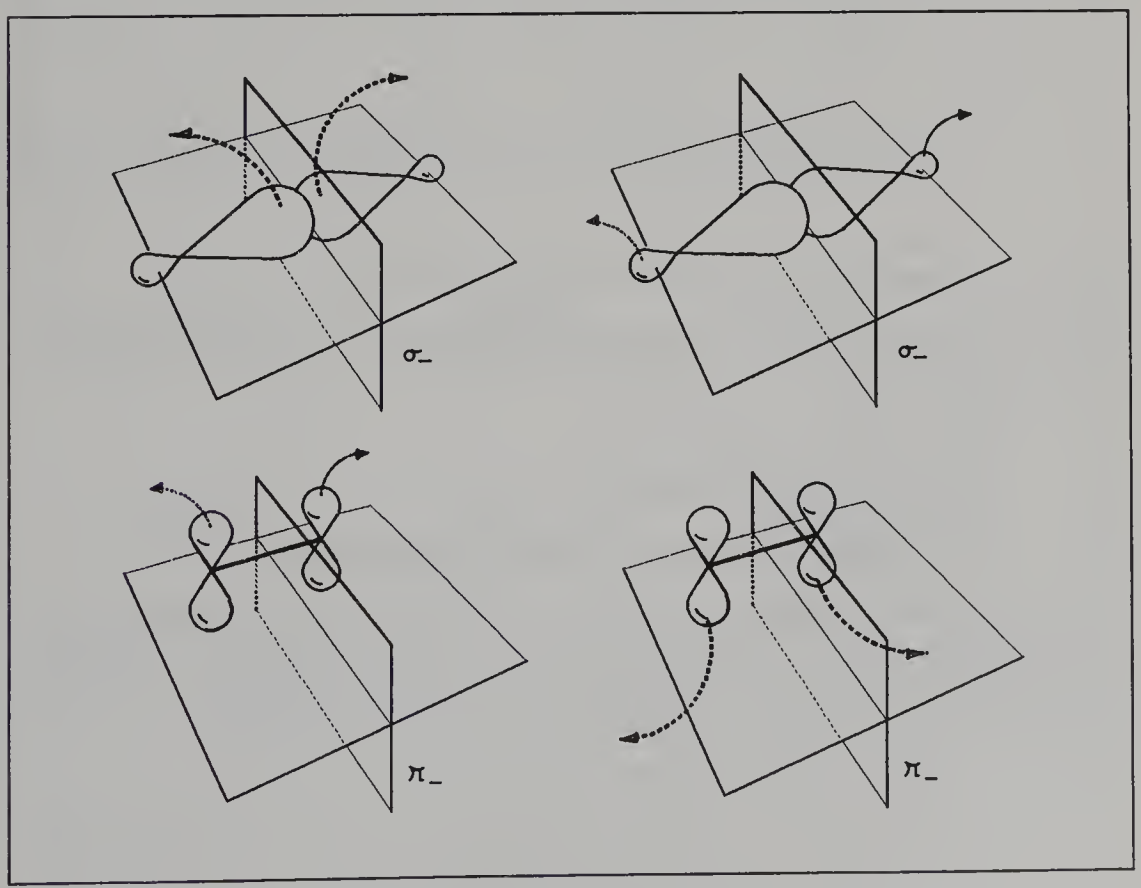


Figure 4.13: *Molecular orbitals (components) interacting suprafacially.*

A component is said to interact antarafacially if the interaction (overlap) occurs at two lobes located on the opposite side of the nodal plane. Figure 4.14 depicts an antarafacial interaction of different components with their neighbours. It should be noted that an *s* orbital may interact or overlap only in a suprafacial fashion due to its spherical symmetry.

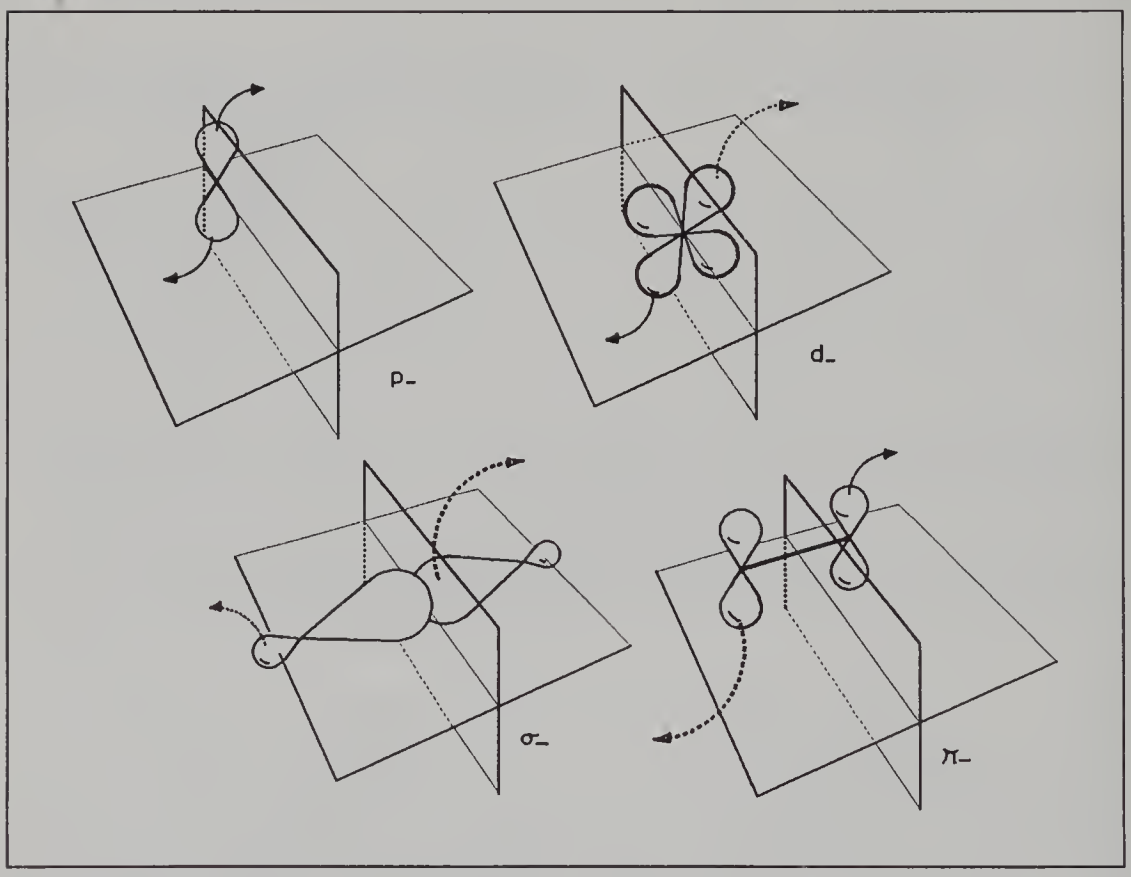


Figure 4.14: *Different components interacting antarafacially.*

During a chemical reaction two components may interact with, or add to, each other in three distinct ways:

i) Both components suprafacially

ii) Both components antarafacially

iii) One component suprafacially and the other antarafacially

The faciality of a component is depicted by a subscript *s* or *a* for suprafacial and antarafacial interactions, respectively. Thus, $[\pi_s+\pi_s]$ means that both π-components are interacting suprafacially while $[\pi_s+\pi_a]$ means that one π-component is interacting suprafacially while the other π-component is interacting antarafacially.

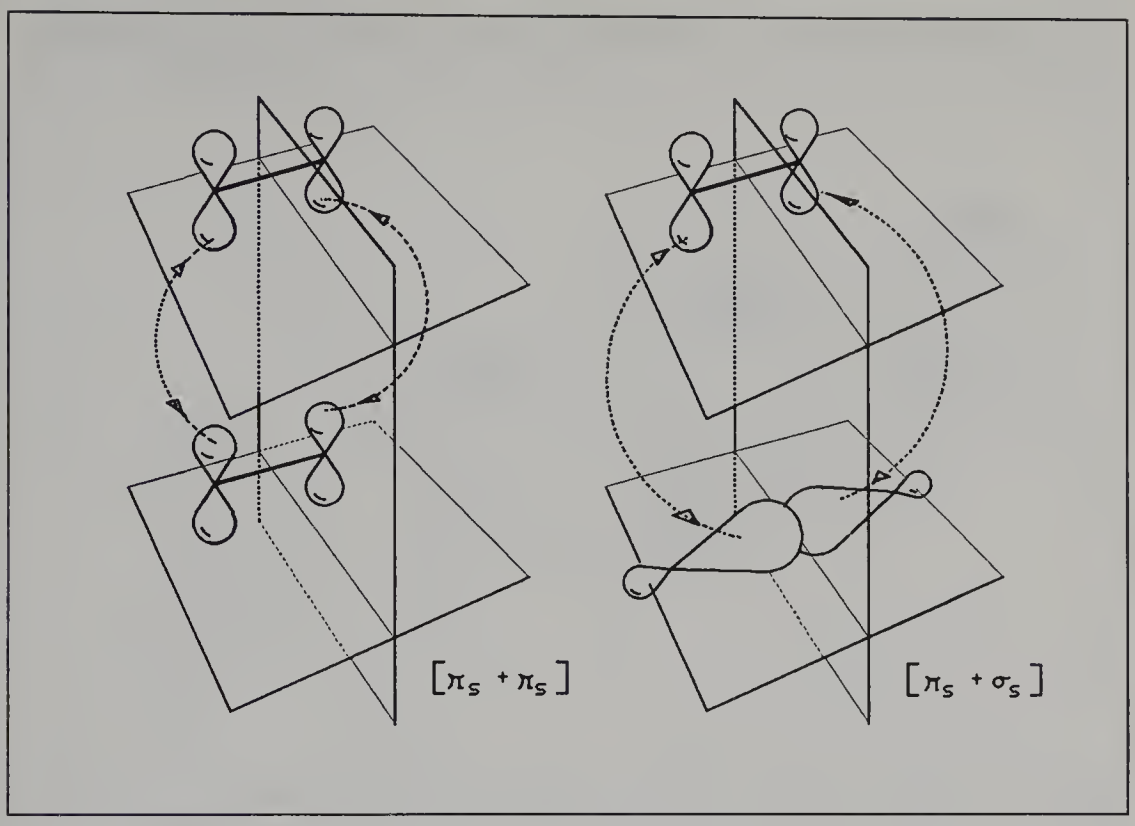


Figure 4.15: *Interactions between two π-components and between a σ- and a π-component.*

The dimerization of two olefins to form cyclobutane is an example which illustrates the three geometrical ways of the interactions between two π-components.

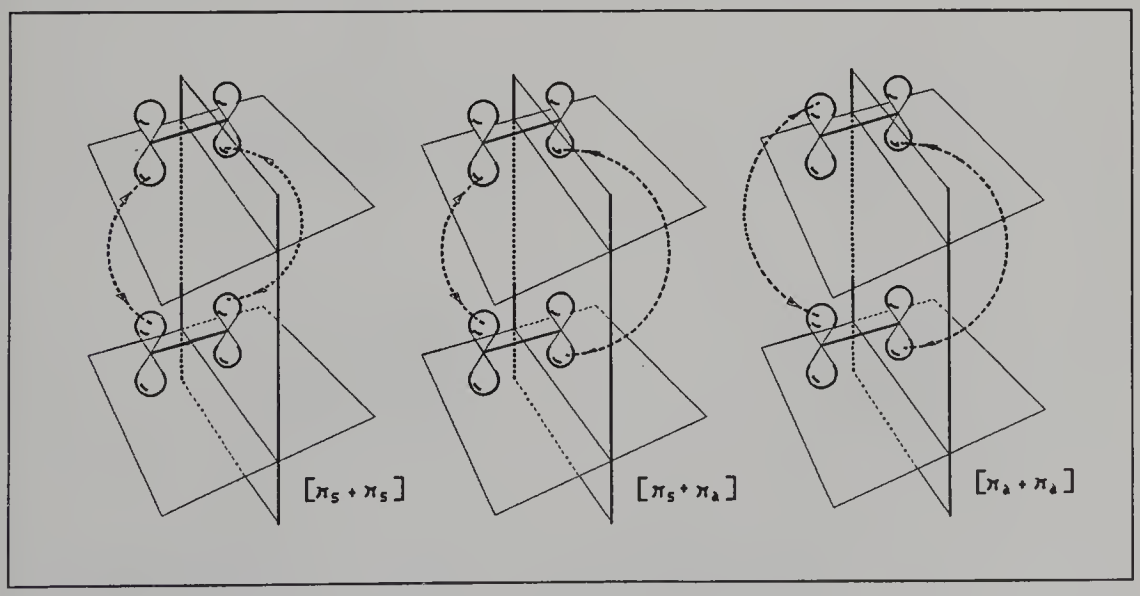


Figure 4.16: *Different modes of interactions between two π-components.*

Electrocyclic ring opening of cyclobutene provides an example of an intramolecular interaction of a σ-component and a π-component as shown in Figure 4.17.

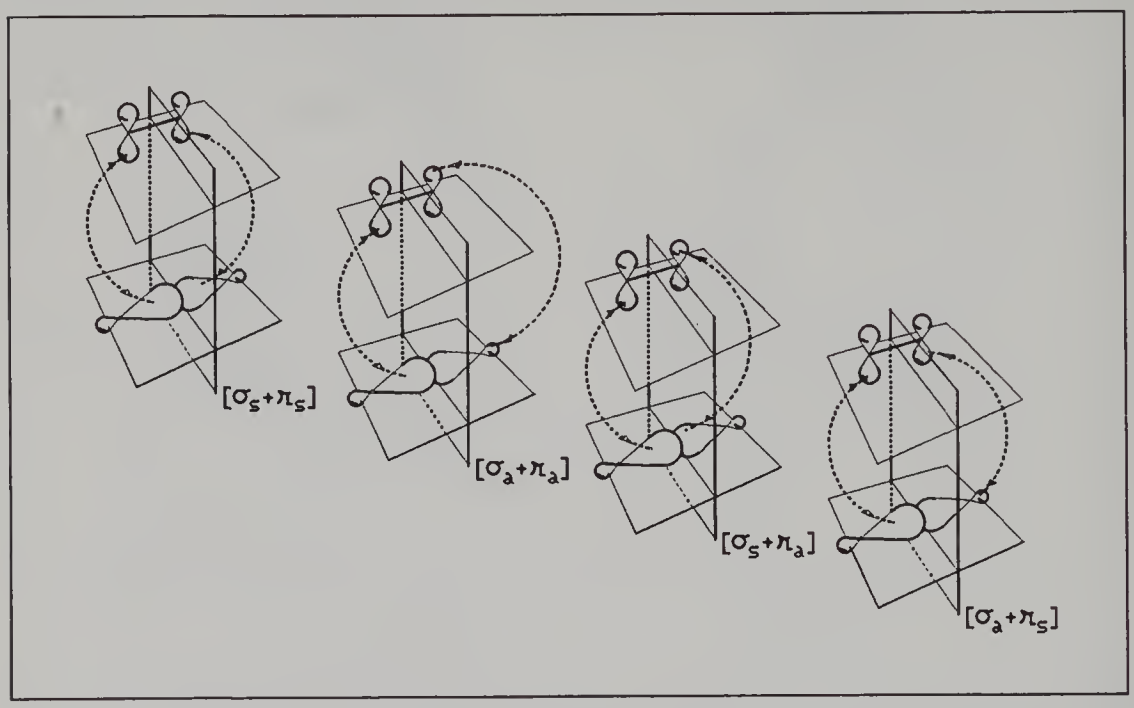


Figure 4.17: *Different modes of interactions between a σ-and a π-component.*

Sigmatropic hydrogen shifts provide an example of the interaction of an *s*-component with a π-component.

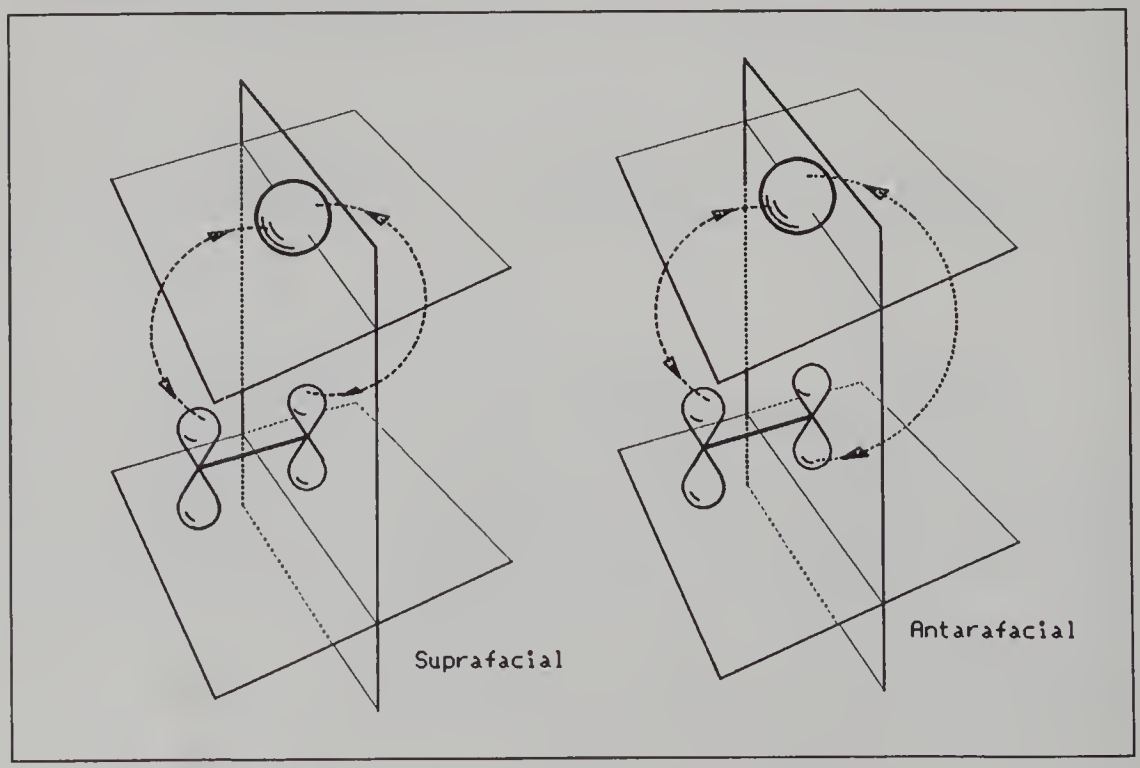


Figure 4.18: *Migration of hydrogen over a π-orbital system.*

Likewise, the interactions between a migrating alkyl group during sigmatropic shifts can be conceived.

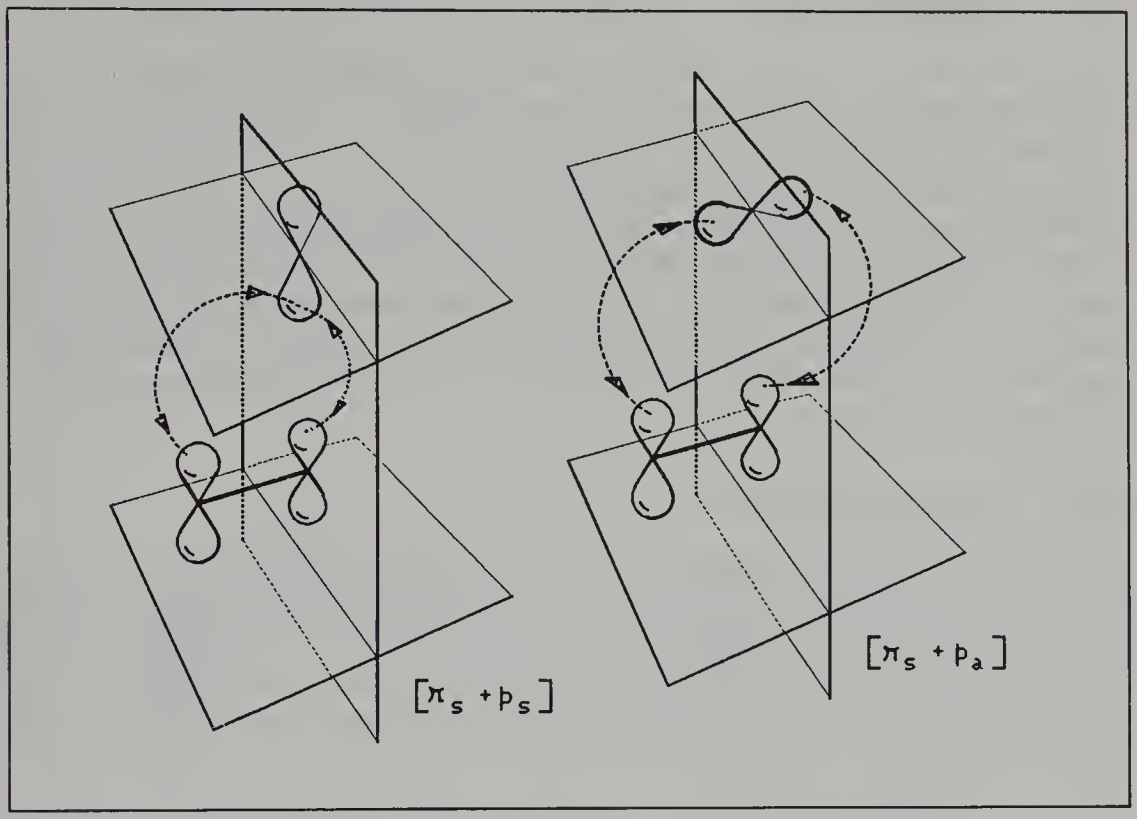


Figure: 4.19: *Two modes of interactions between a π-and a p-component.*

4.2 Applications

The importance of orbital interactions, particularly between the HOMO of one component with the LUMO of the other, during chemical reactions is evident. The physical grounds for HOMO-LUMO differentiation were discussed. The possibilities of the geometrical approach of the interacting orbital system, i.e. suprafacial and antarafacial geometries of the reacting species, were also explained. After having discussed the requisite concepts, the *frontier orbitals approach* can, in a unified manner, be applied to interpret or predict the stereochemical pathways of pericyclic reactions. This approach is better understood by its application to cycloaddition reactions and is discussed first. The approach would later on be applied to electrocyclic reactions.

4.2.1 Cycloadditions

Two well known cycloaddition reactions are the Diels-Alder reaction and the dimerization of olefins. It is established that the Diels-Alder reaction proceeds through a concerted mechanism in the ground state, however, the dimerization of two olefins is not observed to be a feasible reaction in the ground state. The mechanism of the two reactions may be understood by carrying out the frontier orbitals analysis of these reactions.

(4.3)

The presence of substituents both on the diene and dienophile is ignored, for the sake of simplicity, and the emphasis is mainly on the diene and the ethylene component. The pertinent molecular orbitals of butadiene and ethylene, as well as their frontier orbitals labels, are shown in Figure 4.20. Moreover, frontier orbitals interactions between these two interacting olefins are also shown.

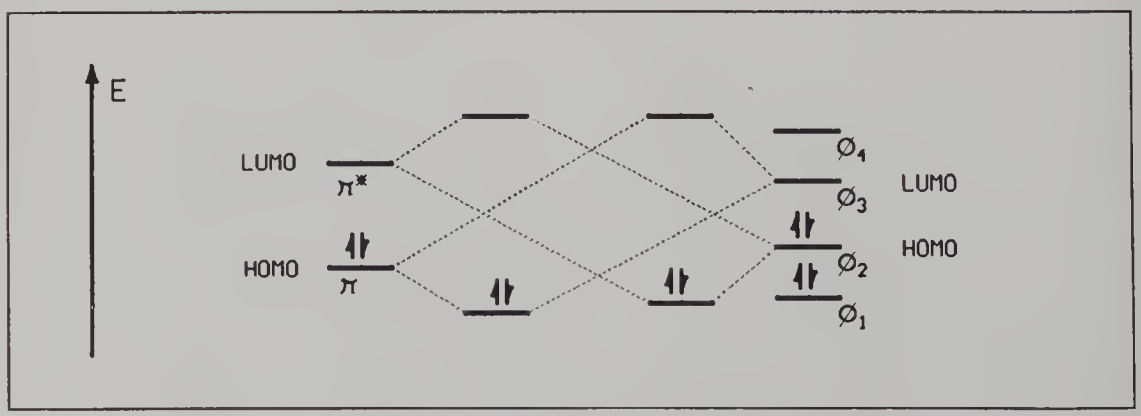


Figure 4.20: *Two possible frontier orbitals interactions during Diels-Alder reaction.*

As mentioned in Chapter 1, the Diels-Alder reaction involves an intermolecular cycloaddition of a diene and an ethylene.

The following two frontier orbitals pairs are possible:

i) $HOMO_{Diene}$ - $LUMO_{Ethylene}$

ii) $HOMO_{Ethylene}$ - $LUMO_{Diene}$

The frontier orbitals interactions between the two possible orbital pairs are shown (Figure 4.21). It is evident that whichever HOMO-LUMO pair is chosen, there are bonding interactions at the two reaction centres where two new σ bonds are being formed. These bonding interactions at both reaction sites are responsible for a low energy barrier to attain a cyclic transition state, and this makes the concerted cycloaddition a thermally allowed process.

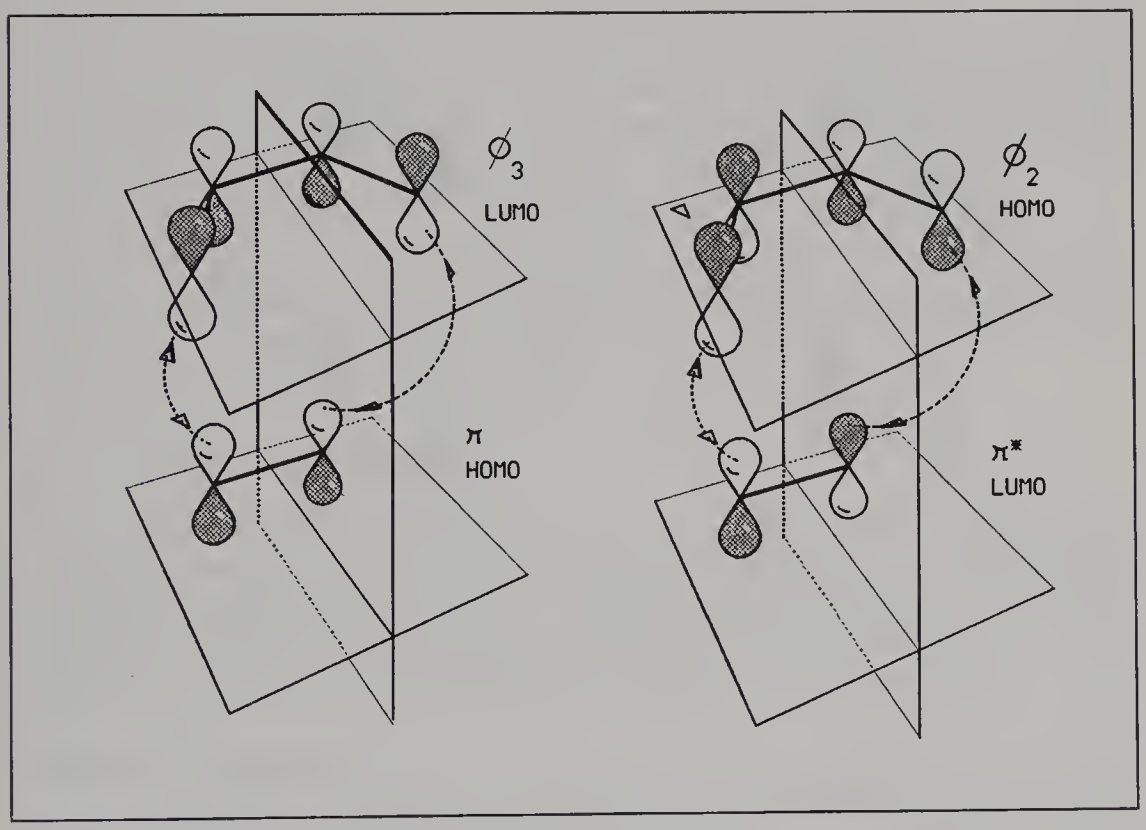


Figure 4.21: *Frontier orbitals interacting suprafacially during Diels-Alder reaction.*

The reaction between a diene and an olefin is designated as a [4π+2π] cycloaddition. This designation defines the number of electrons in the two adding components; one with four electrons, and the other with two electrons. A careful look at the geometrical approach of the two adding components reveals that both components approach and interact suprafacially and that two new σ-bonds are formed on the same face of the π–system. The mechanistic designation for this cycloaddition is represented by $[_4\pi_s+_2\pi_s]$, where the numbers 4 and 2 are the number of participating electrons while the subscript *s* or *a* to the adding component indicates a suprafacial or an antarafacial interaction of the component. Thus, $[_4\pi_s+_2\pi_s]$ expresses a cycloaddition reaction where both the adding components are of π-type; they differ in the number of their electrons and are interacting suprafacially.

The situation, however, in the case of dimerizaton of two olefins is quite different.

(4.4)

The two possible frontier orbitals interactions for a face to face approach of two ethylene molecules is shown in Figure 4.22. A careful look at these interactions reveals that the interactions between these frontier orbitals leads to a bonding interaction at only one of the two reaction centers. This makes the concerted formation of two σ-bonds at the two termini rather difficult. It is clearly due to these reasons that the dimerization of ethylene and related reactions is forbidden in the ground state.

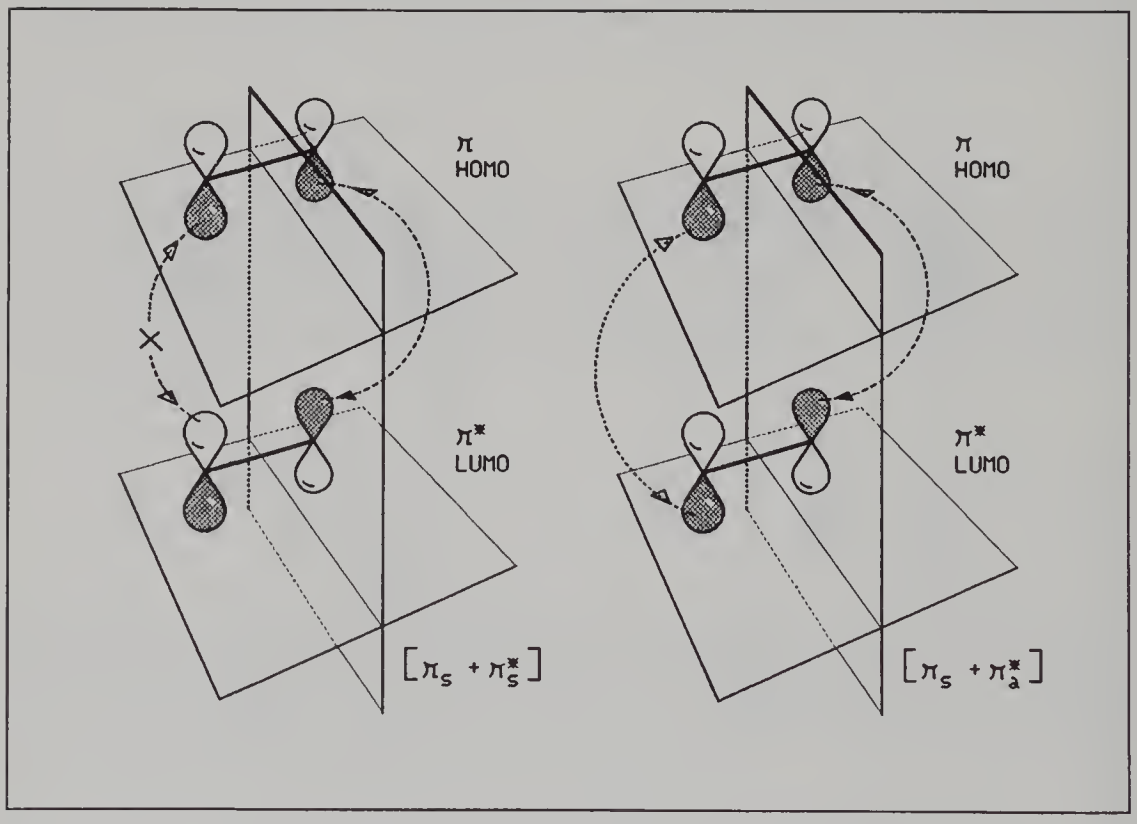
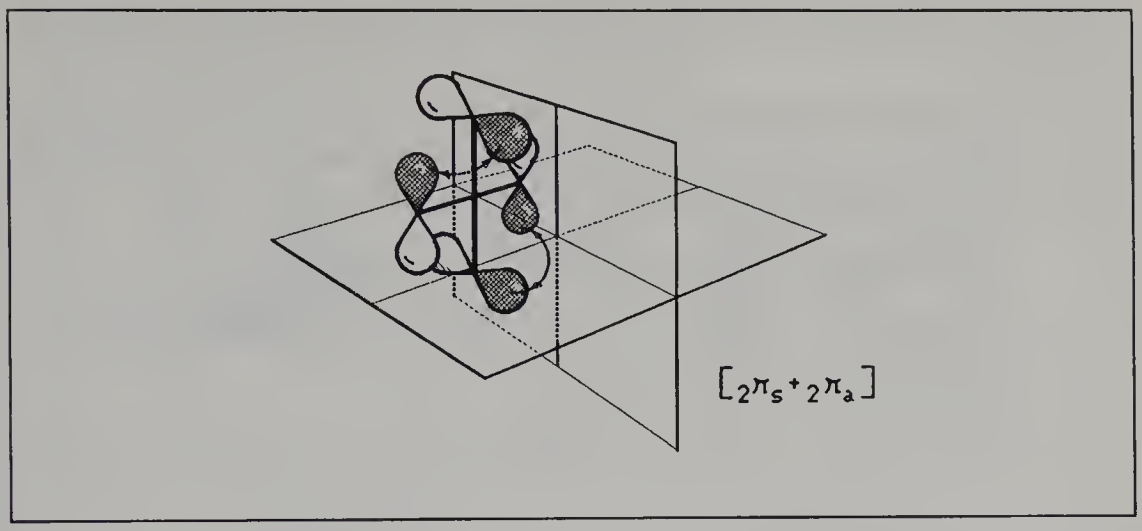


Figure 4.22: *Frontier orbitals interactions during dimerization of ethylene.*

Consider the dimerization of ethylene in an orthogonal approach. During this approach the two double bonds are twisted sufficiently. It is clear that a suprafacial interaction of one component and an antarafacial interaction of the other component leads to bonding interactions at both the reaction centers. A ground state forbidden process thus becomes an allowed process.



During a face to face approach, where the two components interact suprafacially, the mechanistic designation is $[_2\pi_s+_2\pi_s]$ and the process becomes energetically unfavourable. However, when the two ethylene molecules approach in an orthogonal manner, one component interacts suprafacially and the other antarafacially. The mechanistic designation for this energetically favourable process is $[_2\pi_s+_2\pi_a]$.

These arguments are extendable to other cycloaddition reactions having either (4n) or (4n+2) electrons. It might be generalized *that the mechanism for the ground state concerted cycloadditions involving* (4n) *electrons would be* $[_2\pi_s+_2\pi_a]$ *while those involving* (4n+2) *electrons would be* $[_4\pi_s+_2\pi_s]$.

4.2.2 Electrocyclizations

So far the frontier orbitals technique was discussed in terms of intermolecular cycloaddition reactions. However, with a trick, this technique can be applied to electrocyclic reactions which may also be described as intramolecular cycloadditions. During this process the two adding components are present within the same molecule. The reaction may take place either thermally or photochemically.

4.2.2.1 Thermal

4.2.2.1.1 Even-Numbered Polyenes

The interconversion of butadiene and cyclobutene is an example of an even-numbered polyene with (4n) electrons participating in the electrocyclic transformation.

(4.5)

Both the forward and reverse reactions are possible. However, it is more convenient to look at the reaction in the direction of the ring opening. The reaction involves the

conversion of one σ-bond and one π-bond of cyclobutene to two π-bonds of butadiene.

The process may be described as an intramolecular interaction of two components; i.e., a σ-component and a π-component, each with two electrons. The interaction between these two components is possible in three different ways:

i) Both components interact suprafacially.

ii) One component interacts suprafacially while the other antarafacially (two possibilities).

iii) Both components interact antarafacially.

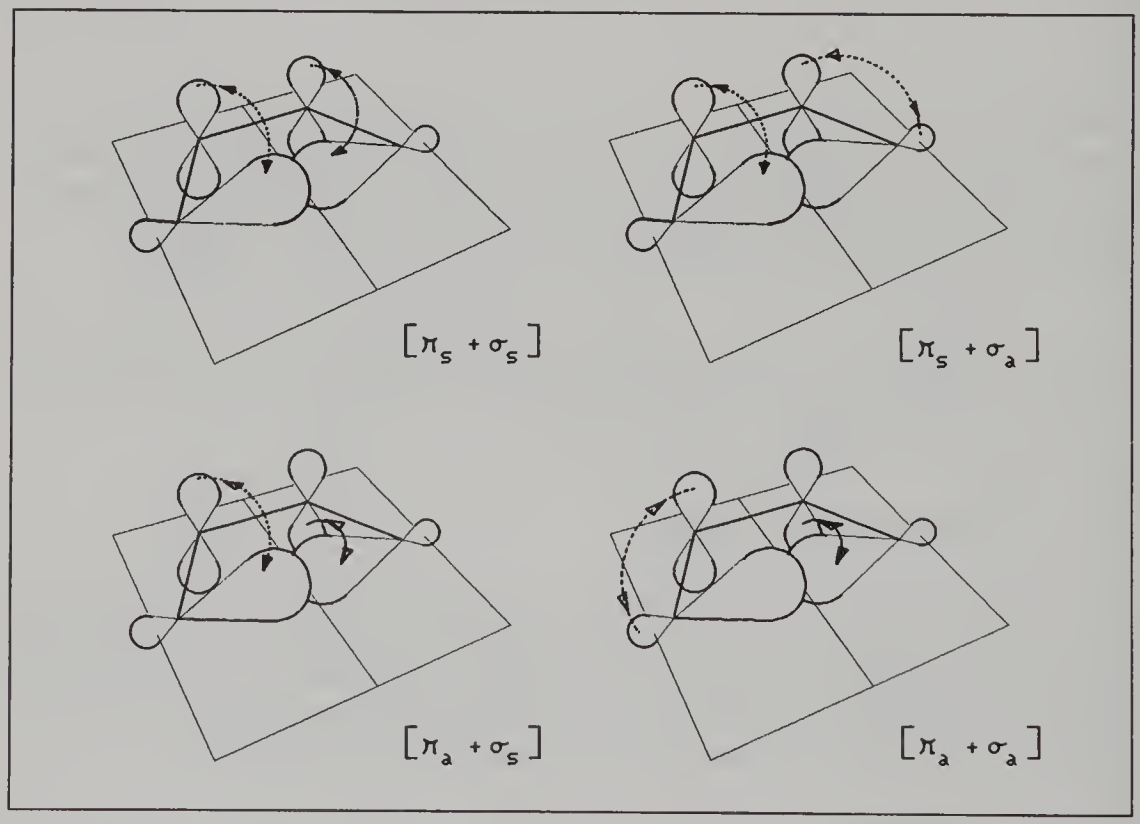


Figure 4.23: *Possible modes of intramolecular interactions between σ- and π-components.*

The stereochemical outcome of all these possibilities may be the same, or different, depending on the nature of the substituents. The following two combinations of the components of the frontier orbitals are possible:

i) $\sigma_{HOMO} - \pi^*_{LUMO}$

ii) $\sigma^*_{LUMO} - \pi_{HOMO}$

The ring opening of cyclobutene is the result of an interaction of a σ-component with a π-component. This intramolecular interaction may take place either in a conrotatory, or disrotatory, manner. Normally, the majority of chemical reactions take place in the direction of maximum HOMO - LUMO overlapping of the reacting species. It would be logical to see which of the two mechanisms results in maximum

bonding at the two reaction centers. The two situations resulting from a disrotatory, and a conrotatory, opening are shown in Figure 4.24.

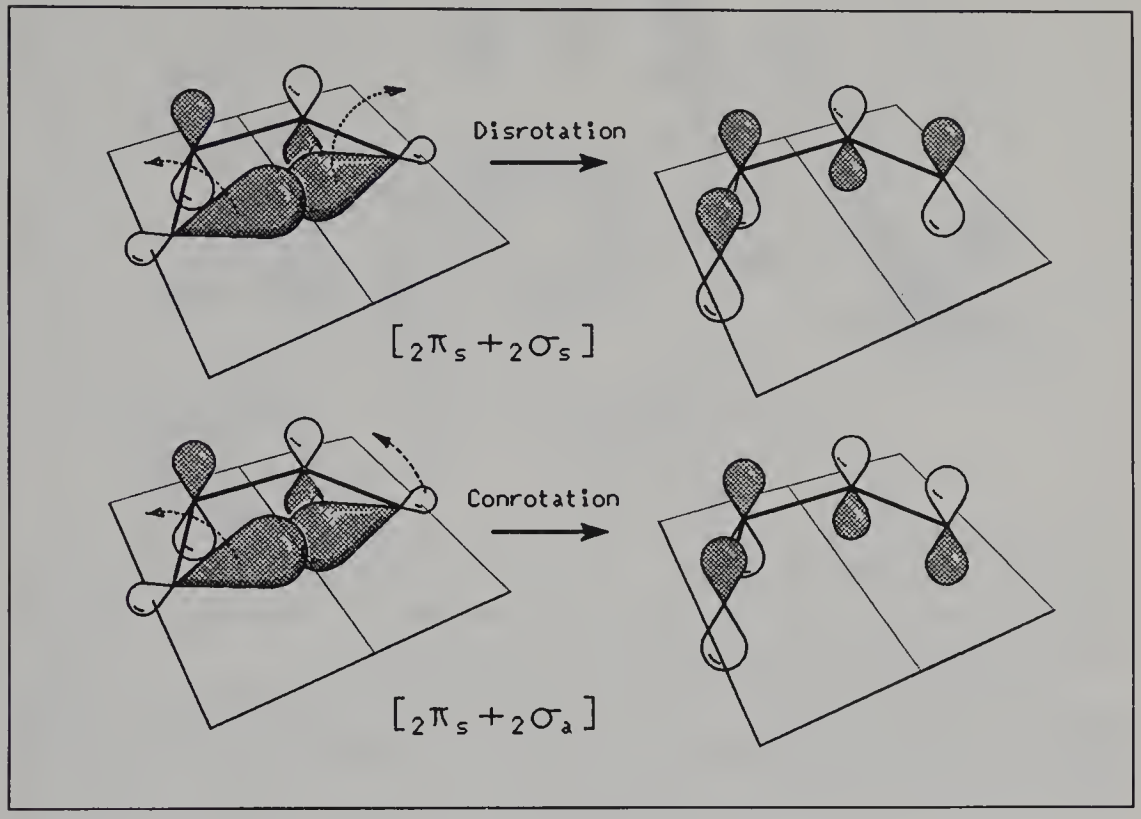


Figure 4.24: *Two possible modes of ring opening of cyclobutene.*

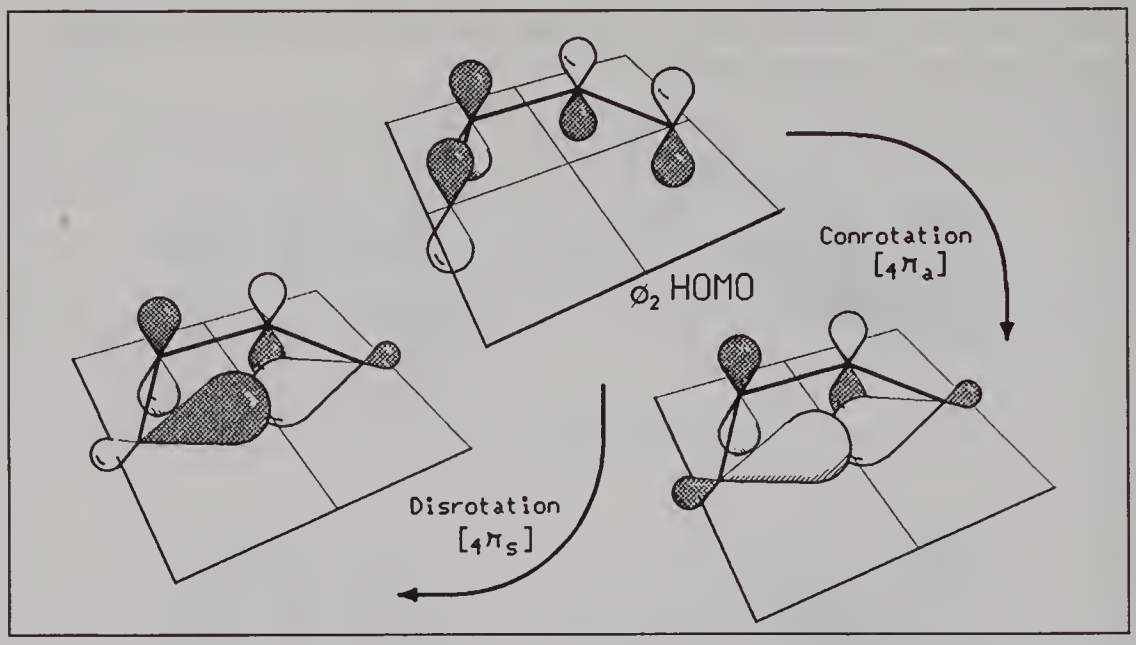
A careful look at the two situations reveals that the conrotatory process leads to bonding interactions at both reaction centres while the disrotatory process results in bonding interaction at only one reaction centre. Hence, the transition state for the conrotatory process is of lower energy and the process becomes energetically favourable.

Problem 4.3:

The frontier orbitals pair shown in Figure 4.24 is σ_{HOMO} - π^*_{LUMO}. Confirm that the alternate set would also lead to the same conclusion. Write the mechanistic designation for the alternate set of frontier orbitals.

It is also evident from Figure 4.24 that during conrotation, the σ-component is interacting antarafacially while the π-component is interacting suprafacially. The mechanistic designation for this process is $[_2\sigma_a + _2\pi_s]$. On the other hand the disrotatory process involves a suprafacial interaction of both components with each other. The mechanistic designation is, therefore, $[_2\sigma_s + _2\pi_s]$.

The same reaction may also be analyzed in the reverse direction, i.e. cyclization of butadiene. The choice between the two alternate mechanisms may easily be made by looking at the HOMO of the diene. Evidently a conrotatory mechanism is the favoured option. The mechanistic designation for cyclization reaction is $[_4\pi_a]$ indicating that the diene having (4π) electrons undergoes cyclization in an antarafacial manner.



It may be concluded that *the thermal ring opening of cyclobutene would be an allowed process through conrotation. The mechanistic designation would be* $[_2\sigma_a+_2\pi_s]$ *for ring opening and* $[_4\pi_a]$ *for cyclization reaction.*

Frontier orbitals analysis of the interconversion of 1,3,5-hexatriene and 1,3-cychlohexadiene may be carried out the same way (Equation 4.6).

(4.6)

The process of ring opening involves an intramolecular interaction of a 2-electron-σ-component to a 4-electron-π-component. It can be seen that a 4-electron-π-component of cyclohexadiene describes the molecular orbital system of butadiene. The two possible sets of frontier orbitals for the reaction are:

i) $\sigma_{(HOMO)} - \phi_{3\,(LUMO)}$

ii) $\sigma^*_{(LUMO)} - \phi_{2\,(HOMO)}$

Using one of the pairs, e.g. $\sigma_{HOMO} - \phi_{3\,(LUMO)}$, the conrotatory and disrotatory ring openings of cyclohexadiene are shown in Figure 4.25. Evidently, a disrotatory mechanism is the energetically favoured process and the mechanistic designation is $[_2\sigma_s+_4\pi_s]$.

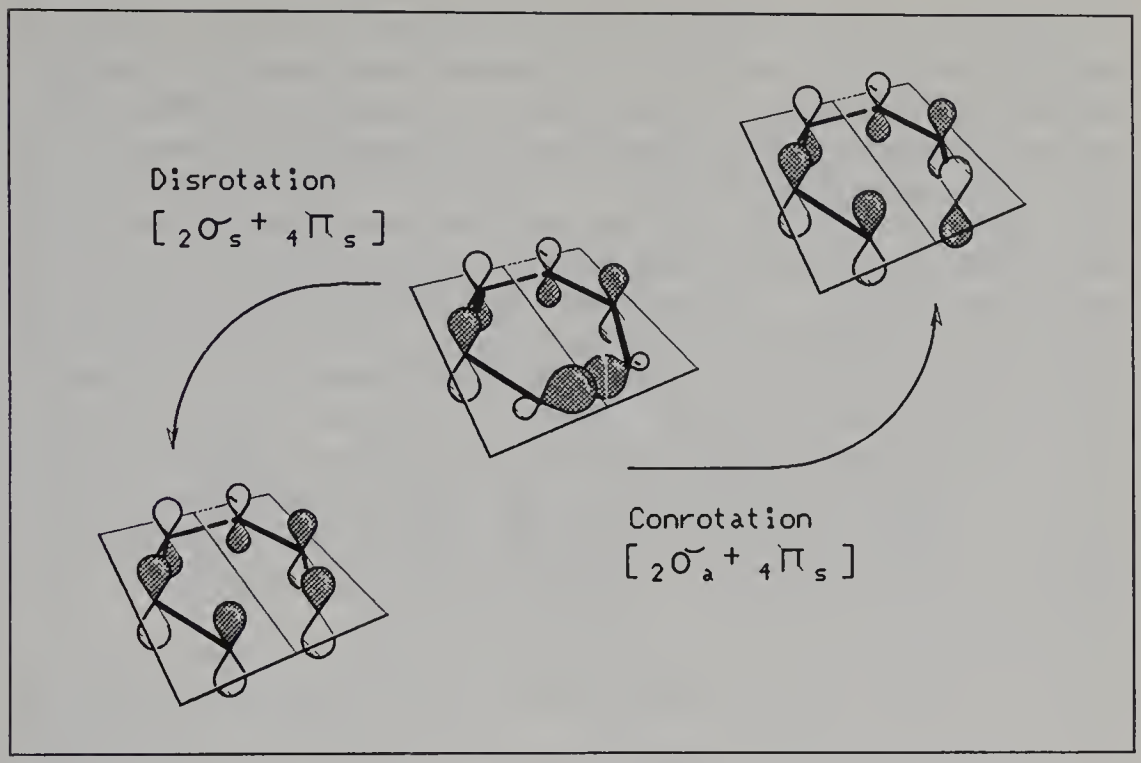


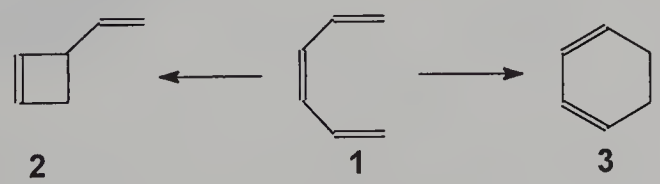
Figure 4.25: *Disrotatory and conrotatory ring opening of 1,3-cyclohexadiene.*

The mechanistic designation for the cyclization reaction may be ascertained again by considering HOMO (i.e. ϕ_3) of the triene. Evidently a suprafacial interaction at the two termini, through disrotation, leads to the formation of a σ-bond at the two reaction centers. Hence, $[_6\pi_s]$ is the favoured mechanism.

Problem 4.4:

Draw the other frontier orbitals pair for 1,3-cyclohexadiene and write the mechanistic designations for the ring opening and cyclization reactions.

There remains another aspect of the problem. The isomerization of hexatriene-cyclohexadiene follows the predicted disrotatory mechanism in a suprafacial manner when all six electrons are taking part in the pericyclic process. However, there might exist the possibility when only a part of the conjugated array of electrons takes part in the pericyclic change. For example, when only four out of six electrons of the conjugated system **1** undergo an electrocyclic change, the product **2** may also be formed in addition to product **3**.



2 **1** **3** (4.7)

The products **2** and **3** are the results of partial and total mobilization of electrons during the reaction, respectively. The number of possibilities increase with an increase in the number of electrons making up the conjugated system.

The results of complete, or partial, mobilization of electrons may lead to a variety of pericyclic products. For example, 1,3,5,7-octatetraene **4** may theoretically undergo a number of pericyclic changes. Experimentally, however, only product **5** is formed as illustrated in Figure 4.26. This observation may be rationalized on the basis of a phenomenon known as *periselectivity* where the whole of the conjugated array of electrons, or a part of them, is mobilized. The Woodward-Hoffmann rules limit the total number of electrons undergoing suprafacial additions to 2,6,10... electrons, i.e. (4n+2), where n=0,1,2... . Likewise they limit the total number of electrons undergoing antarafacial additions to 0,4,8,..... electrons, i.e. (4n). However, the rules do not identify which of the possible (4n+2) electron systems would be formed in case both the processes were feasible. For example, the product **5** is formed when the whole of the conjugated system (8-electrons) of the tetraene **4** is involved in the pericyclic change. However, when only one half of the electrons (4 electrons) of the tetraene are mobilized, products **7** and **8** are formed. The Woodward-Hoffmann rules predict both these possibilities to be thermally allowed in an manner. However, as mentioned above, only product **5** is experimentally obtained.

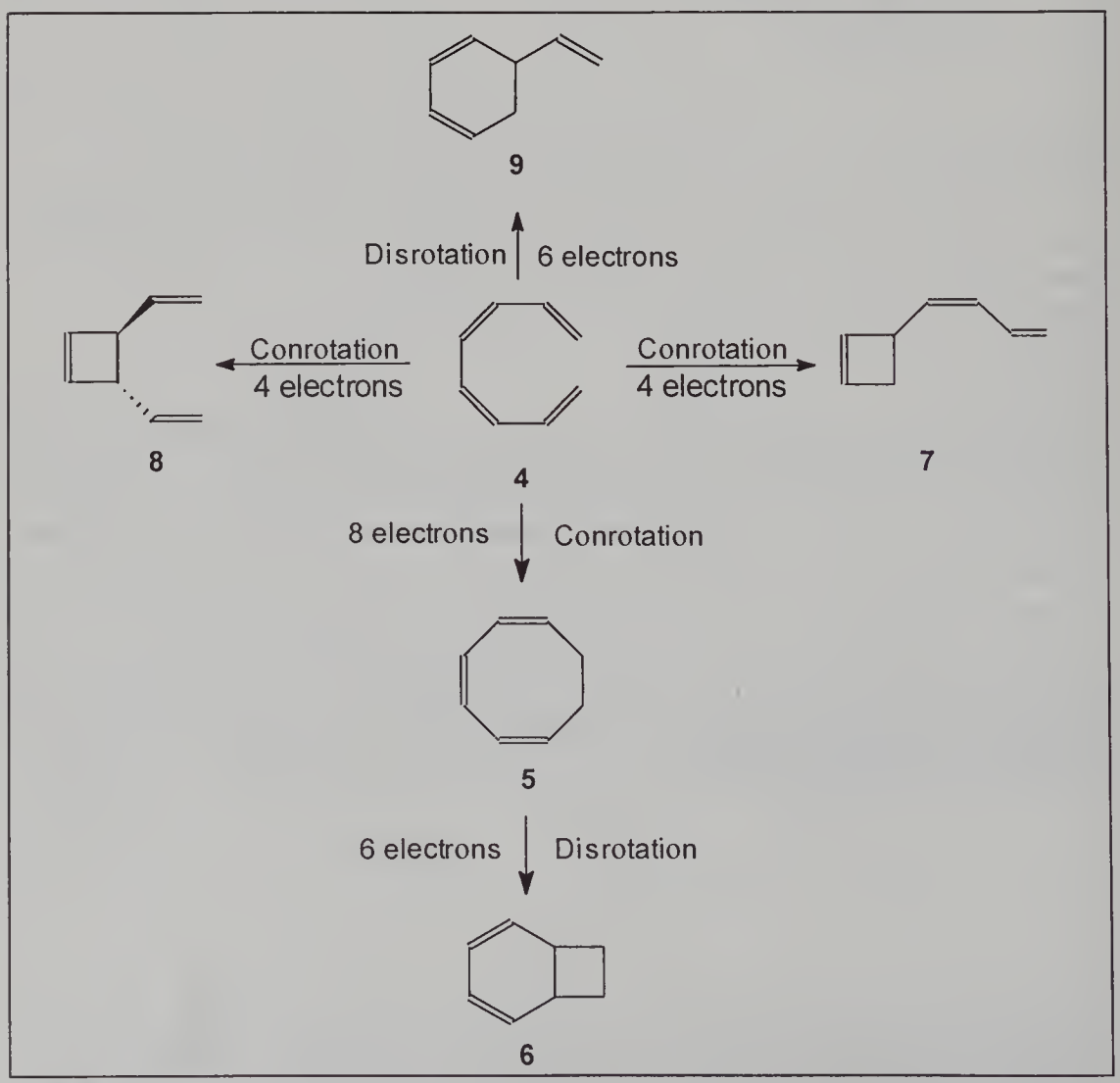
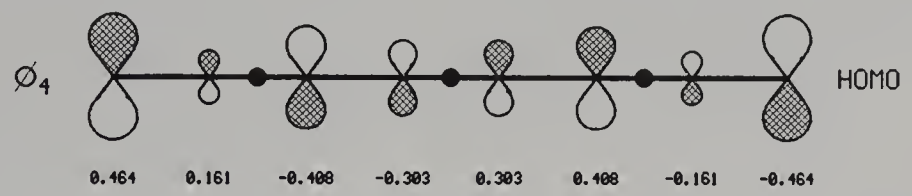


Figure 4.26: *Different possible products of the reactions of 1,3,5,7-octatetraene (**4**).*

The reason for this periselectivity may be understood if the concept of the coefficients of different atomic orbitals, making up the molecular orbital of a polyene, is understood (Appendix A). At this stage, it is sufficient to mention that the bond formation during a reaction normally takes place at those centres where the orbitals carry the largest coefficients. As an example, the HOMO of tetraene **4** is shown with the coefficients of the atomic orbitals. A comparison of the orbital coefficients of the HOMO (shown below) illustrates that the terminal orbitals carry the largest coefficients. Therefore, the formation of the σ-bond during electrocyclization of tetraene **4** should take place at the two terminal carbon atoms.



The formation of the sole product **5** during electrocyclization of tetraene **4** is thus explained [4 a-b].

Problem 4.5:

Write mechanistic designations for all the pericyclic changes shown in Figure 4.26.

4.2.2.1.2 Odd-Numbered Polyenes

The frontier orbitals criterion is also applicable to odd-numbered polyene systems. Cyclopropyl-allyl isomerizations can hence be easily explained by applying the above concepts.

(4.8)

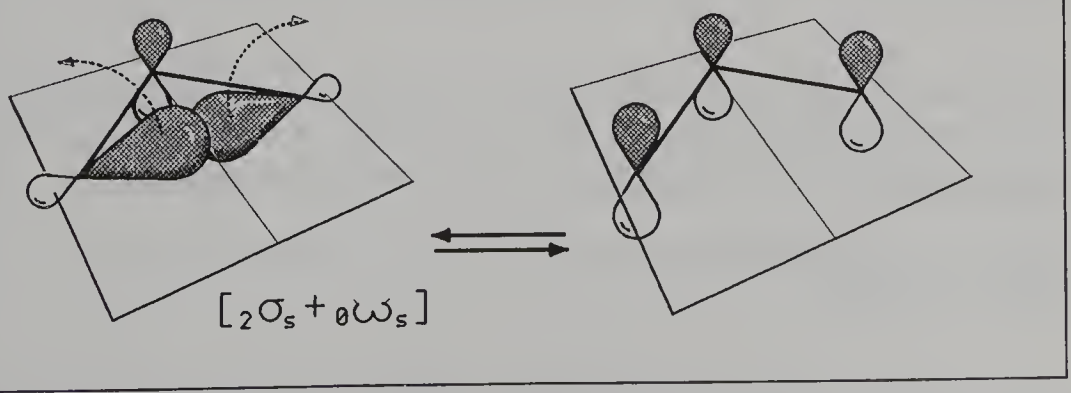


Figure 4.27: *Disrotatory ring opening of cyclopropyl cation.*

Problem 4.6:

Disrotatory ring opening of cyclopropyl cation to allyl cation is shown in Figure 4.27. Write a mechanistic designation for the valence isomerization of the corresponding anion. What would be the conclusions regarding the cyclization processes for the two ionic species?

The ring opening of cyclopentenyl cation to pentadienyl cation may be viewed as an intramolecular interaction of a σ-component to a π-component (allyl) as shown in Figure 4.28. The molecular orbitals of the two species were illustrated earlier in Figure 3.23.

(4.9)

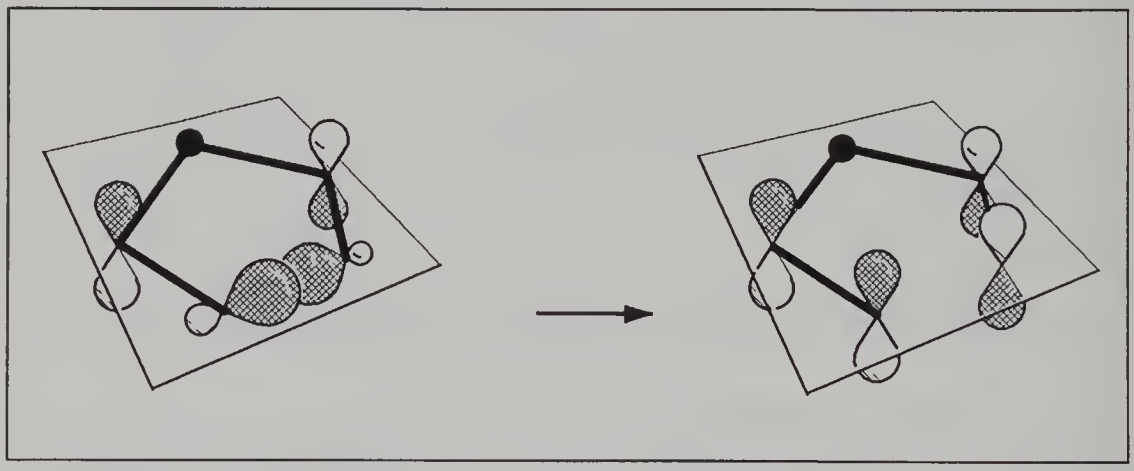


Figure 4.28: *Conrotatory ring opening of cyclopentenyl cation.*

Problem 4.7:

Label the frontier orbitals for the system undergoing an electrocyclic change (Equation 4.5) and show that the ground state reaction would take place through conrotation. Draw an alternate mechanistic possibility for the reaction.

The valence isomerization of 1,3-dipolar compounds can be explained using the same arguments.

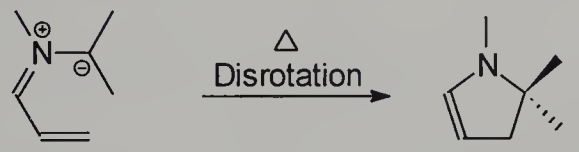
Problem 4.8:

Write the mechanistic designation for a thermally allowed cyclization of a 1,3-dipolar compound.

The analogous cyclization of a 1,5-dipolar system can also be explained using the same arguments.

Problem 4.9:

Draw frontier orbitals for the reaction and predict the course of thermal reaction using FMO concept.



It is evident that the frontier orbitals criterion is equally applicable to both even-and odd-numbered polyene systems, and it may be generalized that *polyenes with (4n) electrons undergo thermal electrocyclic transformation through conrotation, while those with (4n+2) electrons through disrotation.*

4.2.2.2 Photochemical

The frontier orbitals concept is also applicable to photochemical reactions. The photoexcitation of cyclobutene leads to a change in electron occupancies resulting in a new set of frontier orbitals as shown in Figure 4.29.

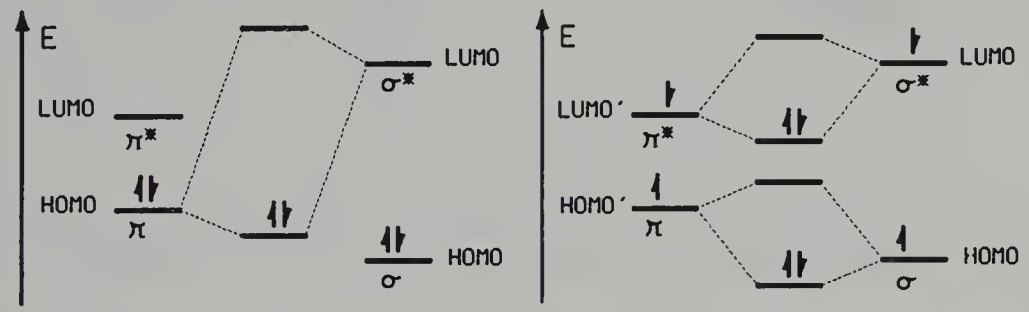


Figure 4.29: *Frontier orbitals interactions in the ground state and excited state of butadiene and cyclobutene.*

Problem 4.10:

Take a look at Figure 4.29 and find the energy-drop as a result of interactions of frontier orbitals in the ground state. Do the same for the excited state process.

Consider the interactions between the HOMO - HOMO′ or LUMO - LUMO′ frontier orbitals pairs as shown in Figure 4.30. It is evident that the disrotatory mechanism, leading to bonding interactions at both the termini, is favoured as was predicted by Woodward and Hoffmann.

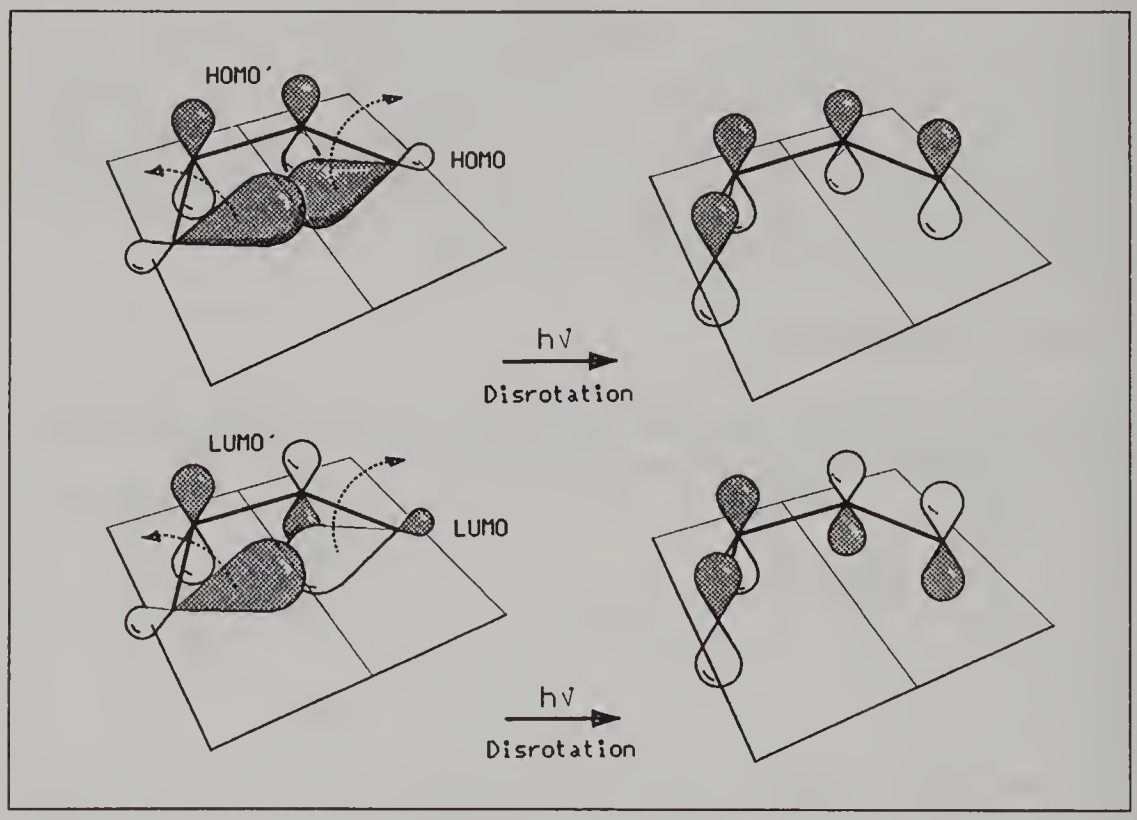


Figure 4.30: *Photochemically allowed disrotatory ring opening of cyclobutene.*

4.3 Generalized Selection Rules

The correlation diagram method based on the principle of orbital symmetry conservation is one way of reasoning. However, the orbitals interaction scheme appears to be more unificative and broader in scope as it gives a direct description of the nature of chemical reactions. The method requires no selection rules and is completely automatic. Usually, a knowledge of the HOMO and LUMO of a very simple system is needed and this makes the theory quite simple and extendable. Contradictions are found between predictions based on the correlation diagram method and on the frontier orbitals method, but the latter are able to treat many problems which are beyond the reach of the former method. An interesting application of this method is in the explanation of the catalytic action of the *d*-orbitals which causes an otherwise symmetry forbidden reaction to become allowed [5 a-d].

The analysis of electrocyclic reactions on the basis of orbital correlation diagrams, and through frontier orbitals approach, is discussed. However, the allowedness and stereochemistry of a pericyclic reaction can also be determined without resort to these theories. A set of generalized rules were derived by Woodward and Hoffmann [6] which exploit the concept of suprafacial and antarafacial component analysis. This simple generalized selection rule is sometimes described as the Odd-Sum rule and may be stated as follows:

A pericyclic reaction is allowed in the ground state if the sum of $(4n+2)_{supra}$ *and* $(4n)_{antara}$ *components is odd. If the above total is even, the reaction is forbidden.*

Odd-electron systems generally conform to the patterns for even-electron systems containing one more electron corresponding to the ground state reaction.

He *et al* [7] have suggested another selection rule which is referred to as the Odd-Even rule which states:

A pericyclic reaction is allowed in the ground state if one half of the total number of electrons taking part in a pericyclic change is odd (or even) and the total number of antarafacial components is even (or odd).

A detailed discussion of the two selection rules follows.

4.3.1 Odd-Sum Rule

Before applying the rule to pericyclic reactions, the concept of antarafacial and suprafacial interactions is revised. A suprafacial interaction is defined as the one in which new bonds are formed on the same face of a π-system while the bond formation for an antarafacial interaction is on the opposite face of a π-system. On the basis of the above definitions a component analysis may be carried out using Figure 4.1. The steps involved are described below;

i) Identify the bonds being formed, or broken, during the course of a reaction.

ii) Draw the constituent *p* orbitals for a π-component and sp^3 hybrid orbitals at each end of the σ-component (disregard the orbital phases).

iii) Identify two orbitals which interact to form the σ-bond of the product, and then connect the two orbitals with a curved arrow. When orbitals overlap in a π manner one may arbitrarily choose the pair of lobes (top or bottom), while making the connections.

iv) Examine the components of the reactants. Each component should have two curved arrows entering it, one to each end. The arrows indicate the stereochemical mode of reaction of each component. If, for a π component, the two arrows are connected to the same face then the mode is *supra,* else, if connected to opposite faces, then *antara.*

For a σ component, if both arrows are connected to the larger (inner) lobes of the sp^3 orbitals or both arrows to the smaller (outer) lobes then the mode is *supra*, else the mode is *antara.*

If the component is a single orbital, then it is called ω. If both arrows terminate to the same lobe, then that component is interacting suprafacially, else antarafacially.

v) Add up (4n+2) supra components and (4n) antara components. If the total is odd, then the reaction is allowed in the ground state, else forbidden.

These steps are illustrated in Figure 4.31 and the result of the stepwise analysis of the reaction is summarized in Table 4.1.

Table 4.1: *Generalized selection rules by Woodward and Hoffmann (The Odd-Sum rule).*

$\sum ({}_{\pi,\sigma,\omega}[4n+2]_s + {}_{\pi,\sigma,\omega}[4n]_a)$	△	hν
odd	allowed	forbidden
even *	forbidden	allowed

* zero is also considered as an even number.

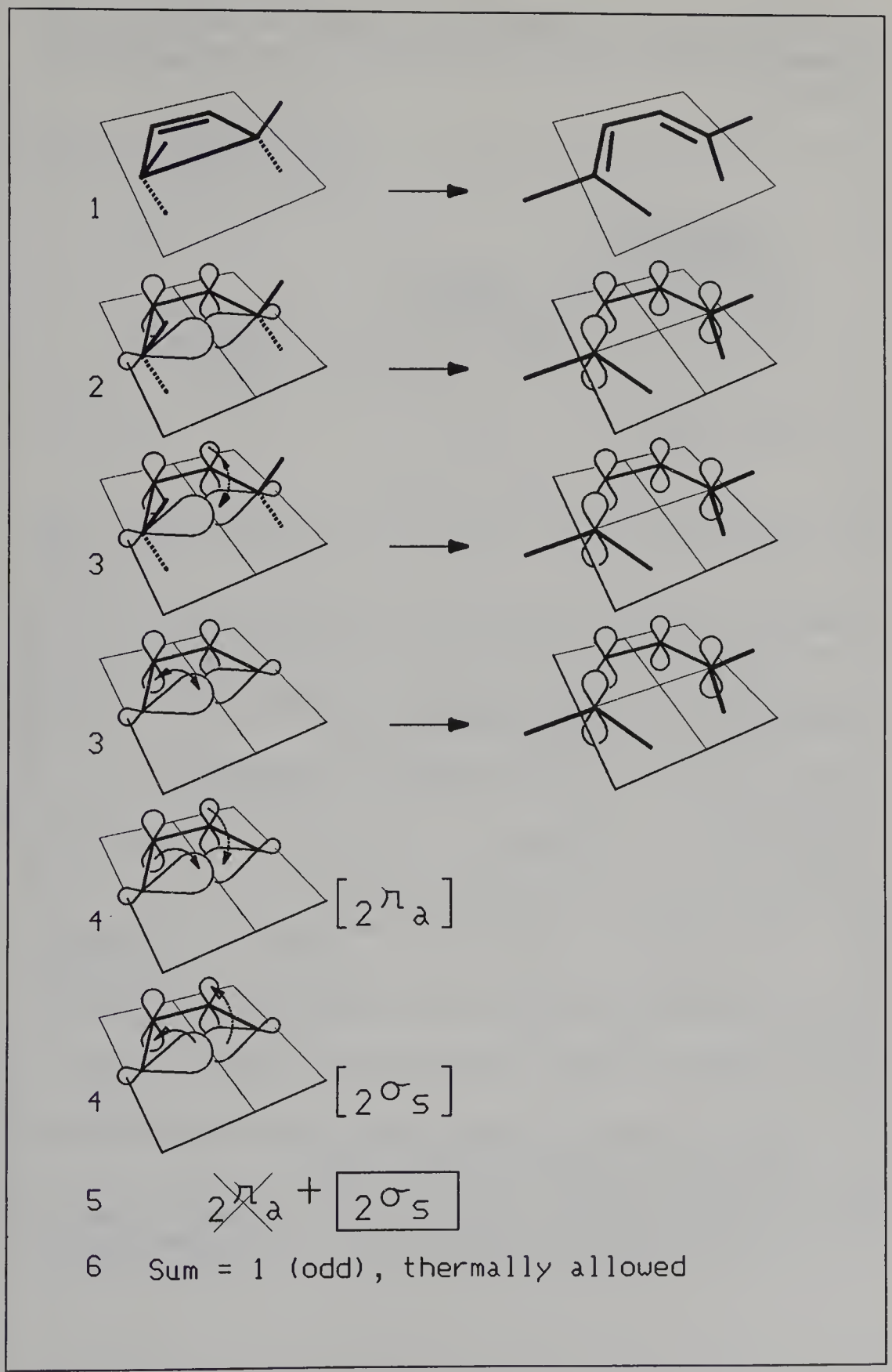


Figure 4.31: *Steps involved during the application of the Odd-Sum rule to electrocyclic reactions.*

Following the steps outlined in Figure 4.31, the analysis of electrocyclic ring opening of cyclobutene is carried out. Three situations may be envisaged as shown in Figure 4.32.

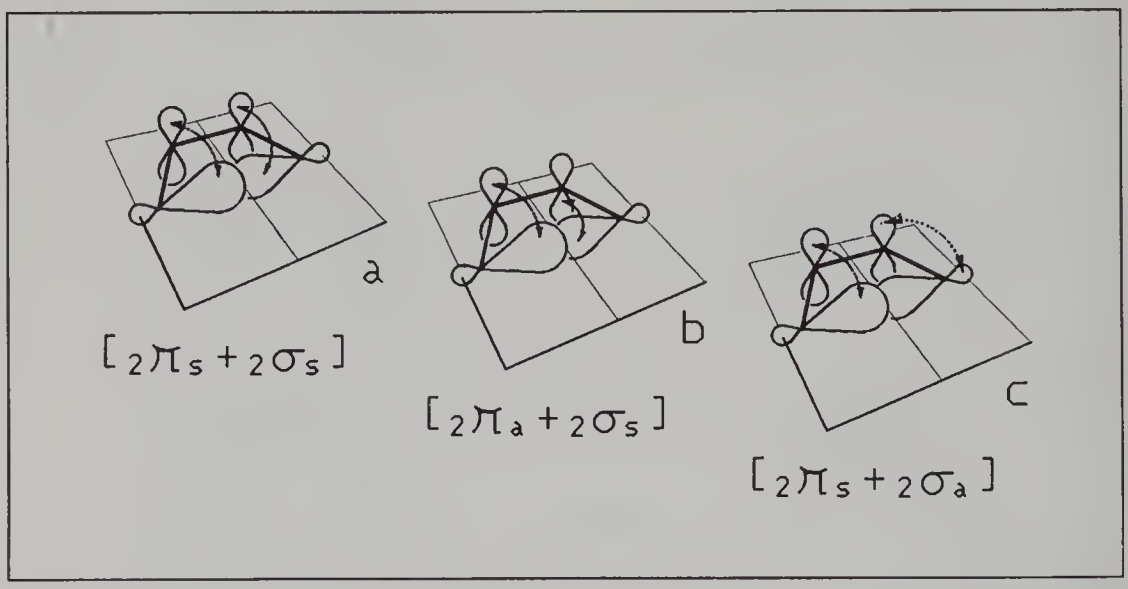


Figure 4.32: *Analysis of electrocyclic ring opening of cyclobutene based on Woodward-Hoffmann rules (Odd-Sum rule).*

On the basis of the Odd-Sum rule, a thermally allowed process would be $[_2\sigma_s + {}_2\pi_a]$, which is obviously a conrotatory mechanism.

Table 4.2: *Predictions based on the Odd-Sum rule for the ring opening of cyclobutene.*

Situation (Figure 4.32)	Faciality		Sum Σ	Prediction
	$_\sigma[4n+2]_s$	$_\pi[4n]_a$		
a	2	0	Even	forbidden
b	1	0	Odd	allowed

Problem 4.11:

i) Apply the rule to Situation **c** (Figure 4.32) and confirm that the reaction is also thermally allowed through this alternate mechanism.

ii) Carry out the component analysis of hexatriene-cylohexadiene isomerization and confirm the conclusions drawn on the basis of frontier orbitals criterion.

Cyclopropyl-allyl cation isomerization may likewise be analyzed (Figure 4.33).

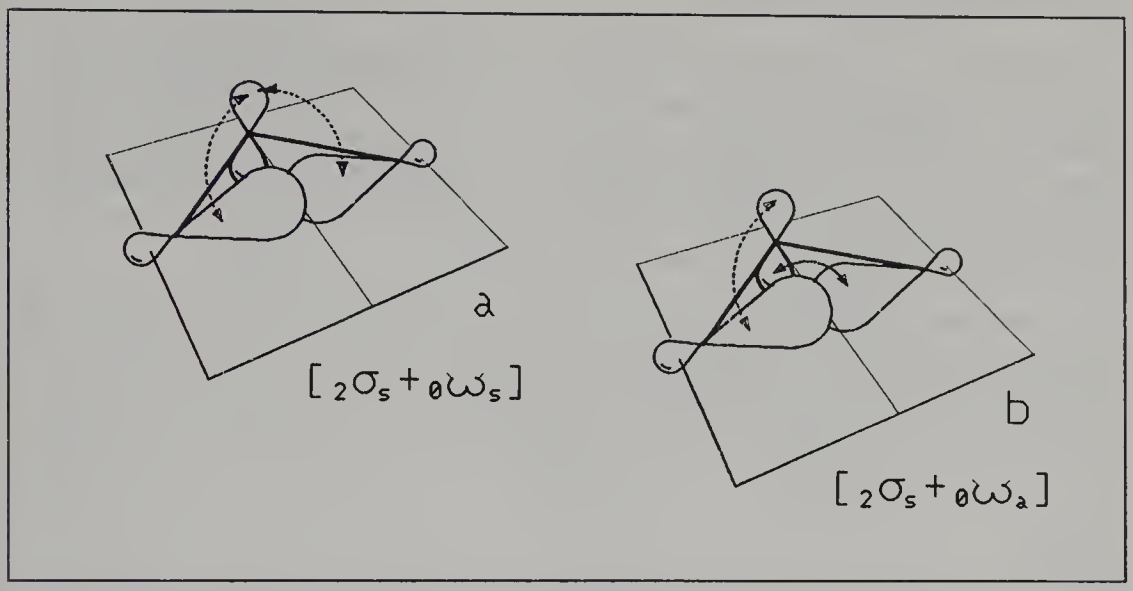


Figure 4.33: *Application of the Odd-Sum rule to cyclopropyl-allyl cation isomerization.*

Table 4.3: *Predictions based on the Odd-Sum rule for the ring opening of cyclopropyl cation.*

Situation (Figure 4.33)	Faciality		Sum	Prediction
	$_{\sigma}[4n+2]_s$	$_{\omega}[4n]_a$	Σ	
a	1	0	Odd	allowed
b	1	1	Even	forbidden

Problem 4.12:

Thermal ring opening of cyclopropyl cation would take place through disrotation:

i) Apply the Odd-Sum rule to the reverse reaction and confirm the above statement.

ii) Confirm the same for the corresponding anion.

iii) What would be the mechanistic designations for the thermal interconversion of both cyclopentenyl cation and anion to that of the corresponding pentadienyl cation and anion?

4.3.2 Odd-Even Rule

The Odd-Sum rule introduced by Woodward and Hoffmann is quite valuable for a detailed consideration of all classes of pericyclic reactions. However, the rule is generally limited to even-electron systems. He *et al* have suggested the validity of a new selection rule for pericyclic reactions which is referred to as the Odd-Even rule. This rule can be applied to pericyclic reactions regardless of whether the number of participating electrons is odd or even. The rule states:

A ground state pericyclic reaction is thermally allowed when only half of the total number of electrons that take part in a reaction is odd (or even) and the total number of antarafacial components is even (or odd).

i.e. H = odd, A = even

or H = even, A = odd

where

H represents one half of the total number of electrons involved in the reaction

A represents the total number of antarafacial components in the reaction.

The rule is applied with the following three considerations:

i) This rule can directly be applied to even-electron systems. However, in odd-electron systems, the rule can still be applied by adding 1 to the total number of electrons involved.

ii) Zero should be regarded as an even number.

iii) If a ground state pericyclic reaction is thermally forbidden, then it is photochemically allowed.

The Odd-Even rule is not only more general than the Odd-Sum rule, but is also very convenient for practical use. This rule is applied to electrocyclic reactions which may be regarded as single-component cycloadditions.

As an example, consider the conversion of butadiene into cyclobutene which can occur either by a conrotatory, or a disrotatory, mode as shown in Figure 4.34.

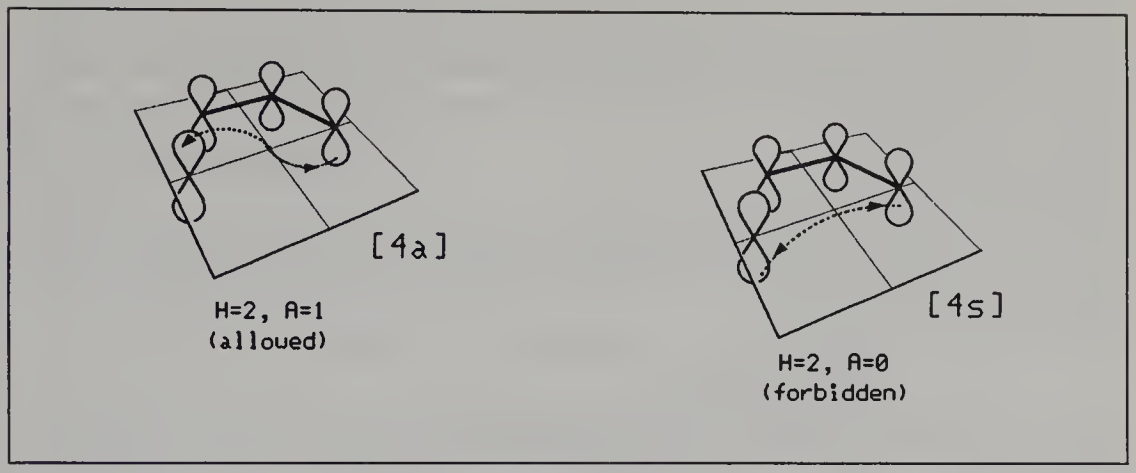


Figure 4.34: *Application of the Odd-Even rule to butadiene and cyclobutene interconversion.*

A conrotatory motion leads to a σ bond formation in the antarafacial sense, and the component is labeled as antarafacial. Conversely, a disrotatory motion of the terminal orbitals leads to bond formation in the suprafacial sense, and the component is thus labeled as suprafacial. In both cases, four electrons are taking part in the reaction, i.e. H=2 (even). The Odd-Even rule demands an odd number of antarafacial components, which is obviously the case for a conrotatory mechanism, i.e. A=1 (odd). Hence, a thermal reaction is allowed through conrotation, which is in conformity with the predictions based on the Odd-Sum rule.

As another example, consider the disrotatory electrocyclization of allyl cation where H=1 and A=0. The Odd-Even rule correctly predicts that the disrotatory path would be thermally allowed .

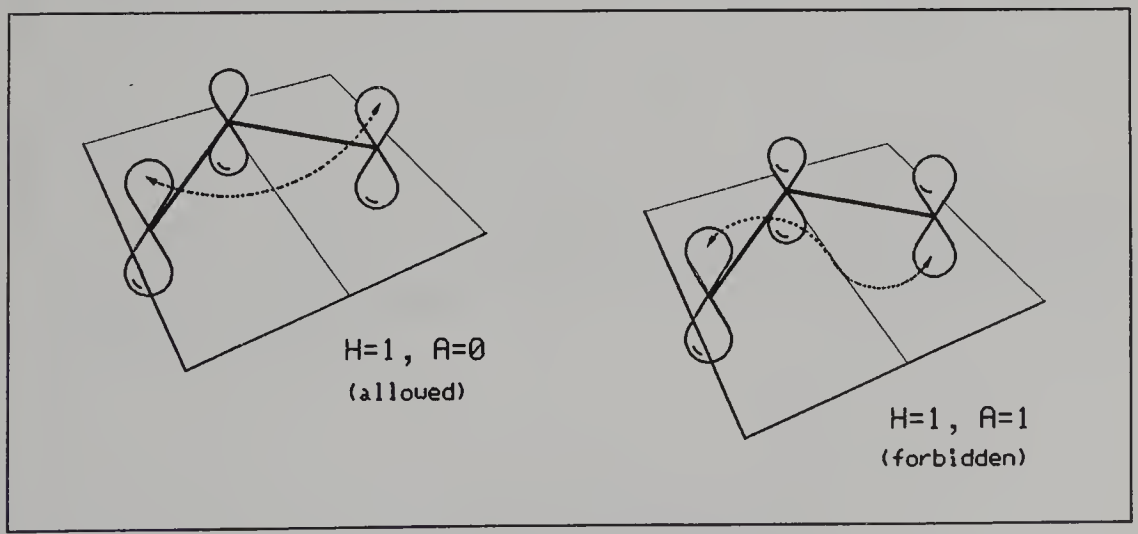


Figure 4.35: *Application of the Odd-Even rule to allyl cation.*

As mentioned earlier, the Odd-Sum rule is applicable to odd-electron systems just as well. Hence, for an electrocyclic reaction involving an allyl radical there are three electrons (odd) and an additional electron has to be added before applying the rule.

For the disrotatory process H=2 and A=0, while for the conrotatory process H=2 and A=1. Thus, it is evident that the conrotatory mechanism is the mechanism of choice. Further discussion [8] on the mechanism of cyclopropyl-allyl radical interconversion follows in Chapter 6.

Problem 4.13:

Using the Odd-Even rule, predict the mechanism of electrocyclizations of the following polyene systems:

i) 1,3,5-hexatriene.

ii) Pentadienyl cation, anion and radical.

The Odd-Even rule is a convenient procedure for predicting the allowedness of pericyclic reactions. Only two easily deduced parameters are employed, i.e. one half of the total number of electrons taking part in the reaction (H) and the number of antarafacial components (A). If the odd, or even, character of these two parameters differs then the reaction is predicted to be thermally allowed. Moreover, systems with an odd number of electrons in the reaction are explicitly considered by adding one additional electron to the ring before applying the rule.

Many more examples showing the application of the generalized rules could be cited, however, space limitations preclude their mention here.

There are many problems which can not be solved on the basis of correlation diagrams or the frontier orbitals method. These problems were discussed by Anh [9] by applying the Möbius-Hückel approach, which is based on the concept of aromaticity. The Möbius-Hückel approach constitutes the subject matter of Chapter 5.

4.4 References

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5. Möbius-Hückel Approach

In Chapters 3 and 4, a thoroughly documented method of Woodward and Hoffmann was presented to determine the favourable paths of electrocyclic reactions. The definitive rules developed by them, based on the conservation of orbital symmetry, are of great interest to organic chemists, since they not only explain the presently known reactions, but also show great predictive power for explaining the hitherto unstudied reactions. The realization of the importance of orbital symmetry to determine the feasibility of pericyclic reactions is considered as a giant breakthrough in the fascinating history of developments in organic chemistry. However, in order to predict whether a reaction is symmetry allowed or disallowed, a knowledge of the symmetry properties of the molecular orbitals of the reactants and products, as well as a knowledge of their relative energies, is required to construct a correlation diagram. For complicated systems it becomes even more difficult to determine the relative energies of their MOs. The frontier orbitals treatment suffers from the basic defect of being inapplicable to systems where there is no symmetry. An alternate approach for predicting the allowedness, or disallowedness, of concerted reactions was advanced by Zimmermann and is based on the concept of aromaticity.

The well known Hückel rule of aromaticity states: *If a cyclic polyene contains (4n+2) electrons it would have a special stability called aromaticity while those with (4n) electrons would not have this stability.* This generalization regarding the stability of cyclic planar conjugated systems seems to hold quite well.

However, this rule is applicable to cyclic systems having a specific topology called Hückel topology and the rings with such a topology are called Hückel rings. A Hückel ring may be formed by joining the two ends of a paper strip. The resulting 'pipe' has two distinct surfaces; an outer and an inner surface. A Hückel ring can also be visualized as a disk with a large hole in it. The resulting 'washer' also has two distinct surfaces; an upper and a lower surface. as shown in Figure 5.1. By analogy, cyclic polyenes whose topology resembles a Hückel ring are called Hückel systems, and it depends on how the surfaces are looked at.

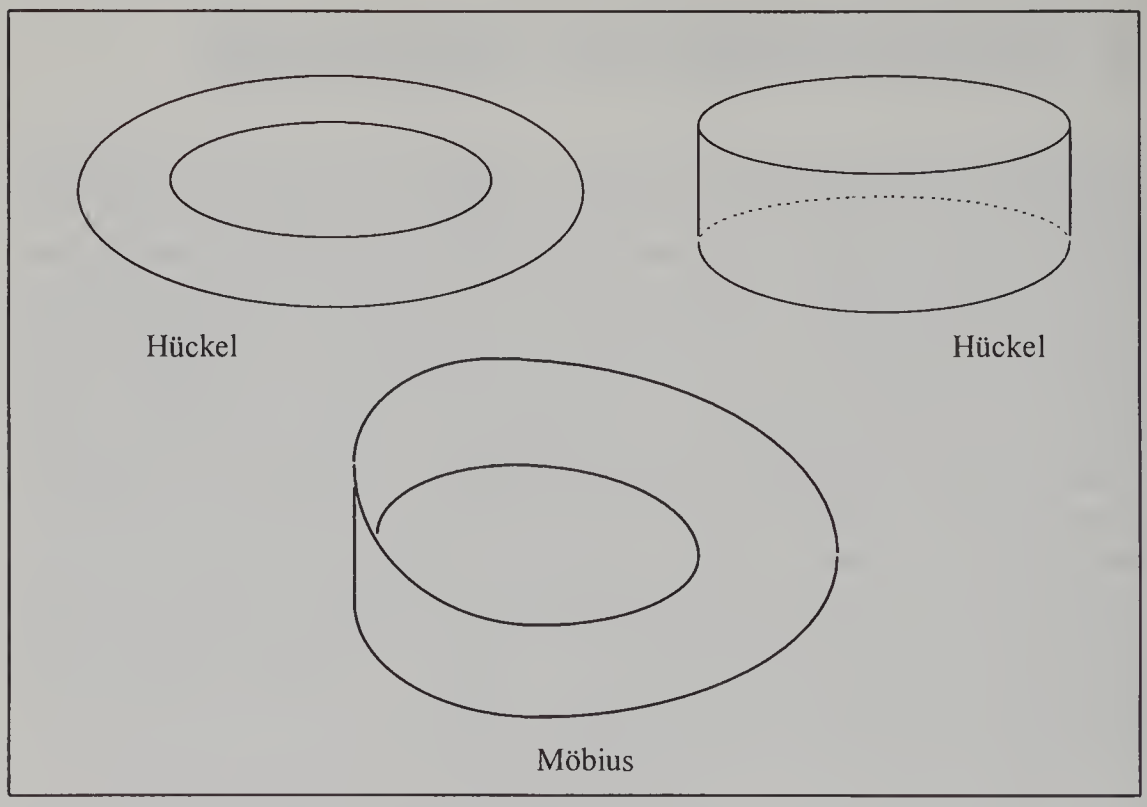


Figure 5.1: *Two Hückel rings, and a Möbius ring.*

There may also exist cyclic polyenes with the topology of a Möbius strip. Such a strip is easily constructed by taking a strip of paper and bringing the two ends of this 'ribbon' together to form a ring. However, it is necessary to first twist the edge of one end of this paper strip through 180°, before joining the two ends together. The result would be a ring of one continuous surface. The resulting 'ring' also has only one continuous edge. Such ring systems are called Möbius systems and depend on the way this single surface is looked at.

The well known Hückel rule of aromaticity as stated is specific for cyclic polyenes with the topology of a Hückel ring.

Heilbronner [1] showed that a linear polyene may also twist through 180° to form the so-called Möbius strip. Such twisted polyenes have aromatic stability when they have (4n) electrons, whereas, those with (4n+2) electrons would be antiaromatic. The criteria for aromaticity as stated for Hückel systems get reversed for the Möbius systems. Based on the topology of the ring, it may be said that *Hückel systems are aromatic with (4n+2) electrons and Möbius systems are aromatic with (4n) electrons.*

Zimmermann [2 a-c] applied this concept of aromaticity to cyclic transition states in concerted reactions. The reactions proceeding through Hückel-type transition states with (4n+2) electrons are thermally allowed due to the aromatic stability of the transition state and those with (4n) electrons are not thermally allowed. For reactions proceeding through the Möbius-type transition states, those with (4n) electrons are thermally allowed and those with (4n+2) electrons are thermally disallowed. For photochemical reactions, the rules are the exact opposite of those for thermal processes.

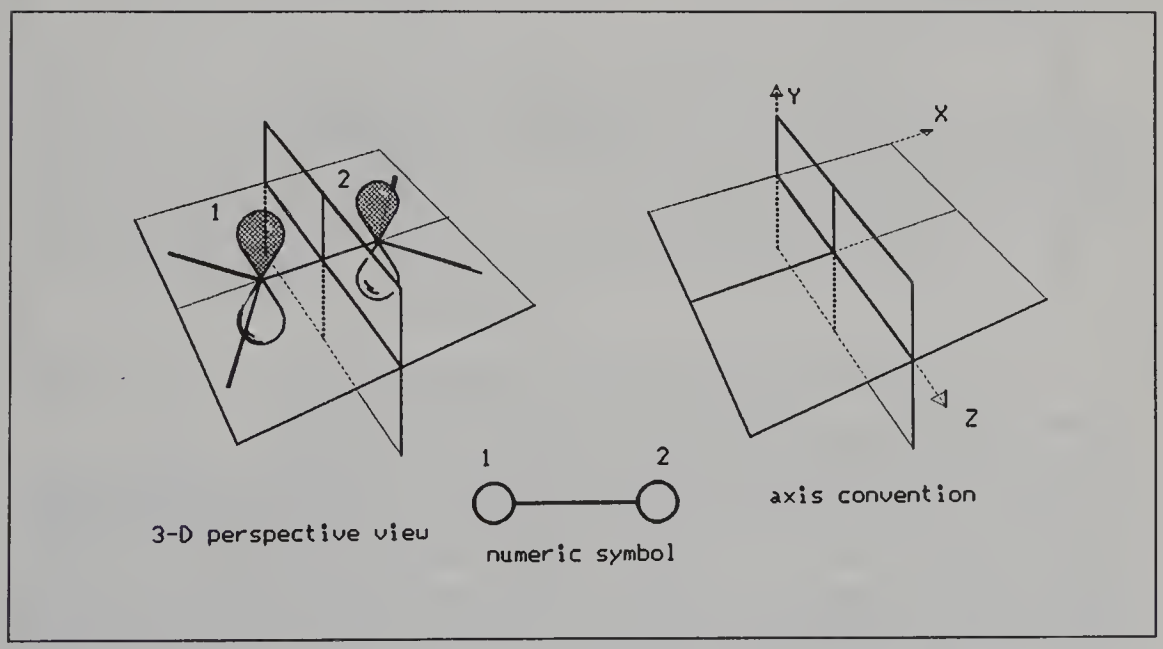
5.1 Basic Concepts

Before analyzing electrocyclic reactions on the basis of the Möbius-Hückel approach, it is important to study some basic concepts.

5.1.1 Hückel Systems

The electronic framework of Hückel systems is made up of trigonally hybridized (sp^2) carbon atoms. The σ-electronic framework of these systems are uninteresting since the properties of σ bonds do not vary. Moreover, atoms which do not have *p-orbital*s may also be omitted.

Consider the simplest case of ethylene where the energy changes are taking place as a result of interactions between two 2*p* atomic orbitals. This system may be described as a σ-skeleton lying in the *xy*-plane containing a core of σ-electrons plus the inner shell electrons. Perpendicular to the molecular plane, on C1 and C2, are two *2p*-orbitals, each having an electron.



Each 2*p*-orbital may be described as an isolated orbital as long as it does not interact with any other *p*-orbital. The energy associated with an electron in an isolated *p*-orbital is called α, the Coulomb integral. It is a measure of the attractive energy between the carbon nucleus and the electron in a *p*-orbital. It is, therefore, a negative quantity and represents the ground state ionization potential of an electron occupying an isolated atomic orbital. Obviously α is proportional to the electonegativity of the atom. Thus, the Coulomb integral for nitrogen, α_N-, has a more negative value than the Coulomb integral for carbon, α-. The formation of a bond between two carbon atoms, each having a 2*p*-orbital of energy α, is shown in Figure 5.2. A face to face approach of these 2*p*-orbitals may take place in two different ways, leading to bonding and

antibonding interactions. The former results in an energy lowering while the latter results in an increase in the energy of the system. These energy changes have already been discussed (Figure 4.3).

When two *p*-orbitals labeled P_a and P_b approach in a bonding way the energy starts decreasing. At the equilibrium distance, interactions are maximum and a new molecular orbital ($P_a + P_b$) is formed. This new molecular orbital is called a bonding molecular orbital (BMO) and is commonly designated as π.

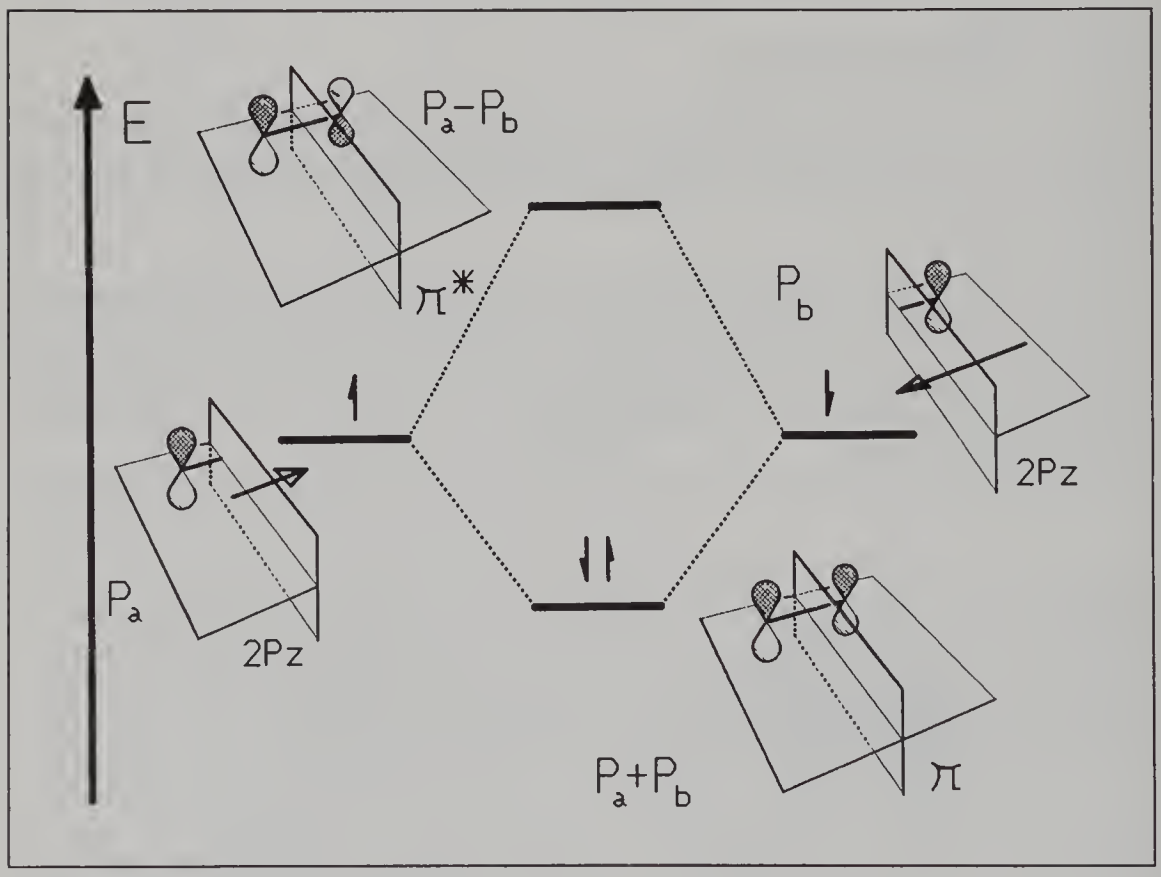


Figure 5.2: *Interactions between two p orbitals to form a π bond.*

The energy associated with the BMO is (α+β), where β is the resonance integral and is a measure of the interactions between two neighbouring *p*-orbitals. Since β is also an attraction energy it should be a negative quantity. However, the approach of two *p*-orbitals in an antibonding manner results in the formation of an antibonding molecular orbital (ABMO) designated as π^*. The energy associated with ABMO is (α-β). The two electrons obviously occupy the lower energy combination. These energy changes are shown in Figure 5.3. An overall energy lowering takes place and a π bond is formed between the two atoms. β is a measure of the strength of the bond thus formed.

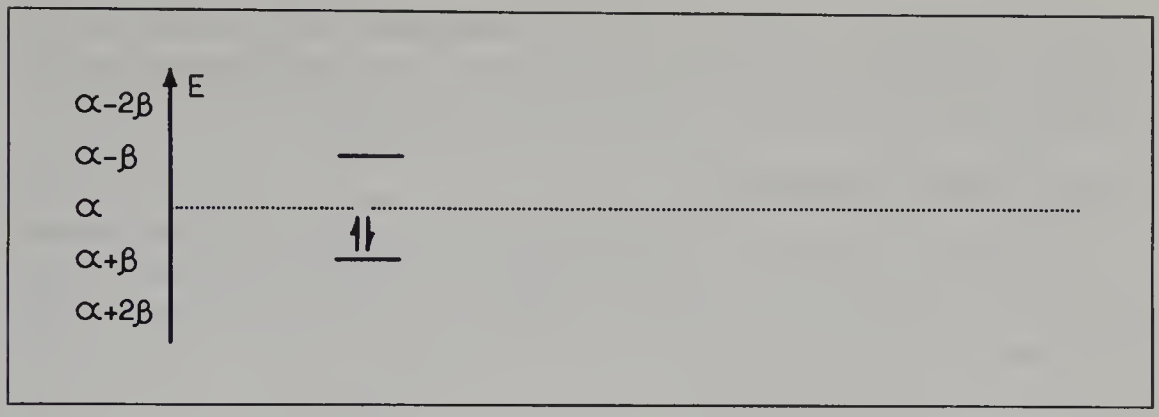


Figure 5.3: *Energy level pattern of ethylene.*

The total π-electronic energy of ethylene, designated as E_π , is given by

$$2(\alpha+\beta) = 2\alpha+2\beta$$

The value E_π for ethylene may be used as a reference value for a completely localized two-center-π-bond. In general, the total electronic energy of any conjugated system may be found using Equation 5.1.

$$E_\pi = \sum_{j=1}^{n_{occ}} n_j E_j \qquad (5.1)$$

where n_j is the number of electrons occupying the jth orbital.

The gain in energy on the formation of an ethylene π-system is called the π-bonding energy (BE). Since the energy of two isolated *p*-orbitals which make up an ethylene molecule is 2α, this energy is described as the energy of an isolated ethylene molecule, and is designated as E_{isol}. The net gain in energy may then be written as

$$BE = E_\pi - E_{isol}$$

where E_π is the total π electronic energy of an ethylene molecule
α is the electronic energy of an isolated AO
E_{isol} is the energy of isolated *p*-orbitals making up the π system

Applying the above equation to ethylene, the bonding energy is

$$BE = (2\alpha+2\beta) - 2\alpha = 2\beta$$

The term 2β is the advantage in energy units, which an ethylene molecule enjoys on the formation of a π-bond.

The above energy needs to be redefined for convenience in applications, where it is important to know the BEPE (Bonding Energy Per Electron) and is given by

$$BEPE = BE/n$$

where n is the total number of electrons in the conjugated system. The BEPE for ethylene would thus be

$$2\beta/2 = \beta$$

This is the simplest case of the formation of a π-bond by the interaction of only two *p*-orbitals. The method to calculate the energy changes, which take place as a result of interactions of more than two *p*-orbitals is discussed below.

5.1.1.1 HMO Relationship

The HMO (Hückel Molecular Orbital) method provides a simple way of calculating the bonding energies of larger conjugated systems and is based on the assumption that atomic orbitals continue to form molecular orbitals [3 a,b]. A simple version of the HMO method is the relationship (Equation 5.2) which may be used to calculate the energies of the conjugated systems.

$$E_j = \alpha - x_j \beta \qquad (5.2)$$

where j may have values 1,2,3,4, . . . , n.

n is the number of π centers, each contributing a *p*-orbital to the conjugated system.

E_j is the energy of the jth. molecular orbital.

α is the energy associated with an isolated *p*-orbital.

β is the interaction energy of two neighbouring *p*-orbitals, i.e., the resonance integral.

x_j is the Hückel energy coefficient which determines the nature of the resultant MO, i.e. whether the new MO is bonding, non-bonding or antibonding. The numerical value of x_j for linear conjugated polyenes is given by

$x_j = -2 \cos(2\pi j) / (n+1)$

It is worth digressing at this point to discuss the physical significance of x_j. It is obvious from Equation 5.2 that

when $x_j = 0$ then $E_j = \alpha$

This implies that the energy of the new molecular orbital formed is the same as the energy of the isolated atomic orbital. In other words, there is no interaction between the two orbitals and the resultant MO is described as a NBMO (Non-Bonding Molecular Orbital). When $x_j < 0$, the resultant MO is called a BMO (Bonding Molecular Orbital). For $x_j > 0$, E_j would be less negative than α and the result would be an antibonding MO.

Substituting the value of x_j in Equation 5.2

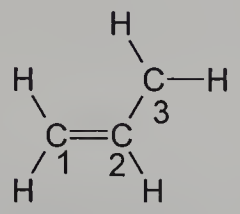
$$E_j = \alpha + (2 \cos(2\pi j) / (n+1)) \beta. \qquad (5.3)$$

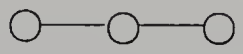
Equation 5.3 may conveniently be used for deriving energy level patterns of linear conjugated polyenes and helps in calculating the bonding energies of these systems.

For a further treatment of the HMO method see Appendix A.

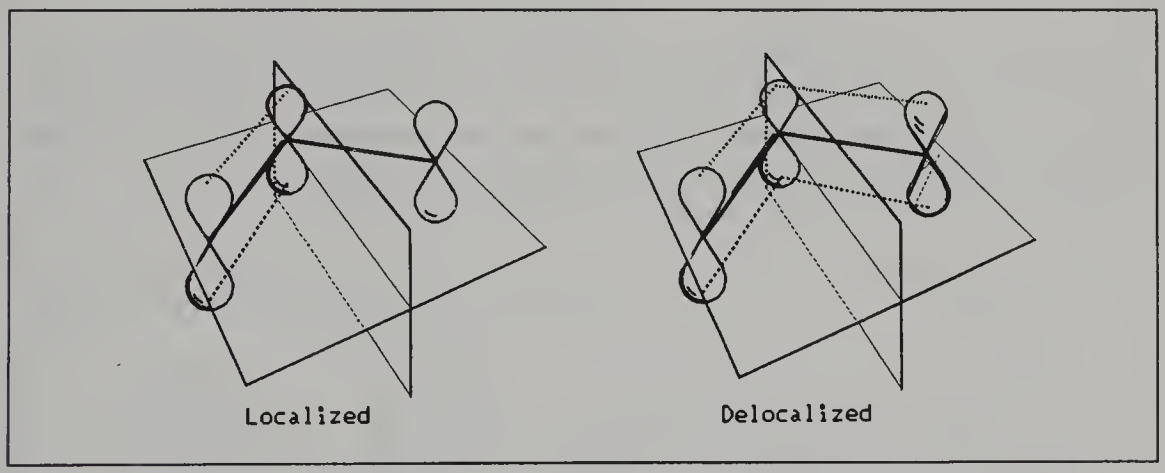
5.1.1.2 Energy Level Patterns

The HMO relationship can be used to calculate the energies of different MOs of linear conjugated systems having more than two carbon atoms. The allyl system is an example of a simple three-carbon system. The σ-framework of the system can be represented either in a linear, or bent, arrangement because it is only the attachment of the π-centers which is important for calculations.





Regarding the formulation of the electronic structure of this system, two approaches are available. One assumes the system as localized where only the orbitals on C1 and C2 are interacting, while the *p*-orbital on C3 behaves as an isolated orbital and does not interact with the other *p*-orbitals thereby confining the double bond on C1 and C2. This illustrates the localized model of the allyl system. The other approach considers an interaction between AOs on all three carbon atoms giving rise to a completely delocalized system.



The relative stability of the two proposed models can be compared by determining their individual electronic energies.

First the energy of the localized model (E_π^{Loc}) of the three allyl systems is determined.

$$E_\pi^{Loc}\ (\text{cation}) = E_\pi\ (\text{ethylene}) + E\ (2p)$$
$$= 2\ (\alpha + \beta) + 0\ (\alpha)$$
$$= 2\alpha + 2\beta$$

$$E_\pi^{Loc}\ (\text{radical}) = 2(\alpha + \beta) + 1(\alpha)$$
$$= 3\alpha + 2\beta$$

$$E_\pi^{Loc}\ (\text{anion}) = 2(\alpha + \beta) + 2(\alpha)$$
$$= 4\alpha + 2\beta$$

The MOs of the allyl system are drawn in Figure 5.4.

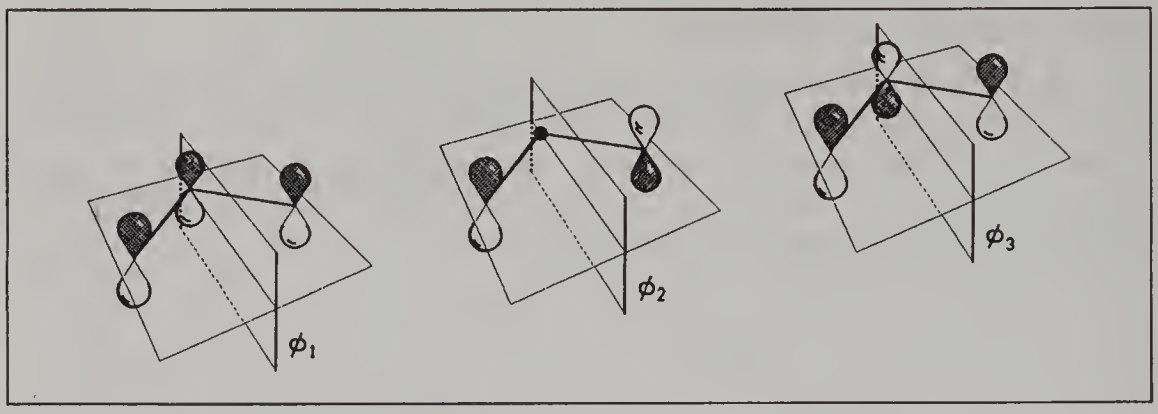


Figure 5.4: *Molecular orbitals of allyl system.*

The energies of these MOs may be calculated using HMO relationship (Table 5.1).

Table 5.1: *Calculations of HMO energies of the allyl system.*

MO	j	X_j	E_j
ϕ_1	1	-1.414	$\alpha + 1.414\ \beta$
ϕ_2	2	0	α
ϕ_3	3	+1.414	$\alpha - 1.414\ \beta$

The energy level patterns of the allyl cation, radical and anion are similar; however, the electron distribution is different in the three systems as shown in Figure 5.5. Since there are three systems with two, three and four electrons for the cation, radical and anion respectively, three electron occupancy patterns are possible.

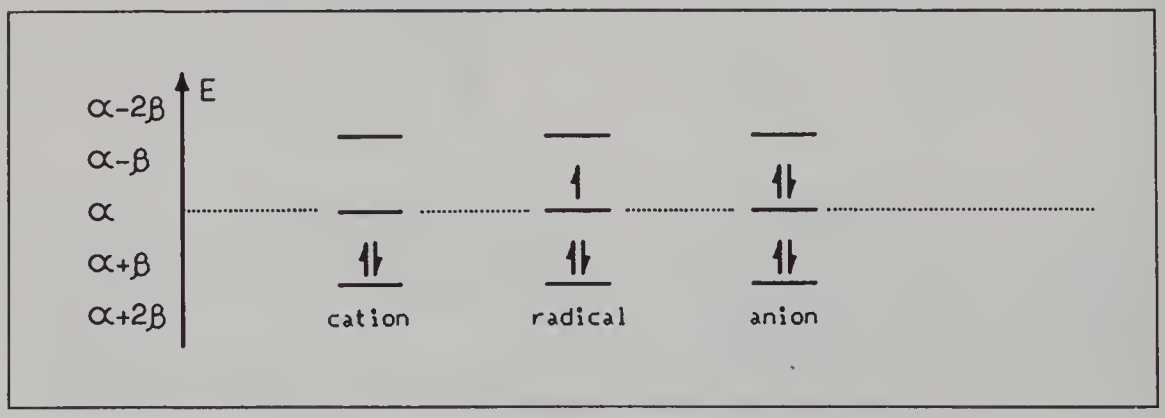


Figure 5.5: *Energy level patterns of three allyl systems.*

Total π energies of the three allyl systems are calculated using Equation 5.3.

For the cation

$$E_\pi = 2(\alpha + 1.414\beta)$$
$$= 2\alpha + 2.83\beta \qquad (\phi_1 \text{ is doubly occupied})$$

for the radical

$$E_\pi = 2(\alpha + 1.414\beta) + 1(\alpha)$$

$= 3\alpha + 2.83\beta$ (ϕ_1 is doubly occupied and ϕ_2 is singly occupied)

and for the anion

$$E_\pi = 2(\alpha + 1.414\beta) + 2(\alpha)$$
$$= 4\alpha + 2.83\beta \quad \text{(both } \phi_1 \text{ and } \phi_2 \text{ are doubly occupied)}$$

It may be noted that the total π energy E_π of the three allyl systems differ only in the α term. This is because the additional electrons in the radical and anion occupy ϕ_2 , which, being a non-bonding MO, contributes nothing to the energy lowering.

The total electronic energy (E_π) of each allyl system is calculated on the assumption of a delocalized model of the allyl system. Since E_π^{Loc} of the allyl system has already been determined, the net gain in energy of the delocalized model over the localized one can be calculated by subtracting the energy of the localized model (E_π^{Loc}) from the HMO energy (E_π), based on a completely delocalized model. Thus, the delocalization energy DE is

$$DE = E_\pi - E_\pi^{Loc}$$

The delocalization energies for the cation, radical and anion are

$$DE_{cation} = (2\alpha + 2.83\beta) - (2\alpha + 2\beta) = 0.83\beta$$
$$DE_{radical} = (3\alpha + 2.83\beta) - (3\alpha + 2\beta) = 0.83\beta$$
$$DE_{anion} = (4\alpha + 2.83\beta) - (4\alpha + 2\beta) = 0.83\beta$$

It is interesting to note that DE is the same for the three allyl systems

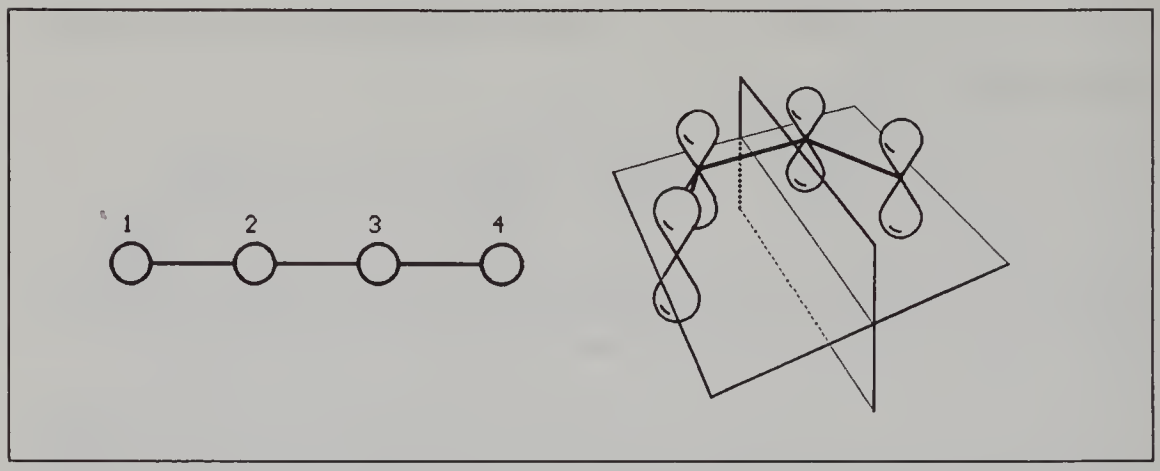
i.e. $DE_{cation} = DE_{radical} = DE_{anion} = 0.83\beta$

As mentioned earlier, a better quantity is needed for comparisons which is defined as the DEPE (Delocalization Energy Per Electron).

i.e.
$$DEPE_{cation} = 0.83\beta/2 = 0.415\beta$$
$$DEPE_{radical} = 0.83\beta/3 = 0.276\beta$$
$$DEPE_{anion} = 0.83\beta/4 = 0.207\beta$$

These calculations for the DEPE reflect a greater stability of the cation, as compared to the radical and anion, which is justified, since the cation is the only system where electrons are present in the BMO. Both the radical and anion have additional electrons in NBMO.

These arguments can also be extended to a four-carbon system. 1,3-butadiene is a typical example of such a system. Both s-*cis* and s-*trans* conformations are equivalent to each other since HMO calculations consider only the point of attachment of atoms.



The HMO energy calculations are shown in Table 5.2 and the MOs of butadiene are shown in Figure 5.6.

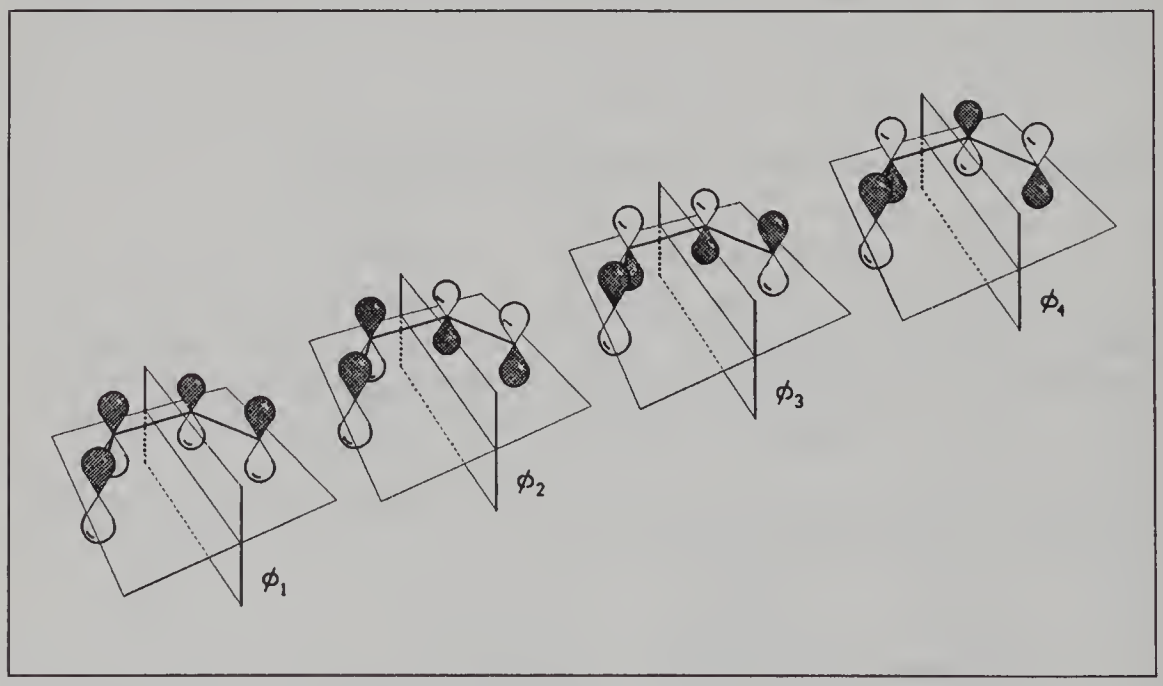


Figure 5.6: *Molecular orbitals of butadiene.*

Table 5.2: *Calculations of HMO energies of butadiene.*

MO	j	X_j	E_j
ϕ_1	1	-1.618	$\alpha + 1.618\beta$
ϕ_2	2	-0.618	$\alpha + 0.618\beta$
ϕ_3	3	0.618	$\alpha - 0.618\beta$
ϕ_4	4	1.618	$\alpha - 1.618\beta$

An energy level pattern based on these HMO energy calculations (Table 5.2), along with the ground state electron occupancy, is shown in Figure 5.7.

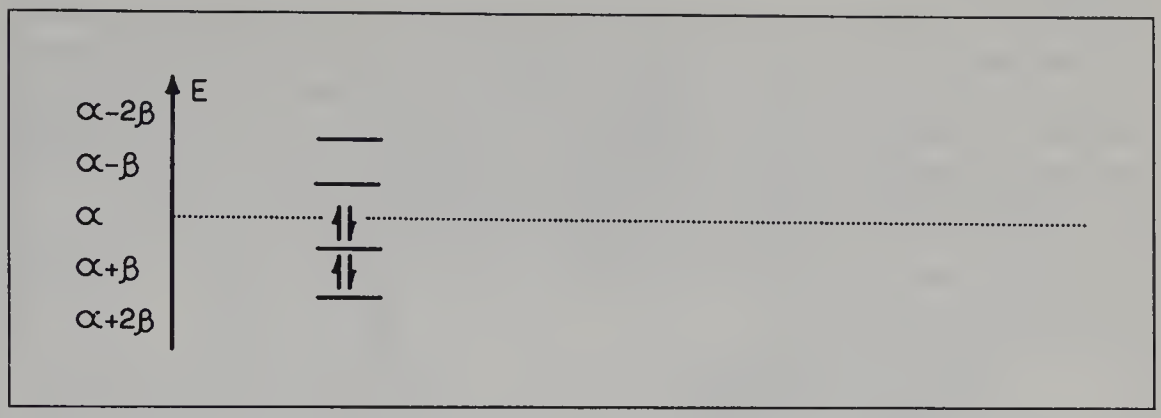
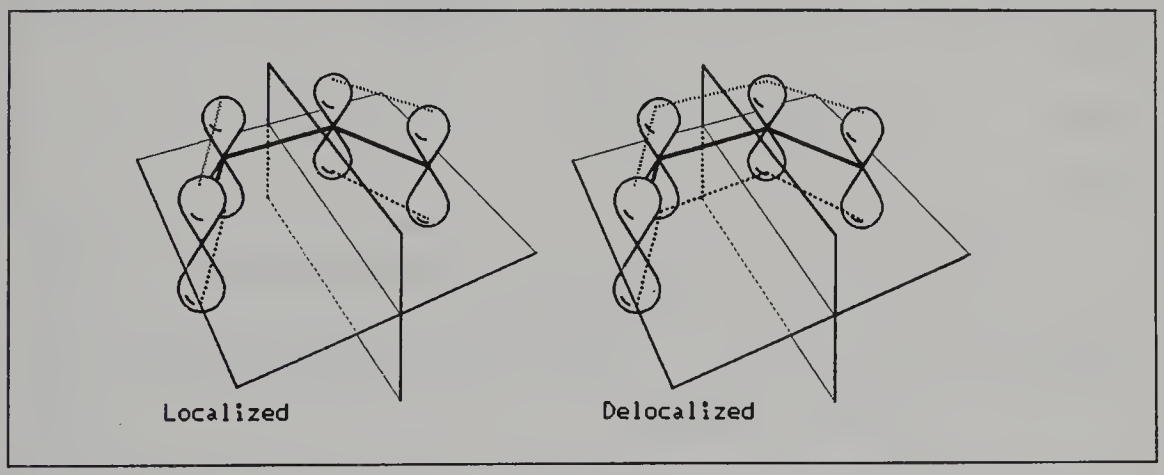


Figure 5.7: *Energy level pattern of butadiene.*

The total electronic energy E_π , based on the delocalized model of butadiene, is

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
$$= 4\alpha + 4.47\beta$$



However, assuming a localized model for butadiene would mean that there are no interactions between two ethylene moieties (i.e. between *p*-orbitals on C2 and C3).

Therefore the energy of the localized model is

$$E_\pi^{Loc} = 2\,(2\alpha + 2\beta) = 4\alpha + 4\beta$$

Thus, the delocalization energy of butadiene is

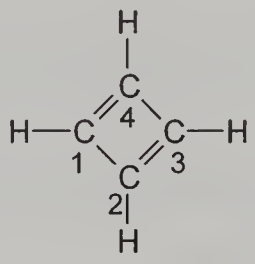
$$DE = E_\pi - E_\pi^{Loc}$$
$$= (4\alpha + 4.47\beta) - (4\alpha + 4\beta)$$
$$= 0.47\beta$$

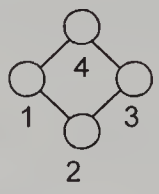
and $DEPE = 0.47/4 = 0.117\beta$

It may be concluded from these HMO calculations that butadiene is stabilized by delocalization to a greater extent than the stabilization of two ethylene molecules.

Problem 5.1:
Calculate the bonding energies BE and BEPE of butadiene. Two canonical structures for butadiene may be written, which would evidently be non-equivalent involving charge separation and would not contribute much to the total hybrid structure. In contrast, the canonical structures for allyl cation are equivalent to each other without any charge separation. Would the results of valence bond arguments (Appendix A) agree with the HMO predictions? Compare these results with those of ethylene.

Consider the case of cyclobutadiene, where the two ethylene double bonds are constrained in a ring,





The HMO energy relationship (Equation 5.3) may be modified for planar conjugated monocyclic systems containing an n number of π-centers and without having any side chain.

Using $E_j = \alpha - x_j \beta$

where

$x_j = -2 \cos(2\pi k) / n$

$k = -n/2, -2, -1, 1, 2, \ldots, n/2$ when n is even and

$k = 0, \pm 1, \pm 2, \ldots, \pm n - 1/2$ when n is odd

substituting the value of x_j, we get

$$E_j = \alpha + 2 \cos(2\pi k/n)\beta \qquad (5.4)$$

Since cyclobutadiene is an even-numbered ring, the values of k would vary from 1 to 4. Substituting different values of k in equation 5.4, the energies of four MOs of cyclobutadiene are calculated (Table 5.3).

Table 5.3: *Calculations of HMO energies of cyclobutadiene.*

MO	k	X_j	E_j
ϕ_1	-2	-2	$\alpha + 2\beta$
ϕ_2	1	0	α
ϕ_3	-1	0	α
ϕ_4	2	+2	$\alpha - 2\beta$

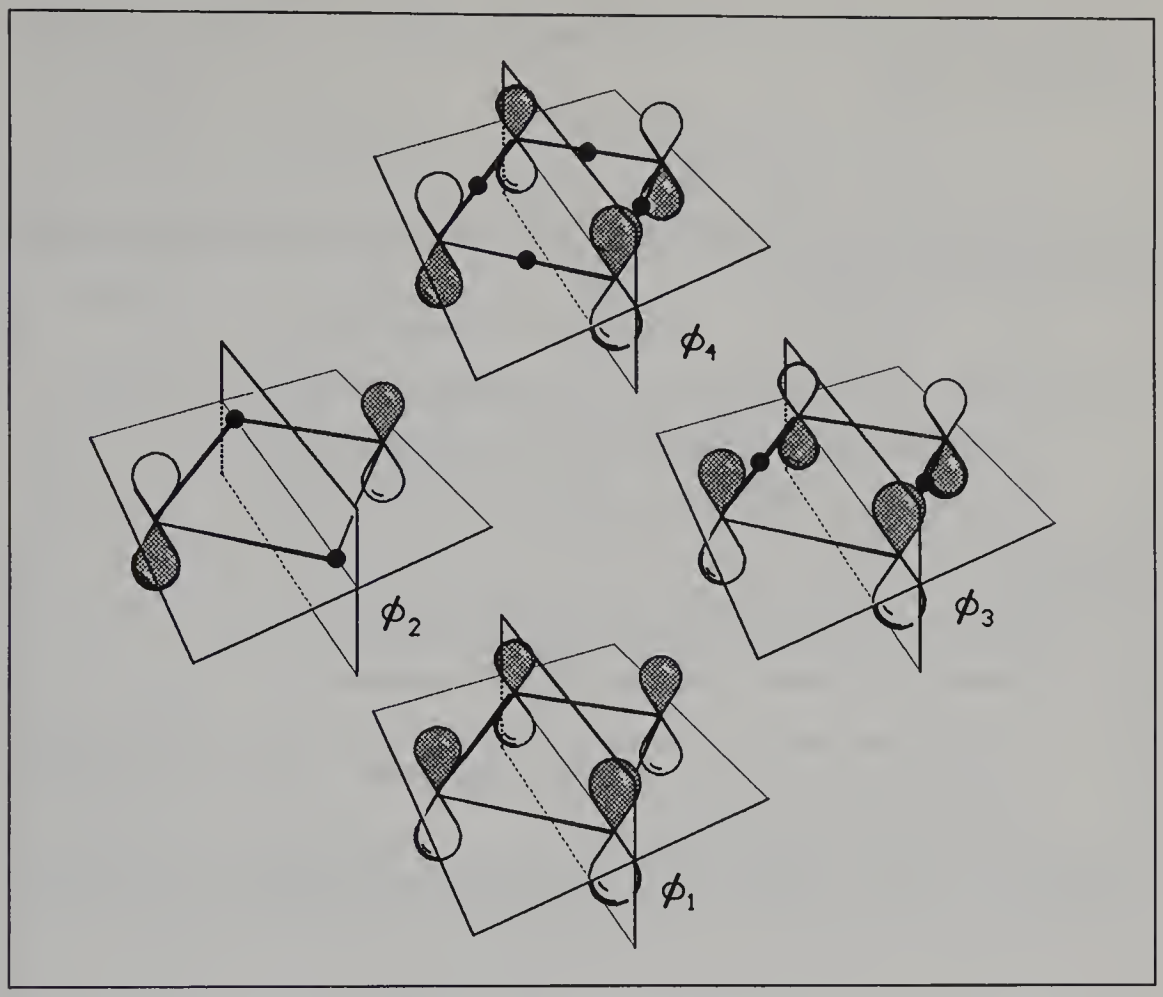


Figure 5.8: *Molecular orbitals of cyclobutadiene.*

As there are two degenerate NBMOs, the energy level pattern predicts that the ground state cyclobutadiene would be a diradical triplet.

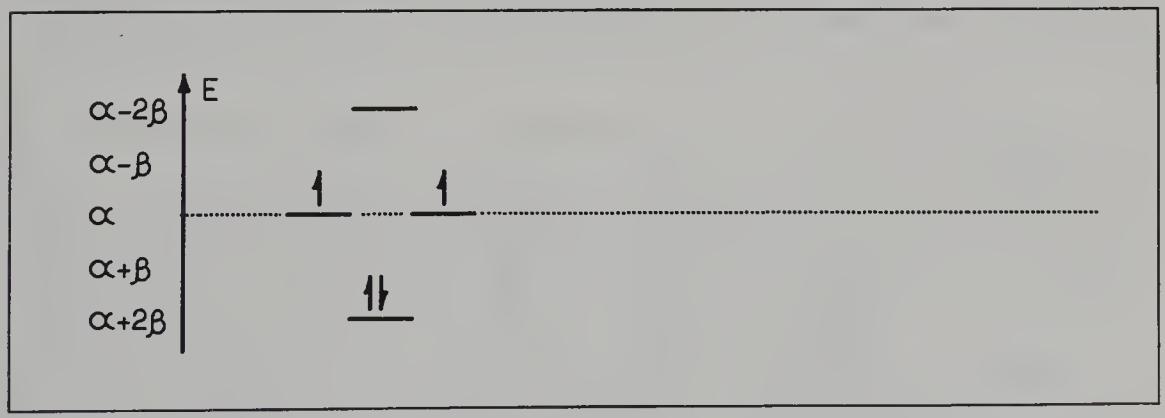


Figure 5.9: *Energy level pattern of cyclobutadiene.*

After having calculated the energies of different MOs of cyclobutadiene, its total electronic energy E_π can be calculated.

$$E_\pi = 2(\alpha + 2\beta) + 1(\alpha) + 1(\alpha)$$
$$= 4\alpha + 4\beta$$

In order to calculate the E_π^{Loc} of cyclobutadiene, assume two ethylene fragments constrained in a ring

$$E_\pi^{Loc} = 2\,(2\alpha + 2\beta)$$
$$= 4\alpha + 4\beta$$

Since in this case E_π^{Loc} and E_π are the same i.e. = $(4\alpha + 4\beta)$, the delocalization energy of cyclobutadiene would be zero.

$$DE = E\pi - E_\pi^{Loc} = (4\alpha + 4\beta) - (4\alpha + 4\beta) = 0$$

From the energy level pattern (Figure 5.9), the following predictions may be made:

i) The ground state of the molecule would be a diradical triplet.

ii) The molecule would have no stability due to π-delocalization.

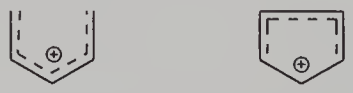
Problem 5.2:

i) Write the valence bond structures for cyclobutadiene.

ii) Would these results be consistent with HMO predictions?

iii) Cyclobutadiene has never been prepared as a stable molecular species, except as a transient species at very low temperatures. Explain the instability associated with this molecule.

The HMO relationship is equally valid for odd-numbered polyenes, e.g. pentadienyl cation or anion and its isoelectronic cyclic analog, i.e. cyclopentadienyl cation.



The E_j values for the five MOs of pentadienyl systems based on HMO calculations are -1.732, -1, 0, +1 and +1.732. Based on these values, energy level patterns of three pentadienyl systems, along with their electron occupancies, are drawn in Figure 5.10.

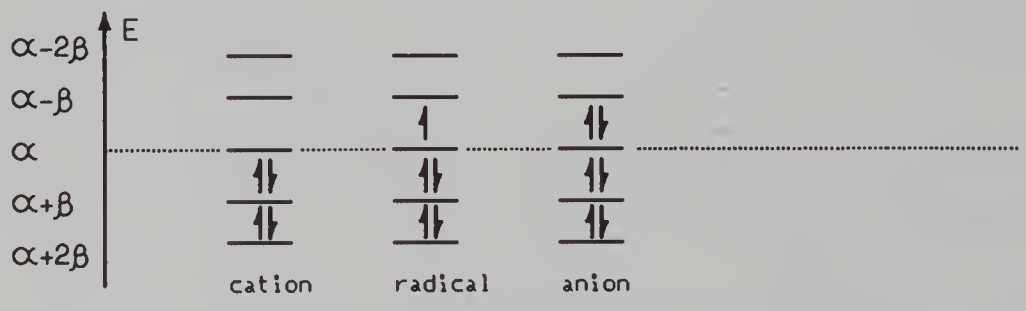


Figure 5.10: *Energy level patterns of three pentadienyl systems.*

Likewise, the E*j* values for the five MOs of the cyclic analog are calculated as -2.0, -0.618, -0.618, 1.618 and 1.618, indicating the presence of two sets of degenerate orbitals. The energy level patterns of the three cyclopentadienyl systems are drawn in Figure 5.11.

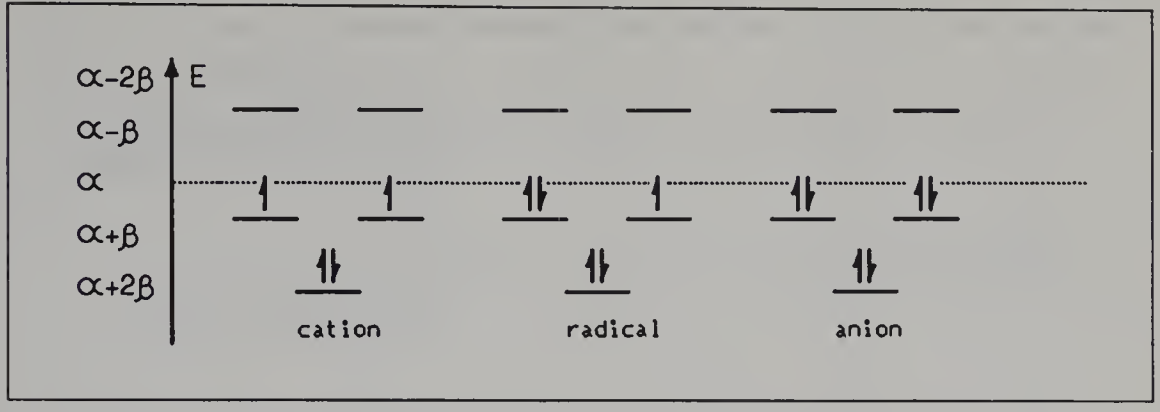


Figure 5.11: *Energy level patterns of cyclopentadienyl systems.*

Problem 5.3:

The energy level patterns along with their electron occupancies for the three pentadienyl and cyclopentadienyl systems are shown in Figure 5.10 and 5.11, respectively. Calculate the total electronic energies of these systems. Also determine the DE's for these two systems. Compare the results of open chain systems with their cyclic analogs.

Problem 5.4:

Calculate the energies of MOs of 1,3,5-hexatriene and the corresponding cyclic analog. Which of the two systems would you predict to be more stable?

Problem 5.5:

Draw an energy level pattern for the cyclooctatetraene molecule and compare the relative stability of its dianion and dication.

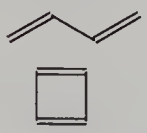
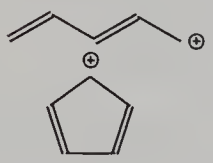
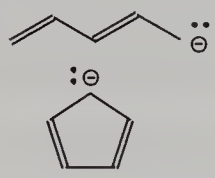
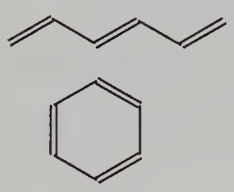
The results of HMO predictions obtained so far regarding the relative stability of linear conjugated polyenes, and their cyclic analogs, with an even-number of electrons are summarized in Table 5.4.

These results reflect an important generalization which may be stated as follows:

Planar, monocyclic systems of the Hückel topology and an odd number of electron pairs (4n+2) are more stable than their open-chain analogs. Such systems possess extra stability called *aromaticity* and the systems are called *aromatic systems*. Conversely, cyclic conjugated systems with an even number of electron pairs (4n) are less stable than their open-chain analogs and are called *antiaromatic systems*.

A simple justification of the stability of aromatic systems relative to antiaromatic systems may be found, if electrons are filled in the energy levels as obtained from HMO calculations. The generalized energy level patterns for even- and odd-numbered cyclic conjugated polyenes which emerge from HMO calculations are shown in Figures 5.12.

Table 5.4: *Results of HMO predictions for conjugated polyenes.*

System	DE (β units)	No. of electrons	HMO Prediction
	0.83 2.00	2	both are stabilized, but the cyclic system is considerably more so.
	0.48 0	4	acyclic system is clearly more stabilized.
	1.464 1.236	4	acyclic system is somewhat more stabilized.
	1.464 2.472	6	cyclic system is much more stabilized.
	0.99 2.00	6	cyclic system is much more stabilized.

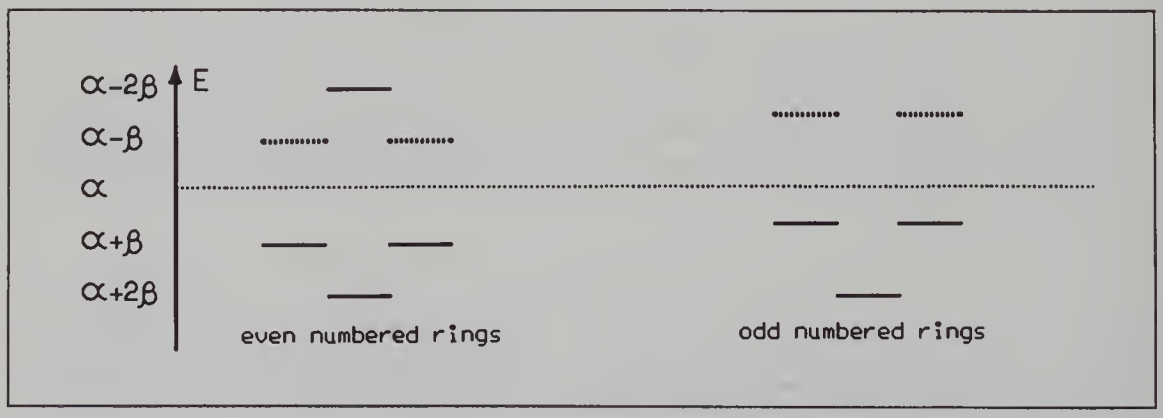


Figure 5.12: *Generalized energy level patterns of even - and odd - numbered rings.*

The filling of electrons in these energy levels is shown in Figure 5.13 and it is evident that the cyclic systems with (4n+2) electrons have all their electrons paired in different energy levels. This type of electronic arrangement is known as a closed-shell configuration which accounts for a greater stabilization of aromatic systems.

The most commonly known Hückel rule of aromaticity can now be stated as:

Planar, monocyclic, conjugated systems having a closed-shell configuration with (4n+2) electrons possess special stability called aromaticity *and the systems are called* aromatic systems. *Conversely planar monocyclic systems having an open-shell*

configuration with (4n) electrons do not possess this special stability and are called anti-aromatic systems [4 a-d].

These rules are valid for cyclic systems having the topology of a Hückel ring.

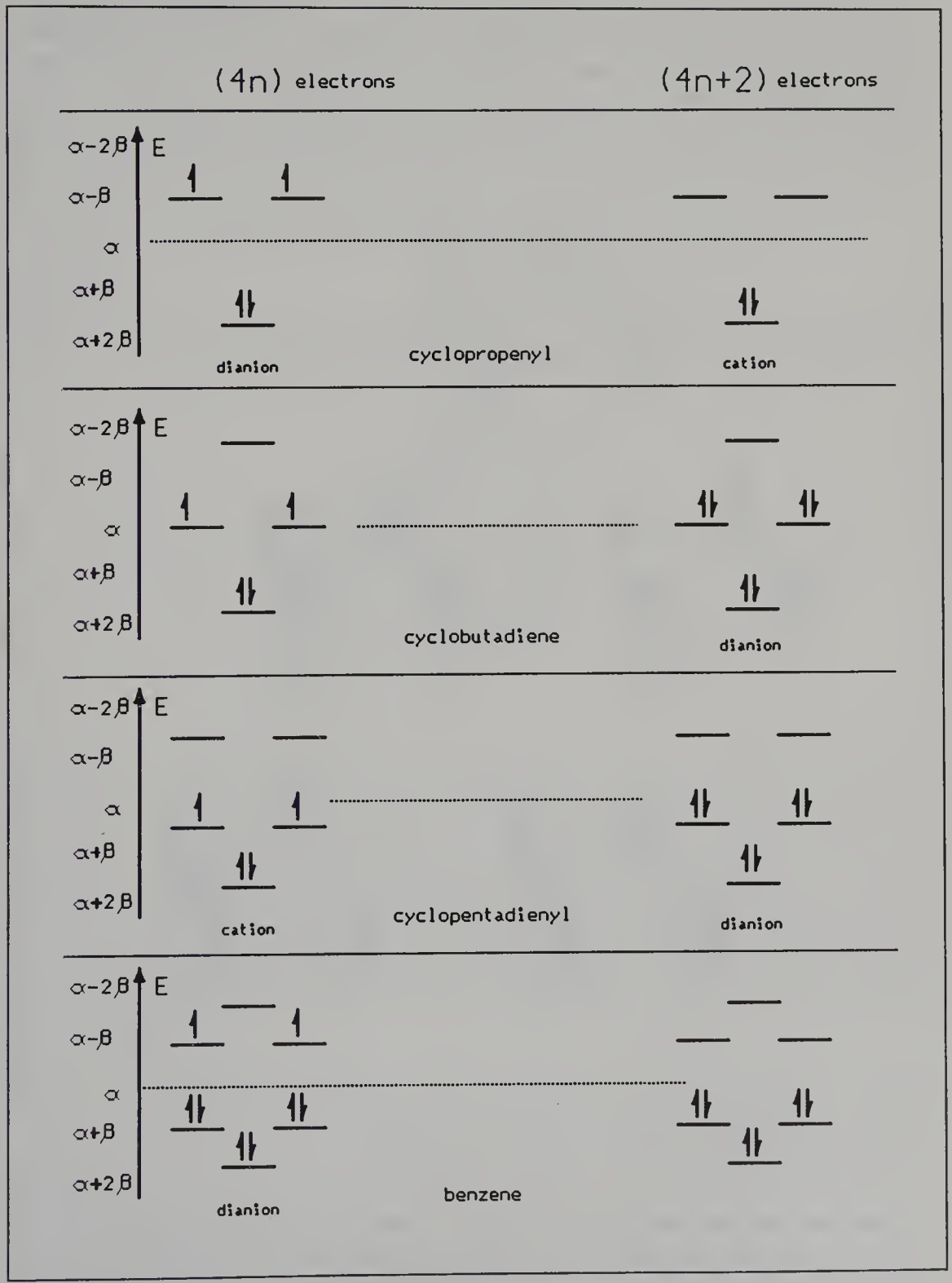


Figure 5.13: *Filling-in of (4n) and (4n+2) electrons in Hückel systems.*

5.1.2 Möbius Systems

The Hückel rule of aromaticity as stated above is appropriate for a special class of cyclic systems known as Hückel systems. Such systems are composed of an array of *p*-orbitals present on carbon atoms of any ring. This set of *p*-orbitals is called the set of *basis orbitals* (starting orbitals). Consider the example of cyclobutadiene, which has four *p*-orbitals on four carbon atoms of the ring. This forms a set of basis orbitals as shown in Figure 5.14 (Set a).

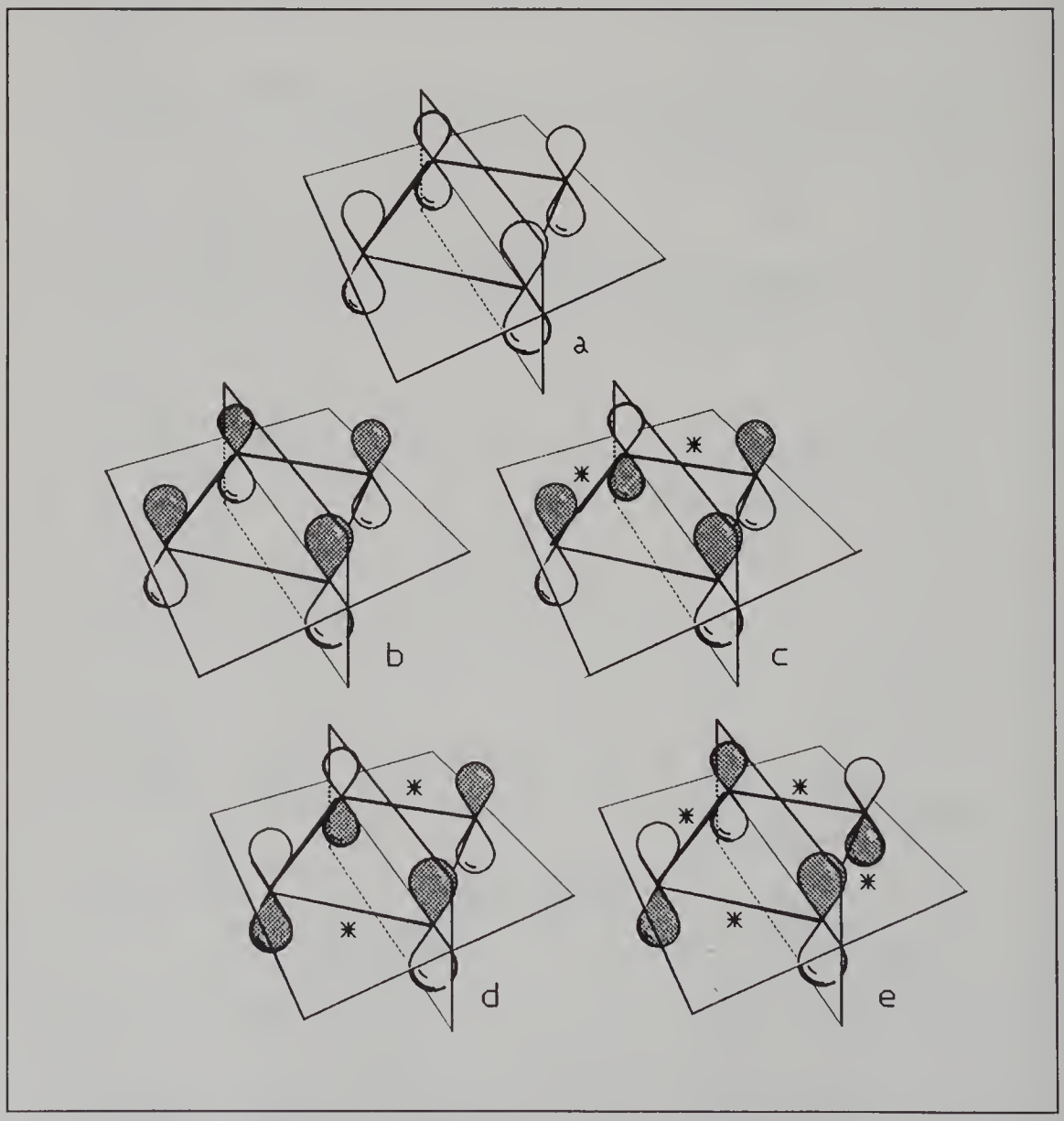


Figure 5.14: *Different orbital arrays of cyclobutadiene.*

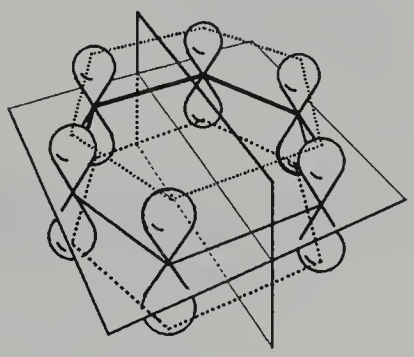
By arbitrarily choosing the sign of four *p* orbitals, different arrangements of this set of basis orbitals are possible. For example, Set b shows all bonding interactions between neighbouring *p*-orbitals, thus having no sign inversion (node) or phase dislocation at all. Changing the sign of any one of the *p*-orbitals leads to an introduction of two phase dislocations, or nodes, in the system as shown by an asterisk (Set c). The simultaneous inversion of two orbitals leads to a further increase in the number of nodes (Set e). It

may readily be seen that turning any *p*-orbital upside down, i.e., changing its sign, does not change the even-ness, or odd-ness, of inversions. This is because two new sign inversions are introduced, if the orbital turned is not adjacent to a node. If it is adjacent to a node, no new nodes result (Set d).

A warning note should be sounded here. These basis orbital arrays are not the actual MOs of the system; but are sets of basis orbitals, prior to MO calculations, and are chosen arbitrarily. The MOs of a molecule are formed by a specific arrangement of basis orbitals with the nodes (sign inversions) placed symmetrically about the central mirror plane passing through the entire molecular system. The results of MO calculations are independent of the selected set. In all these systems there are either zero, or an even number of sign inversions.

Problem 5.6:

Given is a set of basis orbitals composed of an array of six *p*-orbitals on six carbon atoms. Show how the sign inversions appear, disappear or shift in such a system.



It is evident that whichever basis set of *p*-orbitals of a conjugated system is chosen, it would always have either zero, or an even, number of sign inversions. Such arrays of basis orbitals which have either 0,2,4. . ., or any even number of sign inversions are known as Hückel arrays and the planar monocyclic systems, having this unique characteristic, are described as Hückel systems. Both even-numbered cyclic polyenes (e.g., cyclobutadiene, benzene) and odd-numbered polyenes (e.g., cyclopropenyl-, cyclopentadienyl- or cycloheptatrienyl- cations or anions) fit this requirement. These molecular systems have a closed-shell electronic arrangement with (4n+2) electrons as discussed earlier.

Hückel systems may be envisaged as being made up of a conjugated chain of atoms whose ends are joined end to end. These systems have a continuous, parallel π orbital overlap and have two distinct surfaces as shown in Figure 5.15 (compare with Figure 5.1).

However, systems with an odd number of sign inversions may also exist. Consider a linear conjugated chain of atoms in which all AOs have the same overlap characteristics, twist one end of the chain through 180^0 and then join the two ends of the chain. The resulting ring thus formed is a cyclic system with one phase dislocation, or sign inversion, as indicated by an asterisk in Figure 5.15.

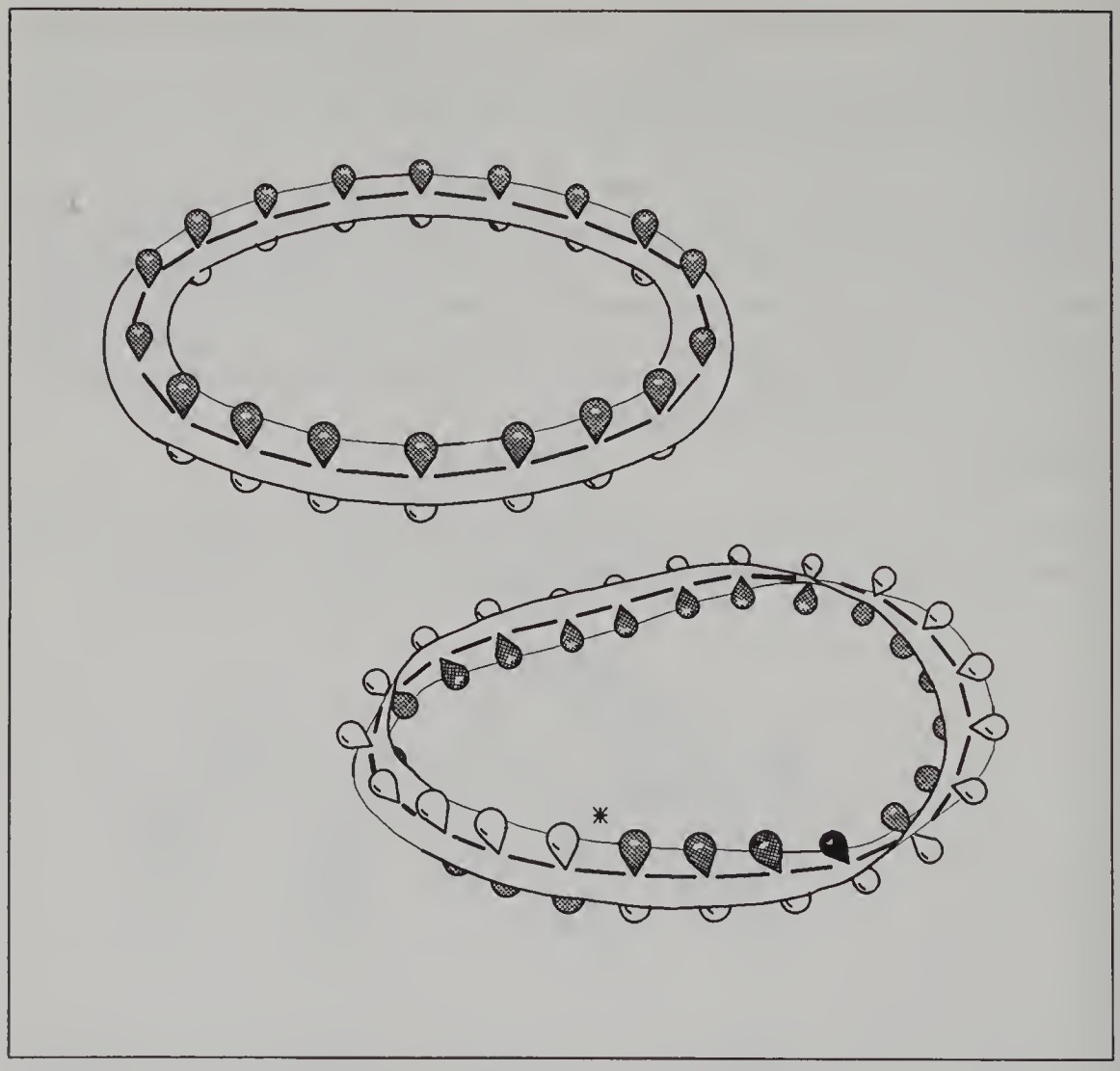


Figure 5.15: *The Hückel surfaces and a Möbius surface.*

The orbitals in the twisted ring form a continuous ring with the topology of a Möbius strip (compare with Figure 5.1). Such ring systems are described as Möbius rings [5].

As mentioned earlier, Hückel systems are composed of an array of only $2p_z$ atomic orbitals, while Möbius systems may also have other types of orbitals such as *s*- or *d*-atomic orbitals, or π-molecular orbitals, as part of a basis orbital set. It is interesting to note that the introduction of a *d*-orbital into a ring of *p*-orbitals would introduce one phase dislocation, or sign inversion [6], resulting in a Möbius ring system as shown in Figure 5.16. Such systems may possibly exist in large polyenes, for example: annulenes with ten or more carbon atoms.

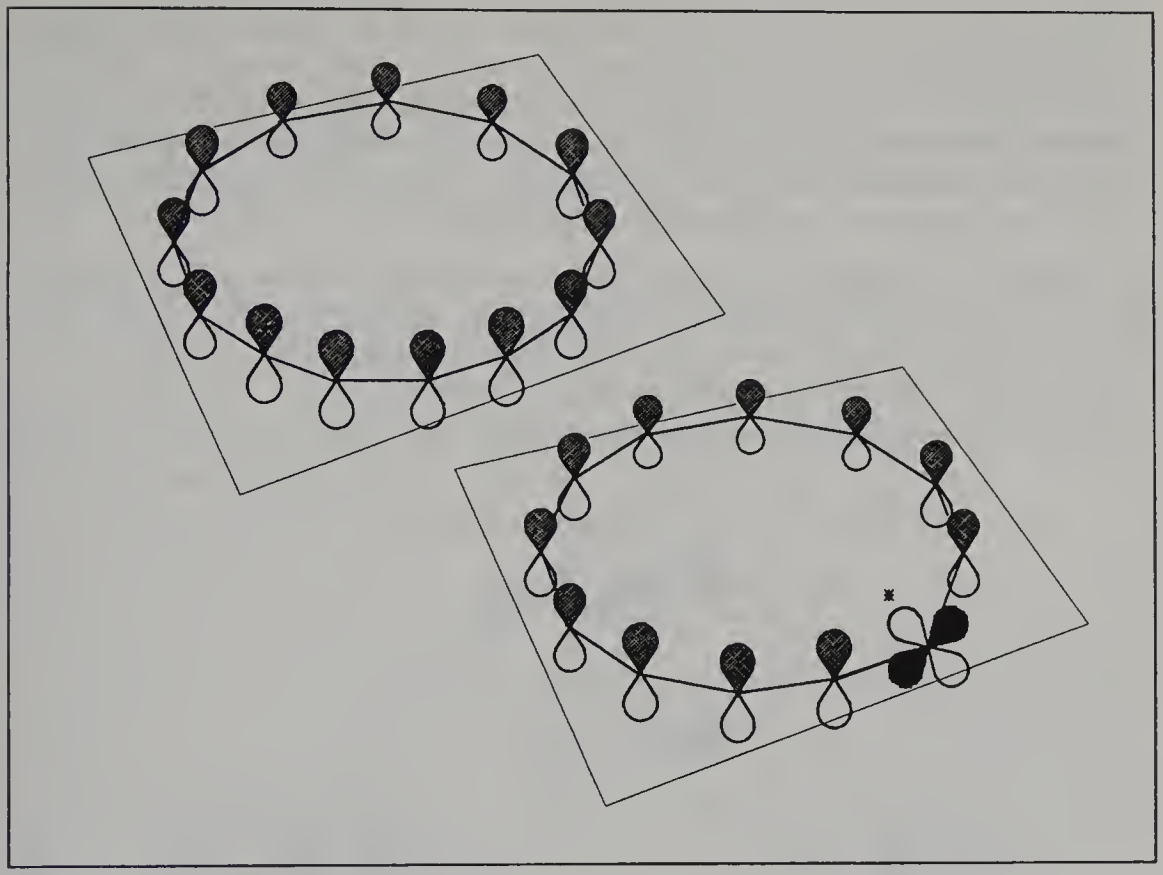


Figure 5.16: Hückel and Möbius rings.

5.1.2.1 Ground State Examples

The concept of Möbius topology can be explained with the help of some specific examples of ground state molecular systems. An instructive molecular system is *twist* trimethylenemethane (Figure 5.17).

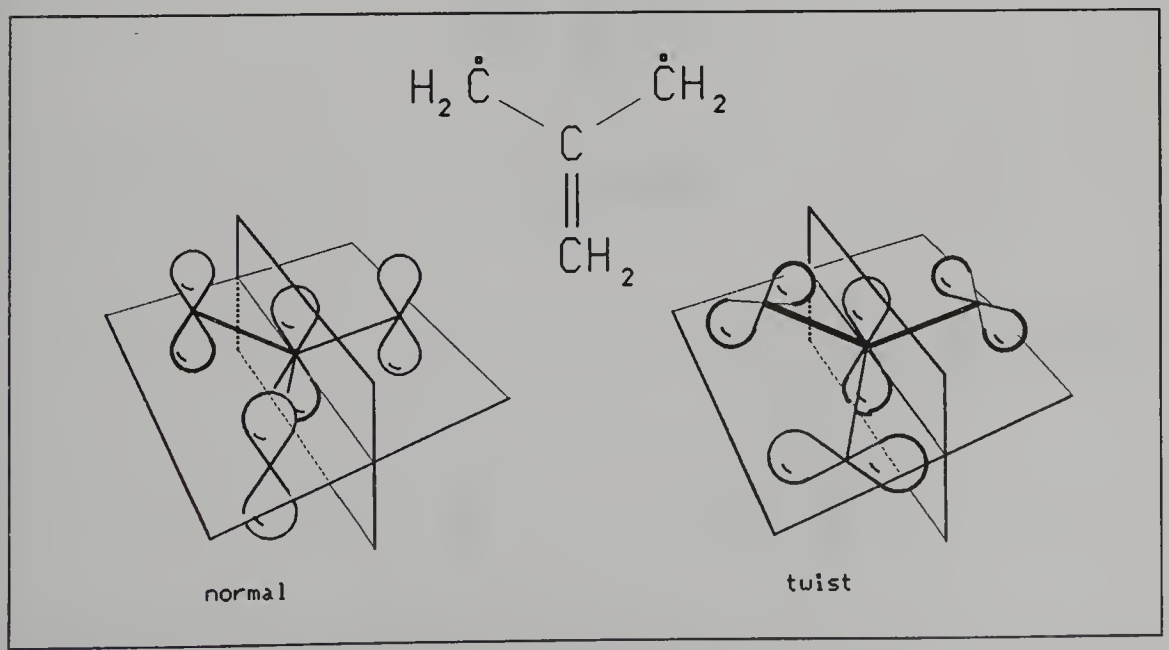


Figure 5.17: Two orbital arrays of trimethylenemethane.

Normal trimethylenemethane may be envisioned as an array of four *p*-orbitals which are normally set up in such a way that there is no sign inversion. However, if the outer three sp^2 centers are twisted through 90° each, a planar array of three *p*-orbitals is formed with the result that the *p*-orbital on central carbon atom gets orthogonal to the outer array composed of three sp^2 orbitals. This is the situation in *twist* trimethylenemethane, as was illustrated in Figure 5.17.

It is clear that the planar array of three *p*-orbitals as shown in Figure 5.18 necessarily has one or three sign inversions in proceeding around the array. Thus, *twist* trimethylenemethane may be envisioned as a Möbius system, which is made up of a monocyclic array of three *p*-orbitals having an odd number of sign inversions.

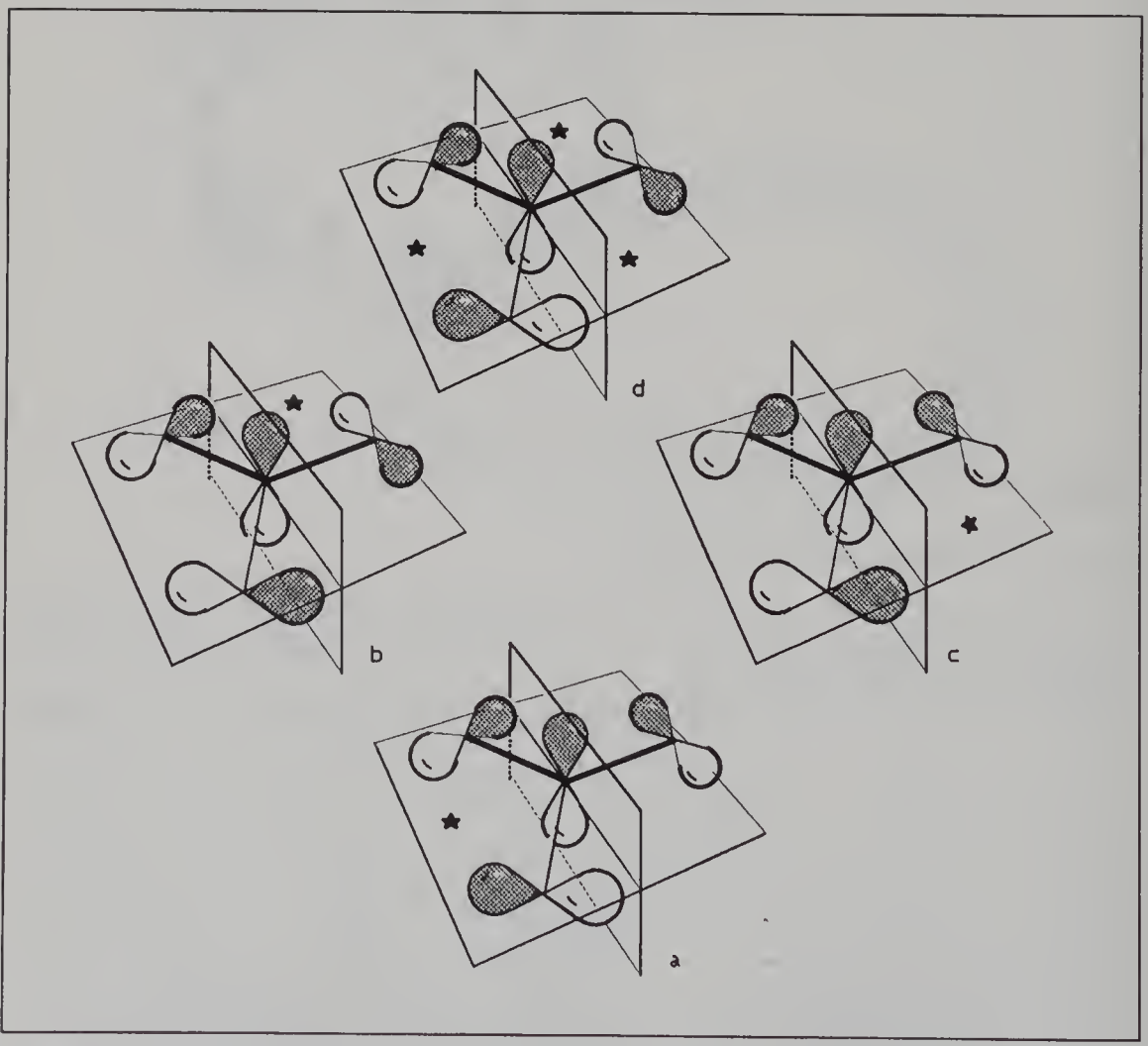
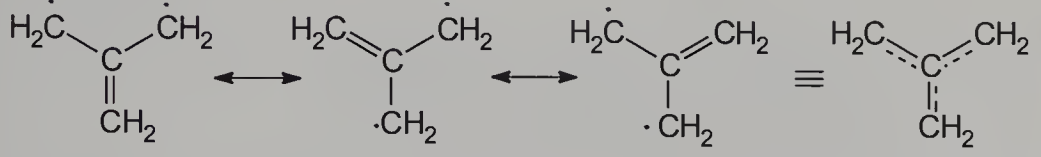


Figure 5.18: *Orbital arrays of twist trimethylenemethane.*

Problem 5.7:

The cyclic structure is not a necessary criterion for aromaticity. The idea of acyclic aromaticity was proposed by Gund [7 a-c] in 1972. Trimethylenemethane *(normal)* may be quoted as an example of a system exhibiting acyclic aromaticity, due to the presence of a Y-structure or Y-delocalization.



The E_j values of the molecular orbitals of normal trimethylenemethane using HMO relationship are calculated to be 1.732, 0, 0, -1.732.
Confirm that it has a high delocalization energy due to Y-delocalization.
Hint: See ref [7a].

Problem 5.8:

The Möbius strip is a unique structure with novel and aesthetically pleasing symmetry properties. An exotic synthesis of the first molecular Möbius strip was reported by Walba [8] by the treatment of *tris*-tetrahydroxymethylethylene (THYME) ditosylate ***a*** with a base, under high dilution conditions, producing two topological isomers, a Hückel ring ***b*** and a Möbius ring ***c,*** in equal amounts (Figure 5.19). Suggest a chemical reaction to confirm that the two products ***b*** and ***c*** are topomers.
Hint: See ref [8],

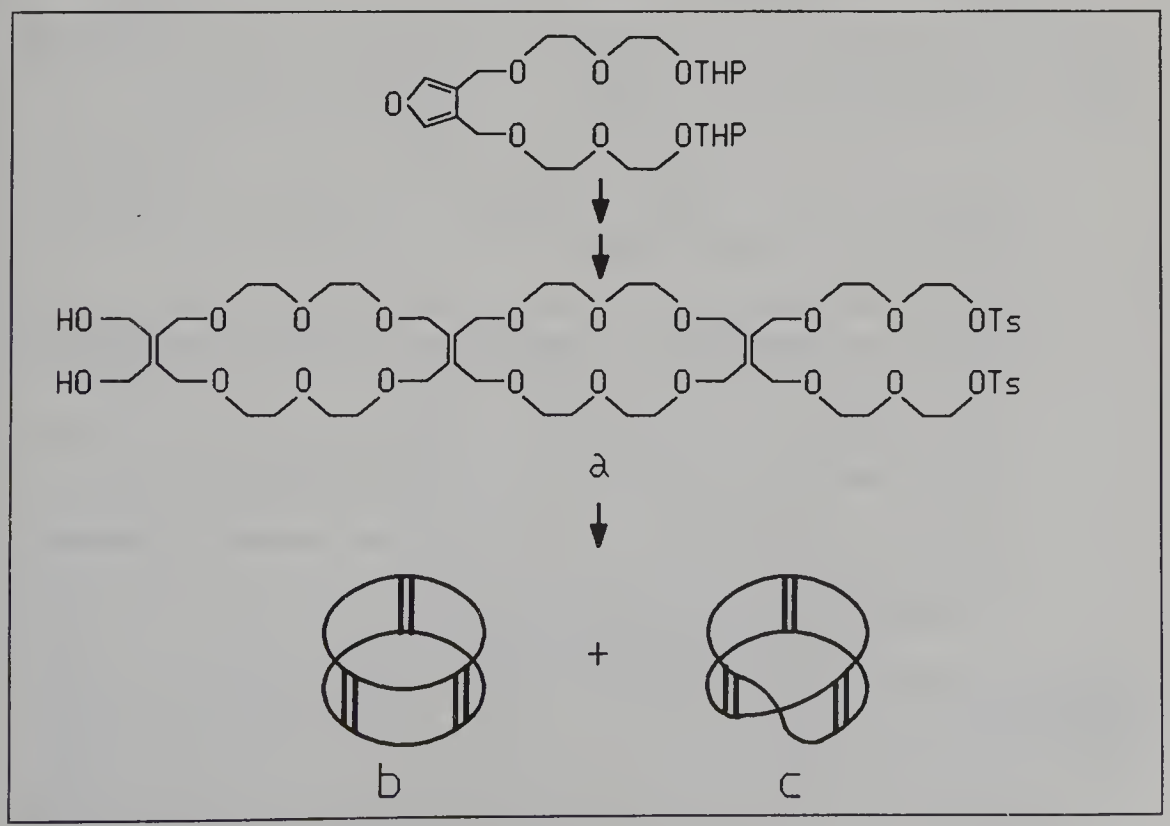


Figure 5.19: *Synthesis of a molecular Möbius strip.*

5.1.2.2 Energy Level Patterns

Heilbronner [1] in 1964 gave an expression for calculating MO energies of a Möbius system using

$$E_j^m = \alpha - x_j \beta^m \qquad (5.5)$$

where x_j $= -2 \cos(2j+1)\, \pi / n$

E_j^m is the energy of jth orbital of a Möbius ring.

j is the MO number ranging from 0. . . (n - 1).

n is the number of basis orbitals forming a Möbius ring.

α is the Coulomb integral

β^m resonance integral between two p orbitals,
$\beta_m < \beta$ due to reduced overlap characteristics in a Möbius ring.

This expression is quite similar to the Hückel expression as derived for ordinary cyclic polyenes. Energy calculations of Möbius systems may be done, as before, using Equation 5.5.

However, both Hückel and Heilbronner mathematical expressions may be expressed graphically in the form of a geometrical projection which is commonly known as the polygon rule (circle mnemonics) [9]. This rule simplifies the derivation of energy level patterns of both planar and twisted cyclic polyenes.

- ***Circle mnemonics (Polygon Rule)***

The polygon rule is used to derive Hückel MO energy levels for a planar monocyclic system, containing an *n* number of π-centers. These π-centers do not have any side chains on the π-carbon atoms. The essential steps involved are the following:

i) Draw a regular *n*-fold polygon where *n* is the number of π-centers in the cyclic system. Thus, a triangle is drawn for a cyclopropenyl system and a square for a cyclobutadiene system.

ii) Draw a circle of radius 2β with its center at energy level α, where α is marked on the ordinate of the energy level diagram and 2β is twice the magnitude of resonance integral between two adjacent orbitals.

iii) Inscribe the polygon into the circle in such a way that one apex of the polygon touches the lowest point of the circle, which is (α + 2β).

iv) Mark all those points where the apex of the polygon touches the circle. Each such point corresponds to one energy level and the vertical displacement of each intersection gives the energy of one MO.

Following these steps energy level patterns of Hückel systems are drawn as shown in Figure 5.20.

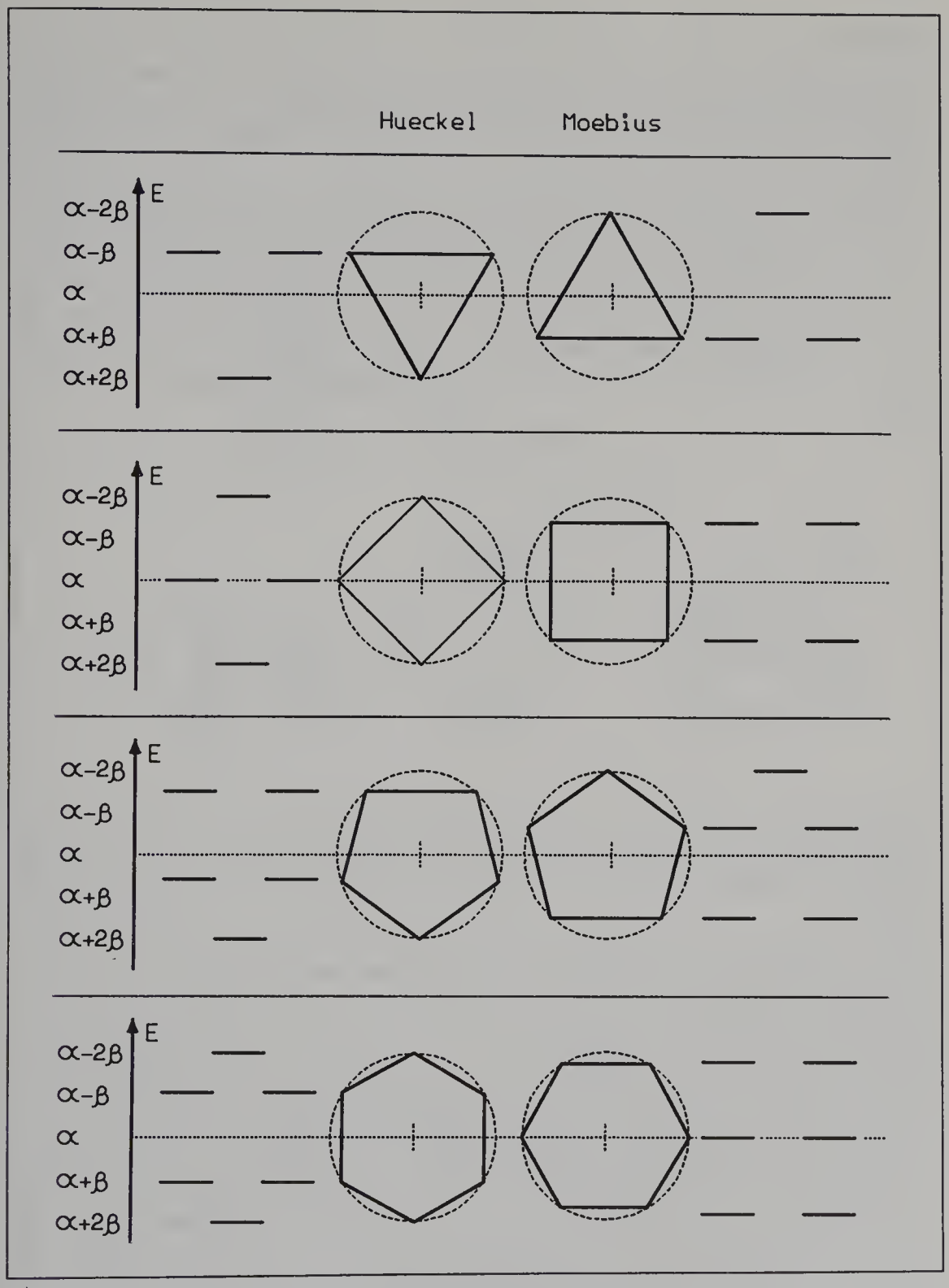


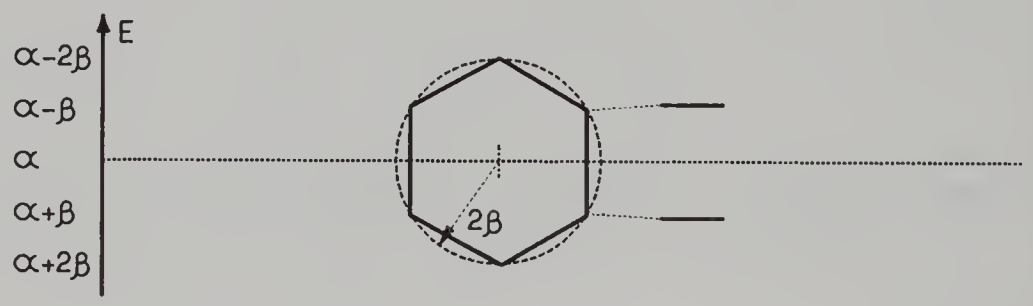
Figure 5.20: *Energy level patterns of Hückel and Möbius systems.*

A similar mnemonic device is possible for Möbius systems, which paraphrases the Heilbronner formula and enables one to derive the energy level patterns of Möbius systems. However, in this case, a side of the polygon is inscribed at the bottom of the circle to obtain the energies of the Möbius systems. This is also illustrated in Figure 5.20.

Problem 5.9:

Draw an energy level pattern for Hückel cycloheptatrienyl system. How does this pattern differ from that of the cycloheptatrienyl system, if it were to exist in a Möbius form? Also compare the energy level patterns of Hückel and Möbius cyclooctatetraene systems.

The polygon rule is also applicable to open-chain systems [10]. For deriving the energy level pattern of an open chain polyene of n atoms, add $(n+2)$ fictitious atoms and construct a ring of $(2n+2)$ atoms. The n atoms of the open chain would be represented by n positions on one side of the ring. These n positions lie between the lowest and the highest points on the ring. For example, in order to derive the energy levels of ethylene (where $n=2$), a ring is constructed with six-atoms $(2n+2 = 6)$ as shown.



Problem 5.10:

Use the above formula to draw the energy level patterns of butadiene and 1,3,5-hexatriene.

The cyclopropane molecule offers a very illustrative and fascinating example of a composite of Hückel and Möbius ring systems present within a single molecule. This molecule has attracted a great deal of interest, because of its highly strained bond angles and its unusual chemistry! which is, in several respects, similar to that of alkenes. Walsh [11 a,b] proposed an orbital model to explain the similarities in the chemical properties of alkenes and cyclopropanes. Since the H—C—H angle in cyclopropane is close to 120°, Walsh proposed sp^2 hybridization for the ring carbon atoms: Two sp^2 hybrid orbitals are involved in C—H bond formation and the third, pointing directly into the center of the ring, is involved in bond formation with the ring carbon atom. These three sp^2 hybrid orbitals make up a Hückel array as shown in Figure 5.21. The three unhybridized p-orbitals are also shown lying in the plane of the ring and are arranged as in *twist* trimethylenemethane to form a Möbius array.

The energies of the resulting MOs of the two arrays can be derived using circle mnemonics as shown in Figure 5.22.

Since sp^2 hybrid orbitals are lower in energy than p orbitals, the Hückel circle is placed lower on the energy scale than the Möbius circle. Moreover, the radius of the Hückel

circle, 2β, would be greater than the radius of the Möbius circle, $2\beta^{m}$, due to greater interactions between sp^2 hybrid orbitals in the Hückel ring. From the energy level pattern, it is obvious that six electrons are required for making a closed shell configuration of the σ-framework of cyclopropane. It is also interesting to note that the MO system formed from sp^2 hybrid orbitals is predicted to contain two electrons, while the MOs of the Möbius array should have four electrons. Thus, the electrons in the *p* orbitals of the Möbius array would be exposed and easily accessible to electrophilic reagents. This prediction agrees with the known reactivity of cyclopropane.

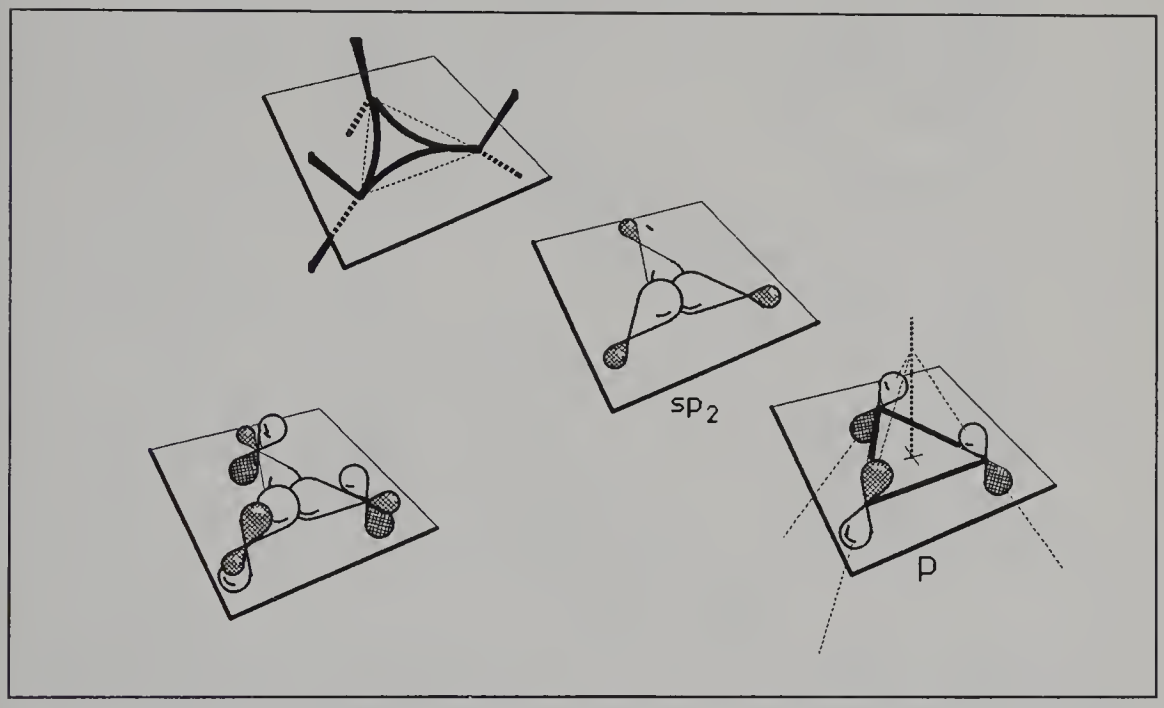


Figure 5.21: *Cyclopropane ring system shown as a composite of Hückel and Möbius ring systems.*

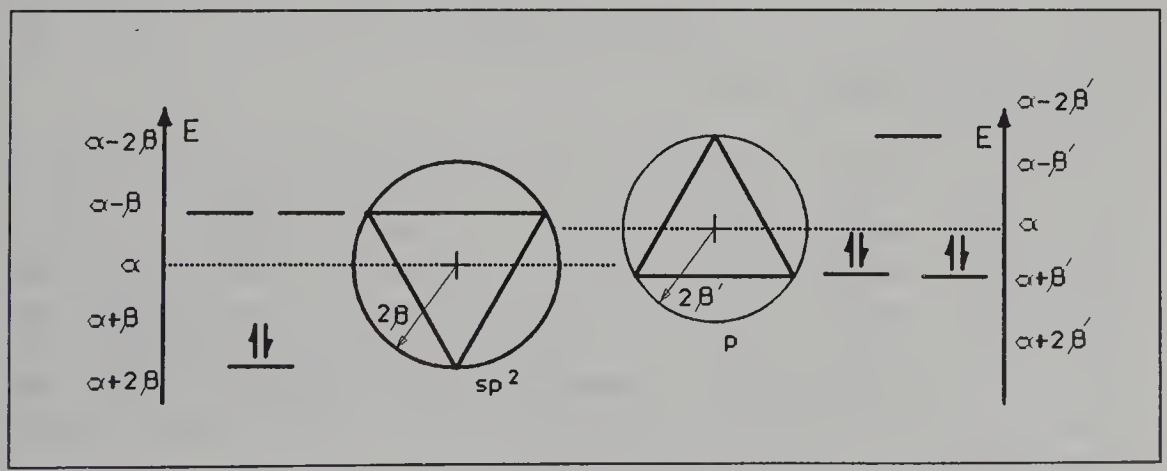


Figure 5.22: *Energy level pattern of cyclopropane derived by circle mnemonics.*

Problem 5.11: Look carefully at the electron distributions of the two orbital systems shown in Figure 5.22 and explain the unusual properties of cyclopropane.

A comparison of the generalized energy level patterns of Hückel and Möbius ring systems, which emerge from the application of the polygon rule is shown in Figure 5.23.

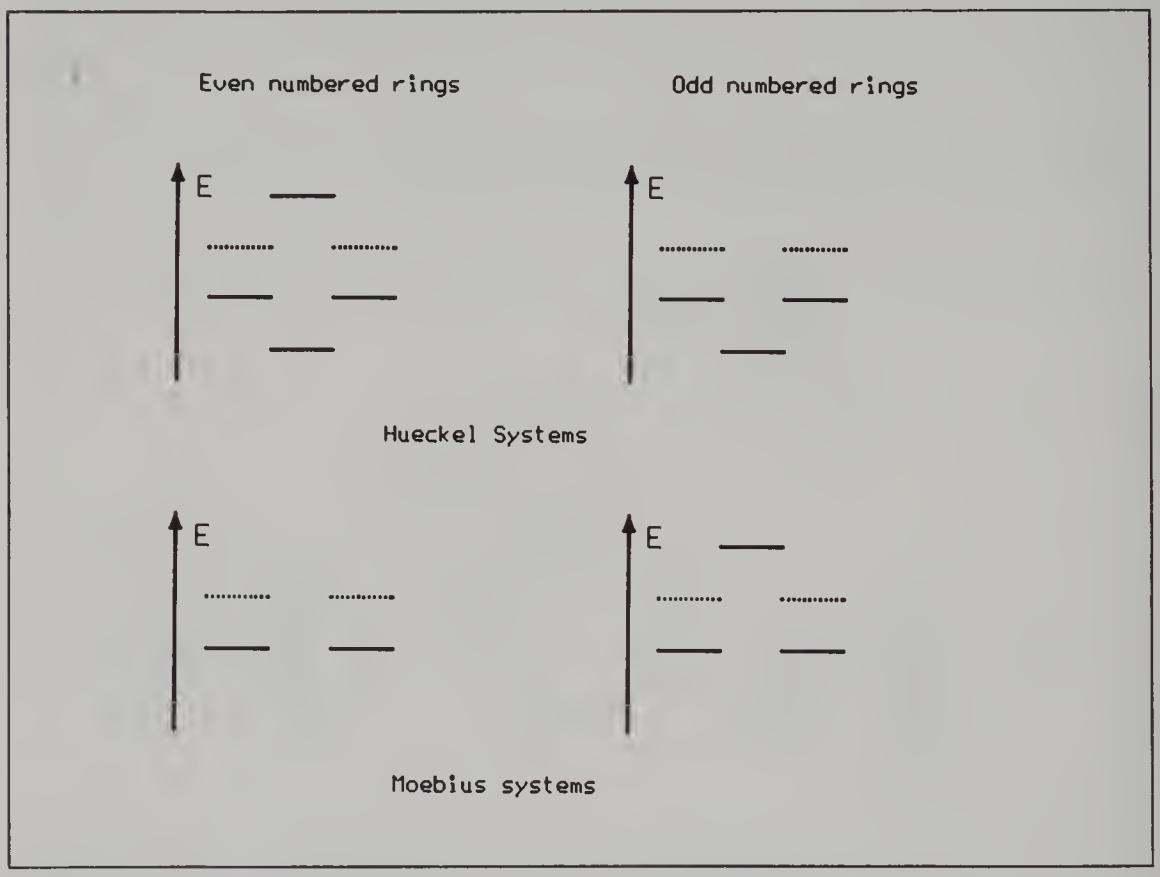


Figure 5.23: *Generalized energy level patterns of Hückel and Möbius systems.*

Problem 5.12: A necessary criterion for a Möbius system is an inevitable phase dislocation (sign inversion). In spite of this fact, Möbius systems really do exist. Take a careful look at the energy level patterns of Möbius and Hückel systems and find the source of stability of these systems.

It may be noted that a pair of degenerate, non-bonding MOs appear in even-numbered cyclic systems. Therefore, (4n)-electrons make a closed-shell configuration and hence impart a special stability to Möbius systems. This is shown in Figure 5.24, where an even number of electrons (4n), or (4n+2), are systematically filled into different Möbius ring systems, thus giving rise to closed-shell, and open-shell, configurations respectively. It is not out of place to mention here that small ring systems do not necessarily exist as Möbius rings. A comparison of the topologies of the Hückel and Möbius rings simply demonstrates a useful device for determining the relative stability of these systems

Problem 5.13: Predict the stability of the dianion of Hückel and Möbius benzene, with arguments based on the electronic arrangement of the two dianions.

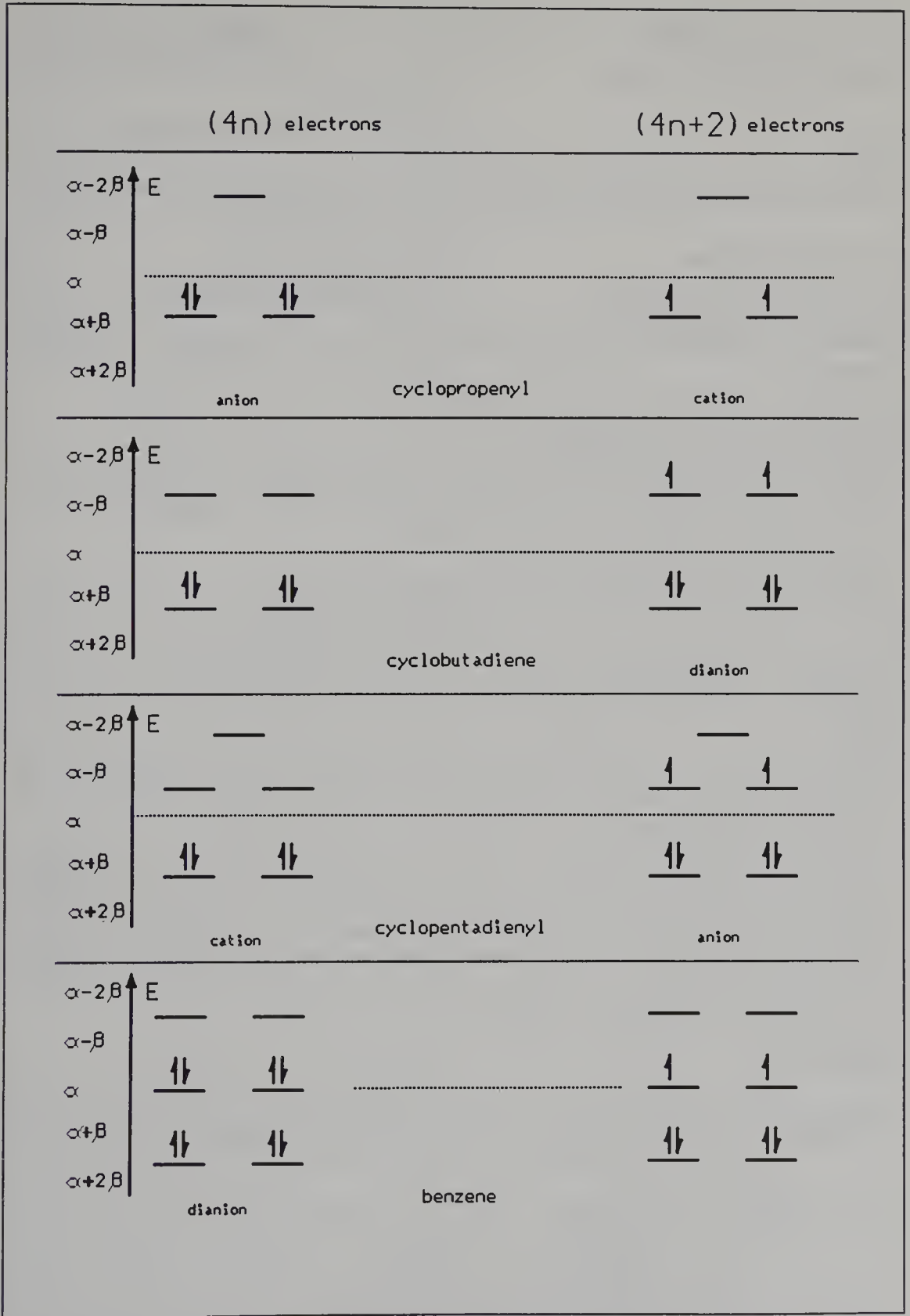


Figure 5.24: *Filling in of (4n) and (4n+2)electrons in Mobius systems.*

A comparison of the general characteristics of Hückel and Möbius systems may now be made, and is given overleaf.

Hückel	Möbius
A cyclic array of basis orbitals.	Any system whose orbitals may form a cyclic array.
Planar.	Twisted.
Composed of an array of only *2p*-orbitals.	An array composed of *p*-orbitals as well as *s-,d-* or any other MO
Two distinct surfaces.	One continuous surface.
Even number of sign inversions.	Odd number of sign inversions.
Closed-shell configuration with (4n+2) electrons.	Closed-shell configuration with (4n) electrons.
The orbital next to the lowest energy MO and the successive MO come in pairs.	Lowest energy MOs come in pairs.

Having made a distinction between Hückel and Möbius systems, it is possible to arrive at a set of general rules for aromaticity for both even-, and odd-, numbered rings with an even-number of electrons, as given in Table 5.5.

Table 5.5: *Rules of aromaticity for even-electron systems* [12].

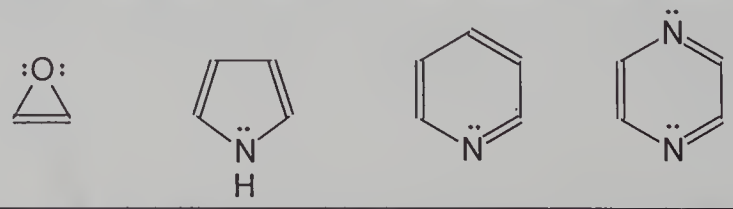
	Even-electron systems	
Topology	(4n) electrons n < > 0	(4n+2) electrons n = 0, 1, 2, . . .
Hückel	AA	A
Möbius	A	AA

* The rules are applicable to both even-(neutral), and odd-, numbered rings (cations or anions).
A = aromatic, AA = antiaromatic

The rules of aromaticity outlined in Table 5.5 for carbocyclic systems are equally applicable to heterocyclic systems. A heterocyclic system would be aromatic if all its heteroatoms are replaced by those carbon atoms that have an equal number of *p*-electrons. For example, the nitrogen atom in pyridine, which contributes a *p*-electron, is replaced by a neutral carbon while the nitrogen atom in pyrrole, which contributes two *p*-electrons, is replaced by a carbanion.

Problem 5.14:

Assuming Hückel topology, predict whether the following heterocyclic systems would be aromatic or antiaromatic. Make use of the rules given in Table 5.5.



It may be concluded that the *aromatic* character of a cyclic system is dependent on its *topology* and the *number of electrons* in the ring. The Hückel rings possess an aromatic

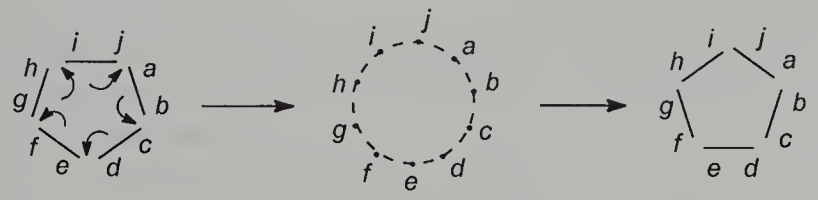
character when they have (4n+2) electrons and Möbius rings possess an aromatic character with (4n) electrons.

5.2 Applications

The Möbius-Hückel approach is applied to predict the mechanisms of electrocyclic reactions.

5.2.1 Thermal Reactions

A pericyclic process may be envisioned as a cyclic permutation of bonds taking place around a ring of atoms as shown.



(5.6)

The emphasis here is mainly on the bonds intimately involved in the pericyclic change. Thus, if atoms *a* and *b* are initially linked by a double bond in the reactant, then they can be linked by a single bond in the product. According to valence bond theory each bond in the reactant, as well as in the product, is formed by an interaction of two AOs, one on each atom. Hence the transition state for any pericyclic process is formed by an interaction of an *n* number of AOs on *n* atoms. This overlap of AOs in a cyclic transition state is in exactly the same manner as the overlap of *2p* AOs in the π-molecular orbitals of a cyclic polyene. The transition state is, therefore, *isoconjugate* with the cyclic polyene. Hence a transition state involving four electrons is isoconjugate with cyclobutadiene, while the one with six electrons is isoconjugate with benzene.

Benzene is regarded as undergoing a rapid oscillation between two Kekule structures through an intermediate called the *resonance hybrid.*

(5.7)

For an aromatic polyene, the hybrid structure would be more stable than either of the classical structures. For an antiaromatic polyene, it would be less stable.

The hybrid structure of a polyene can also be considered analogous to the cyclic transition state of a pericyclic reaction. If the cyclic transition state is more stable than its open chain analog then the pericyclic process is energetically feasible.

The cyclic transition state may be described as aromatic, nonaromatic or antiaromatic, according to whether it is more stable than, as stable as or less stable than the open chain analog, respectively. This generalization had enabled Evans [13 a,b] to formulate

a simple rule for predicting the feasibility of a pericyclic process, which may be stated as follows:

Thermal pericyclic reactions take place preferentially via aromatic transition states.

This concept of the aromaticity of the cyclic transition state is applied to predict the mechanism of pericyclic reactions. The transition states of the electrocyclic transformations of butadiene to cyclobutene, both through conrotation and disrotation, are shown in Figure 5.25. Any set of basis orbitals may be chosen to determine the topology of the transition state.

The thermal interconversion of butadiene and cyclobutene is known to proceed through conrotation while the photochemical interconversion proceeds through disrotation. It needs to be seen whether these observations agree with the predictions based on the Möbius-Hückel approach.

Consider a basis set of four *p* orbitals on four different carbon atoms of butadiene, e.g. ϕ_1. An inspection of the conrotatory transition state of butadiene reveals that there is one sign inversion (indicated by an asterisk in Figure 5.25). Whichever basis set of atomic orbitals is chosen, the result is always an odd number of sign inversions. Thus, the transition state for a conrotatory process is of Möbius type.

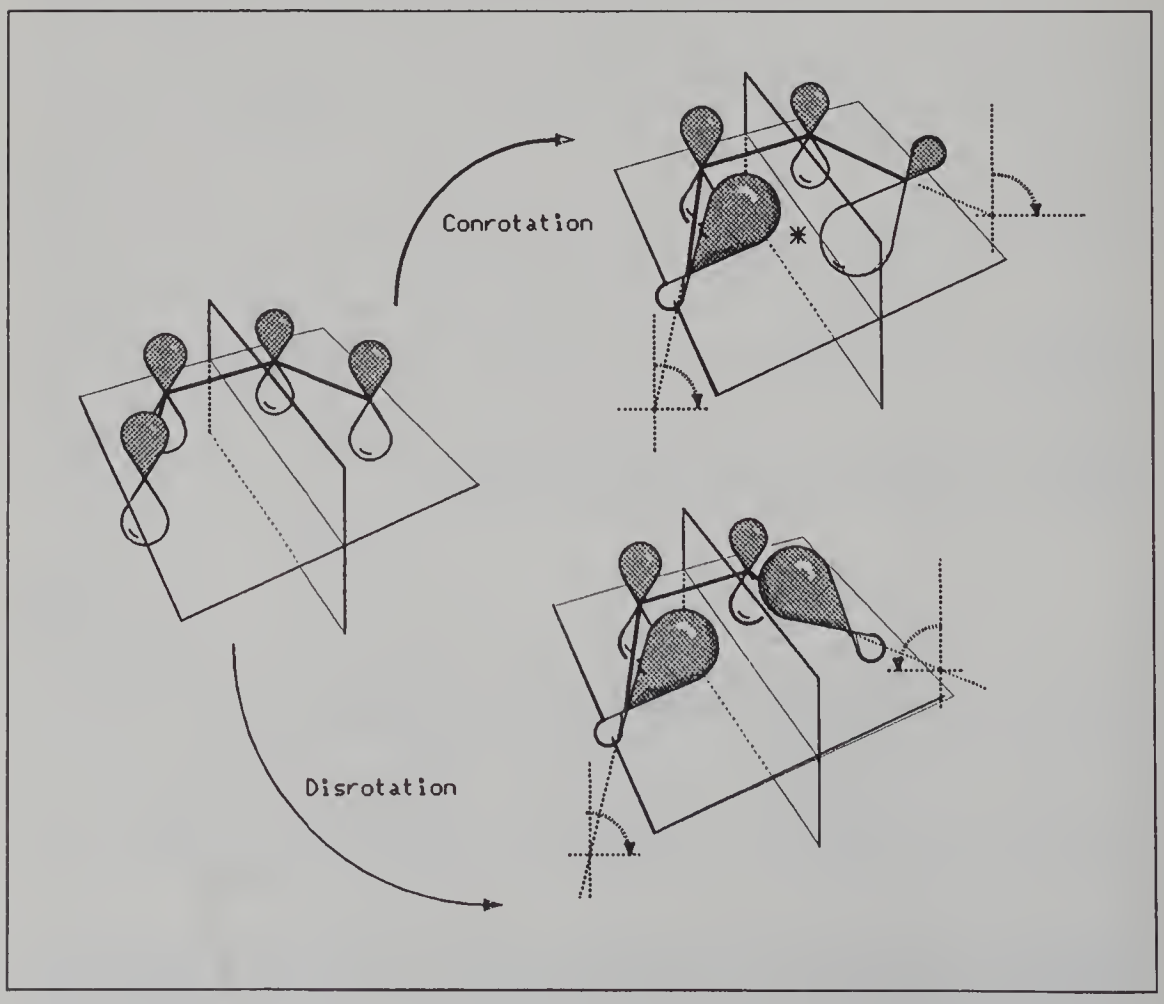


Figure 5.25: *Formation of cyclobutene via Möbius and Hückel transition states.*

As mentioned earlier, Möbius systems have a closed-shell configuration with (4n) electrons and a special stability called Möbius aromaticity is associated with such systems. Thus, a conrotatory transition state of butadiene, being Möbius with (4n) electrons, would be stable and aromatic. Hence, conrotation would be energetically feasible.

Problem 5.15:

Choose different sets of basis orbitals of butadiene and confirm that a conrotatory transition state in each case is Möbius.

A careful look at the disrotatory transition state of butadiene immediately reveals that the orbital array resembles an Hückel array as it does not have any sign inversion (Figure 5.25). Furthermore, whichever set of basis orbitals is chosen, there would always be an even number of sign inversions. Since Hückel systems with (4n) electrons have an open-shell configuration, the transition state for the disrotatory process is unstable and antiaromatic. Hence the disrotatory process would not be energetically feasible.

However, a better comparison may be made if the energy changes are considered during the two processes. The relative energies of the molecular orbitals of butadiene, cyclobutene and the two transition states may be derived using circle mnemonics.

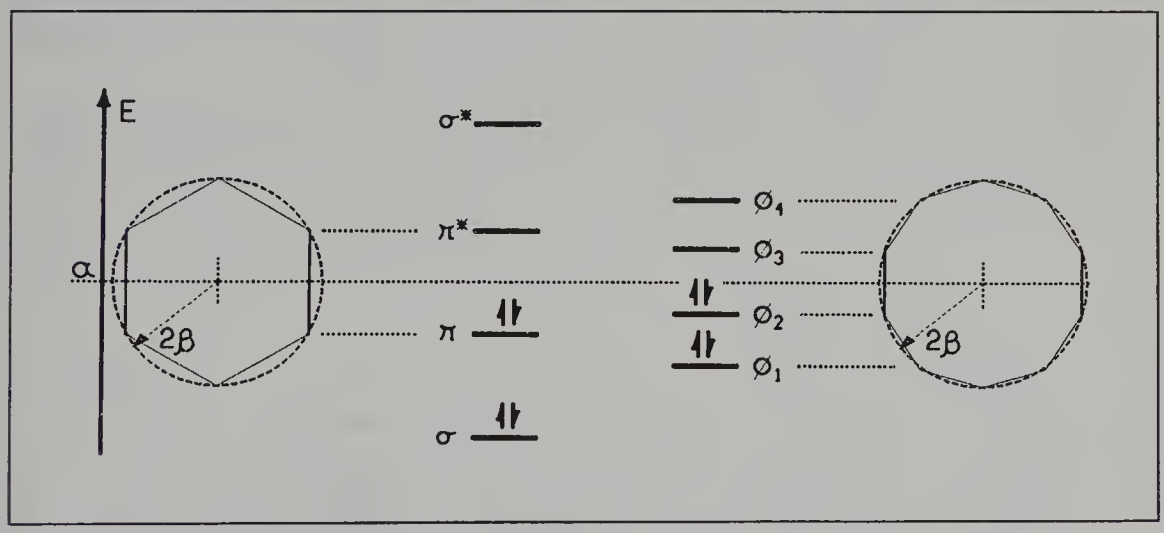


Figure 5.26: *Derivation of energy level patterns of butadiene and a part of cyclobutene using circle mnemonics.*

As mentioned earlier, circle mnemonics are applicable both to the cyclic and open chain polyenes. Hence, for butadiene (where n=4), a ten-membered ring (2n+2 = 10 atoms) is inscribed into the circle. The four points lying between the highest, and the lowest, points on the circle represent the energies of the four MOs of butadiene. The energy levels of cyclobutene can not be obtained by themselves, because of the involvement of σ orbitals. However, the energy levels of the ethylene part of cyclobutene might be obtained using circle mnemonics, i.e. by inscribing a hexagon (2n+2=6 atoms where n=2) into the circle. The σ or σ* orbitals of cyclobutene can then be placed either at a lower, or higher, level than the MOs of either ethylene or those of butadiene (Figure 5.26).

The energy level pattern of the transition state for a conrotatory process may be derived easily by considering it equivalent to a Möbius array that is composed of four *p*-orbitals as in cyclobutadiene (Figure 5.27).

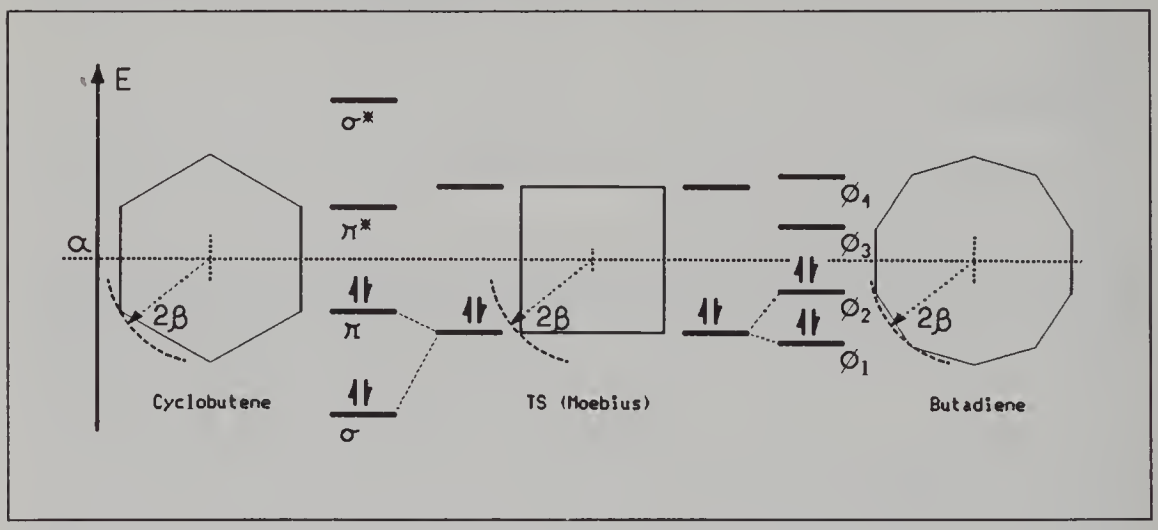


***Figure 5.27**: Energy changes during a conrotatory interconversion of butadiene and cyclobutene via a Möbius transition state.*

It is shown in Figure 5.27 that a Möbius transition state is involved which is aromatic, because it has a closed-shell arrangement of (4n) electrons. Therefore the conrotatory mechanism is an energetically feasible process in the ground state.

The energy level pattern of the disrotatory transition state resembles that of Hückel cyclobutadiene as shown in Figure 5.28.

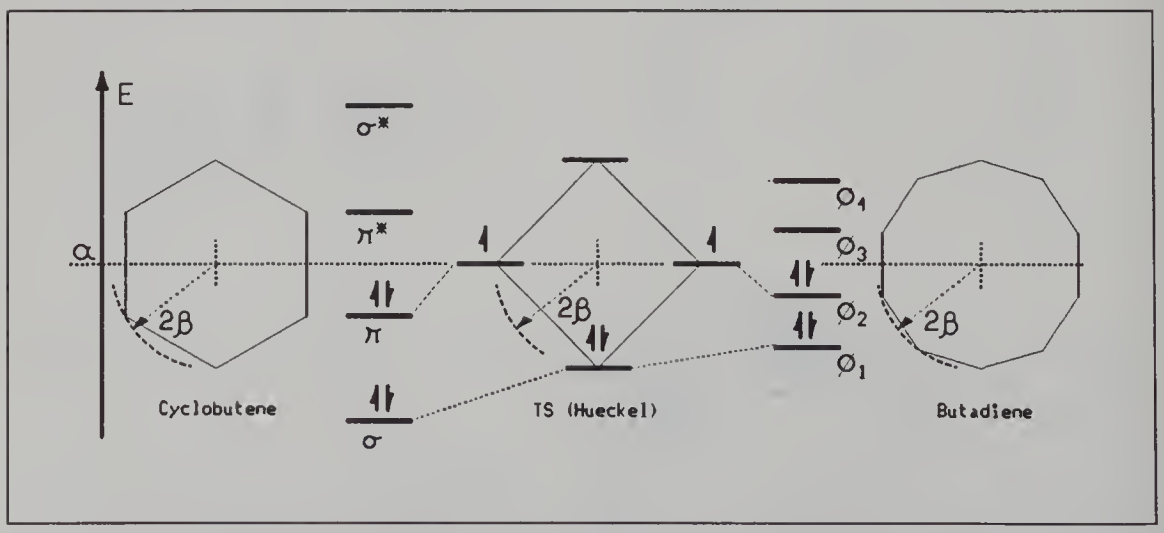


***Figure 5.28:** Energy changes during a disrotatory interconversion of butadiene and cyclobutene via a Hückel transition state.*

A disrotatory process which involves a Hückel transition state is not stabilized because of the open-shell arrangement of (4n) electrons. The energy barrier involved would render this process energetically unfavourable as shown in Figure 5.28.

Thus, polyenes with (4n) electrons undergo thermal electrocyclic change through conrotation. The same conclusion has already been drawn from the two other approaches discussed in Chapters 3 and 4.

The interconversion of 1,3,5-hexatriene and 1,3-cyclohexadiene may also be analyzed using the same arguments as applied to the interconversion of butadiene and cyclobutene.

(5.8)

The transition state may be envisaged as distorted benzene. Evidently, a disrotatory transition state has zero, or an even, number of sign inversions and is of Hückel type, whereas the conrotatory one has an odd number of sign inversions and is of Möbius type. The favourable mechanism is deduced from the rules of aromaticity (Table 5.5).

Problem 5.16:

Draw conrotatory and disrotatory transition states for the interconversion of hexatriene-cyclohexadiene and confirm that the transition state for the disrotatory and conrotatory process is of Hückel and Möbius topologies respectively.

Energy changes both during conrotatory and disrotatory transformations are shown in Figure 5.30 and Figure 5.31 respectively. An explanatory diagram (Figure 5.29) is drawn to show the derivation of the relative energies of the MOs of hexatriene and a part of cyclohexadiene, using circle mnemonics. Using the same device, the MOs of Hückel and Möbius transition states are derived.

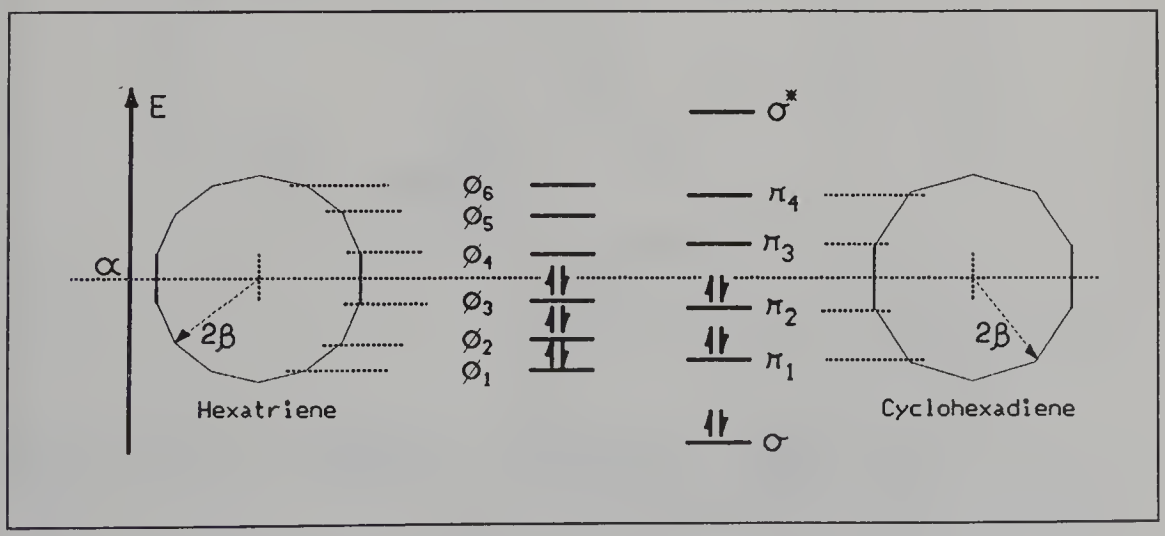


Figure 5.29: *Derivation of the energy level pattern of 1,3,5-hexatriene and a part of cyclohexadiene using circle mnemonics.*

It is evident from Figure 5.30 that the conrotatory process does not appear feasible in the ground state because a Möbius transition state, having an open-shell configuration

with (4n+2) electrons, is formed. This process has to face a large energy barrier during this transition state (Figure 5.30).

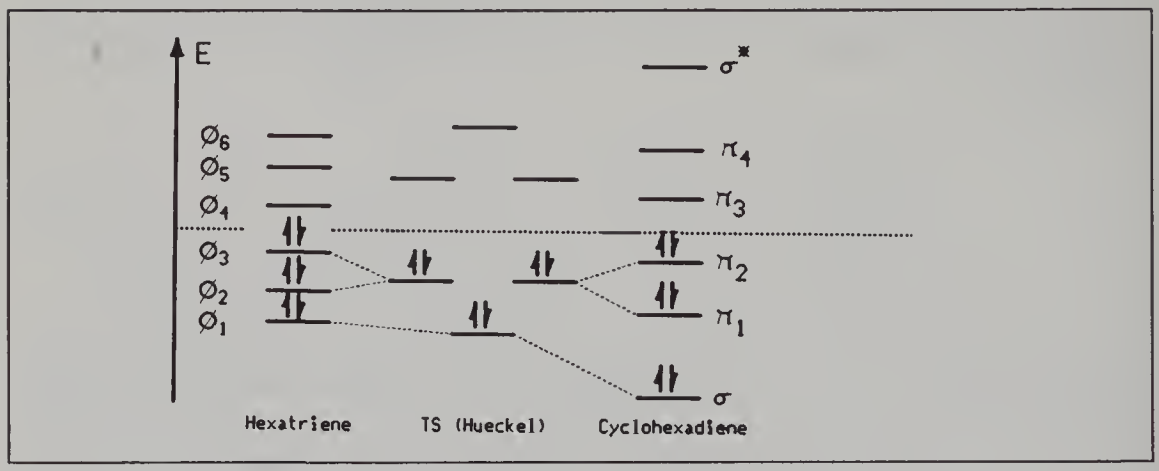


Figure 5.30: *Energy changes during a conrotatory interconversion of hexatriene and cyclohexadiene via a Möbius transition state.*

It can readily be seen from Figure 5.31 that a Hückel transition state is involved during the disrotatory process, which is aromatic, because it has a closed-shell arrangement of (4n+2) electrons. Therefore, the disrotatory mechanism is an energetically feasible process in the ground state.

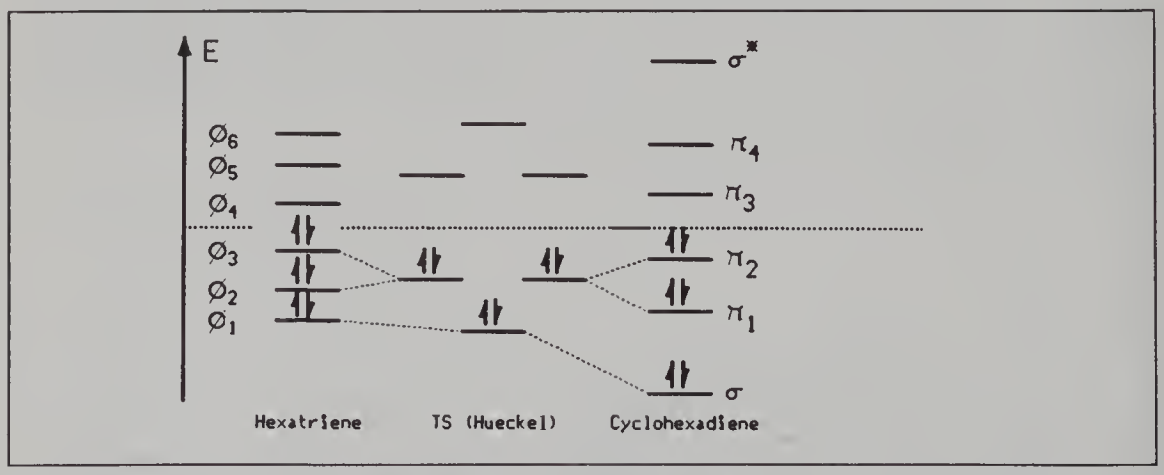


Figure 5.31: *Energy changes during disrotatory interconversion of hexatriene and cyclohexadiene via a Hückel transition state.*

The arguments developed for the ring opening of cyclic systems with either (4n) or (4n+2) electrons are applicable to any ring size. A conrotatory ring opening would always lead to a Möbius ring (an odd number of sign inversions), while a disrotatory to a Hückel ring (Figure 5.32).

It can be concluded that whenever a reaction involves the rupture, or formation, of an even-numbered ring containing (4n) electrons (e.g. cyclobutene) then a conrotatory path would be favoured and if it contains (4n+2) electrons (e.g. cyclohexadiene), then the disrotatory path would be preferred.

The odd-numbered rings, whether cations or anions, follow the same rules and predictions may again be made for the favoured mechanism on the basis of the number of electrons and the topology of the cyclic transition state. These predictions are in agreement with those of Woodward and Hoffmann.

Problem 5.17:
Draw conrotatory and disrotatory transition states for the following ionic systems and confirm the predictions made by Woodward and Hoffmann.

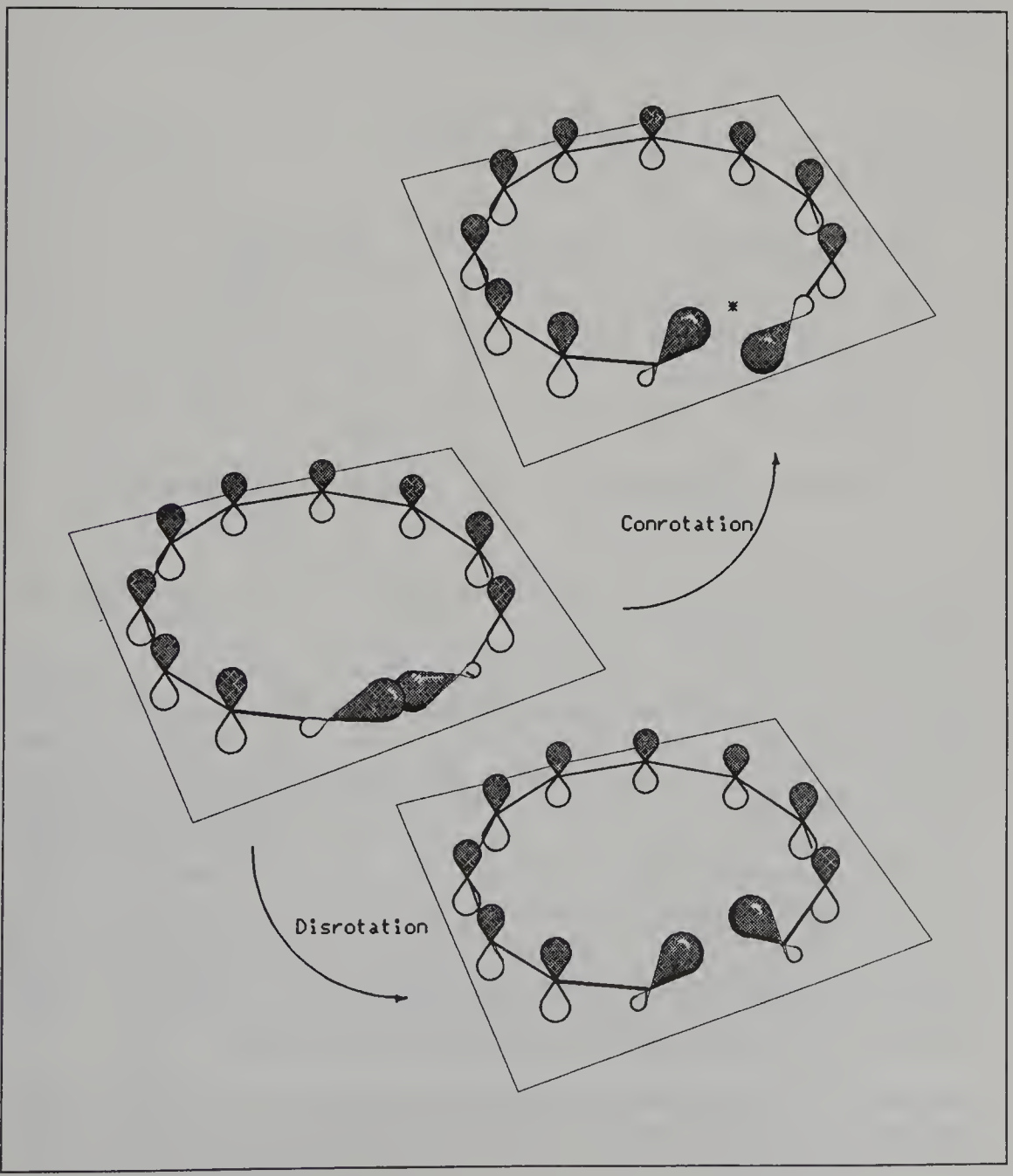


Figure 5.32: *Topology of a disrotatory and a conrotatory transition state.*

The above discussion may be summarized in the form of the following rule: *Thermal reactions prefer Hückel geometries of the transition state when (4n+2) electrons are involved and Möbius geometries of the transition state when (4n) electrons are involved.*

5.2.2 Photochemical Reactions

Thermal reactions prefer aromatic transition states, because such a transition state is of a lower energy and is easier to attain. In contrast, photochemical reactions prefer antiaromatic or less stable transition states. This can easily be justified. An important feature of photochemical reactions is an initial excitation of ground state molecules to their excited states, and then the conversion of these excited species to ground state products, as discussed in detail in Chapter 3.

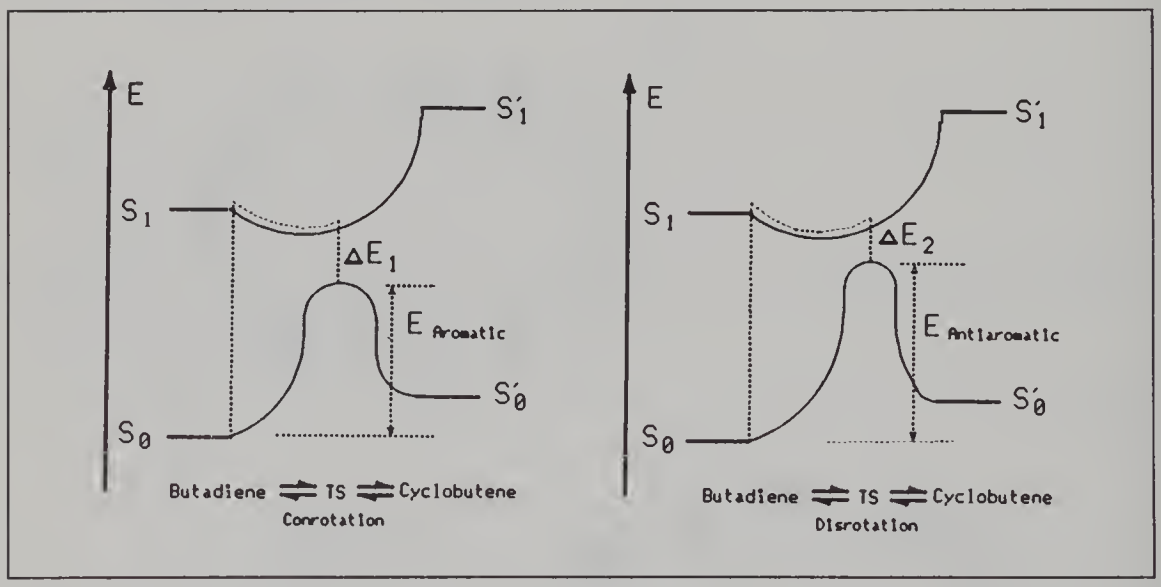


Figure 5.33: *Potential energy curves for photochemical reactions via aromatic and antiaromatic transition states.*

A comparison of the energy changes involved during the formation of an aromatic transition state ($E_{Aromatic}$) and an antiaromatic transition state ($E_{Antiaromatic}$) is shown in Figure 5.33. An aromatic transition state is easier to attain than an antiaromatic state since $E_{Aromatic} < E_{antiaromatic}$. These transition states initially lead to the formation of excited state products, which later decay to the ground state products. However, the conversion of excited state products to ground state products becomes relatively easier for an antiaromatic transition state than for an aromatic transition state because the gap ΔE_2 becomes smaller than ΔE_1. In other words, when the energy of the transition state increases, the potential energy surfaces of the excited state products and the ground state products come close together, thereby facilitating the photochemical process. Since photochemical pericyclic reactions prefer antiaromatic transition states, a rule is formulated which is simply the reverse of that for a thermal process.

Photochemical pericyclic processes prefer Möbius geometries of the transition state when (4n+2) electrons are involved and Hückel geometries of the transition state when (4n) electrons are involved.

5.3 Summary

The steps involved during the analysis of a pericyclic reaction on the basis of Möbius-Hückel approach are shown in Figure 5.34.

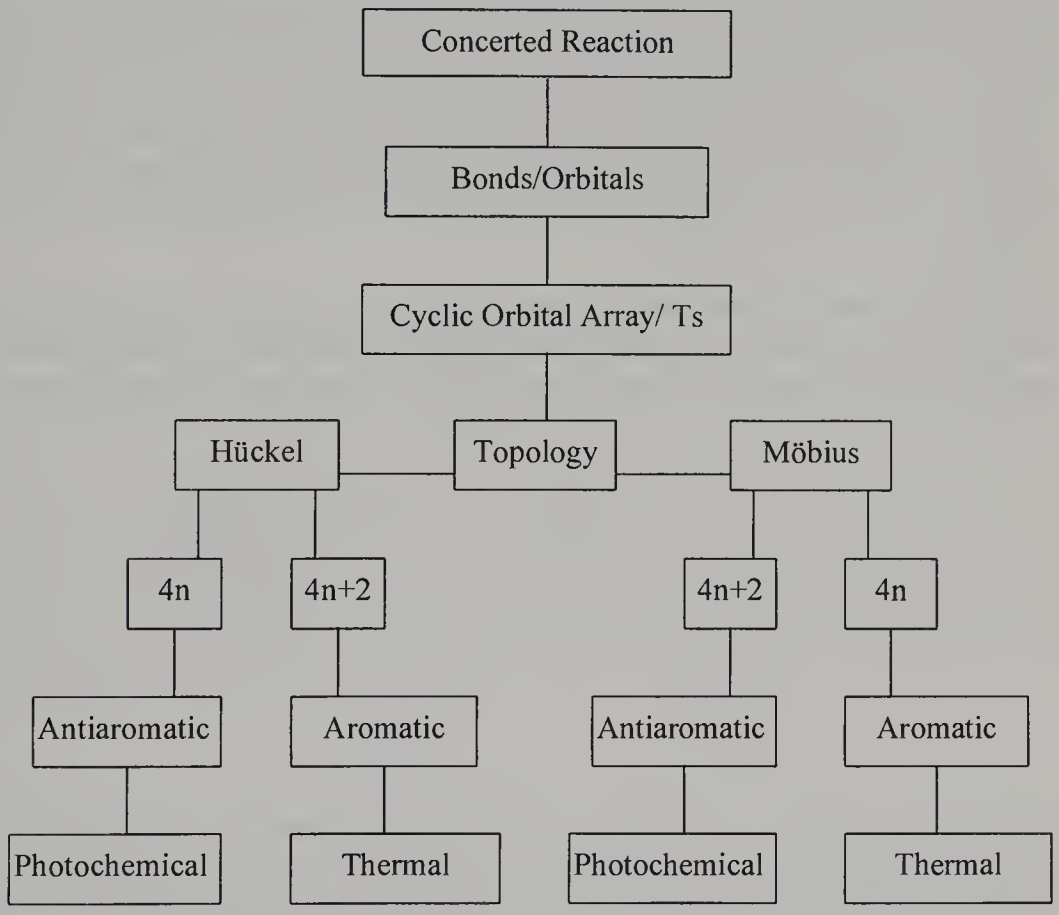


Figure 5.34: *Steps involved during the analysis of concerted reactions through Möbius-Hückel approach.*

However, while applying the approach to concerted reactions the following precautions are required:

i) Sign inversions *within* the atomic orbitals should not be considered.

ii) The reactions which do not possess a cyclic orbital array should not be analyzed through this approach.

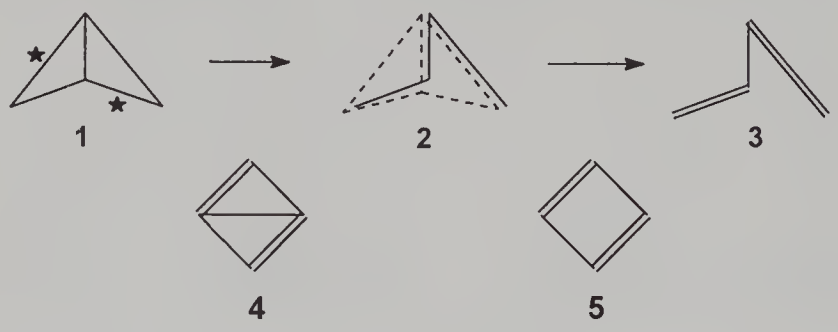
iii) The number of electrons should be carefully counted because a miscount, of just one electron in the total number of electrons, would lead to opposite results.

iv) The behaviour of odd-electron systems would be similar to those closed-shell systems that result after the addition of one more electron, and care should be exercised in identifying them.

The Möbius-Hückel approach uses just one rule, i.e. *(4n+2) electron systems prefer Hückel geometries and (4n) electron systems prefer Möbius geometries*. This analysis is very closely related to the Woodward-Hoffmann version, which is based on the concept of suprafacial and antarafacial interactions between the orbitals making up the transition state of a pericyclic process (as discussed in Section 4.1.2). Hence, each $[_2\pi_a]$ component (frontier orbitals approach) is considered equivalent to one sign inversion (Möbius-Hückel approach).

Both the Woodward-Hoffmann rules, or the equivalent statement embodied in Evan's principle, are valid for both symmetric and unsymmetric systems. Indeed, if this were not the case, they would be far less useful and unimportant. However, the Möbius-Hückel treatment offers the advantage of supplying the underlying reasons for geometric preferences during reactions. Therefore, the approach could be regarded either as providing a satisfactory theoretical basis for Woodward-Hoffmann rules, or as a satisfactory alternative to them.

An added advantage of the Möbius-Hückel approach is that it is also applicable to polycyclic systems since aromaticity, and antiaromaticity, can be predicted with ease for such systems. An interesting example is the conversion of bicyclobutane **1** to butadiene **3** by the breaking of two bonds, indicated by asterisks in Equation 5.9.



(5.9)

The transition state **2** is isoconjugate with bicyclobutadiene **4**. However, since the transannular bond of **1** is an *essential single bond* (i.e., a bond which remains a single bond in all possible structures), omitting this, the transition state becomes an analog of cyclobutadiene **5**. The transition state **2** should, therefore, be of Möbius type. The two σ-bonds may break in the following three different ways:

i) When both bonds break in a conrotatory manner, the breaking of each bond would introduce one sign inversion, and the total number of sign inversions would be even. The corresponding transition state would thus be of Hückel topology.

ii) When both bonds break in a disrotatory manner, no sign inversion would be introduced, and the total number of sign inversions would again be even. The transition state would also be of Hückel topology.

iii) However, if one bond breaks in a disrotatory, and the other in a conrotatory, manner the total number of sign inversions would be odd. The transition state would be of Möbius topology.

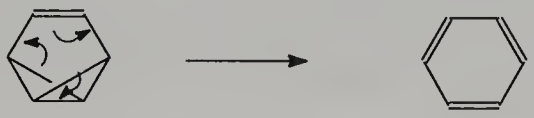
The rearrangement should, therefore, follow a disrotatory opening of one ring and a conrotatory opening of the other ring. This observation was experimentally shown to

be correct [14]. This reaction is of great significance because, being unimolecular, it can not be discussed in terms of the frontier orbitals method. The orbital symmetry conservation technique is also not applicable because symmetry is lost in forming the transition state.

Problem 5.18:

As discussed earlier in Chapter 3, the conversion of benzvalene to benzene (Equation 5.10) takes place readily by the cleavage of the same two bonds as indicated in Equation 5.9 [15].

Would the same mechanism be operative as explained in the preceding paragraph?



(5.10)

The treatment of electrocyclic reactions in terms of the orbital symmetry conservation, the frontier orbitals method and the Möbius-Hückel approach are qualitative. These three approaches predict that the conrotatory opening of cyclobutene would be favoured.

Determination of the numerical values of the difference in activation energies of the transition states of pericyclic reactions is not practically possible, even through approximate calculations. However, with the advent of sophisticated computers, the determination of the structures, geometries and energies of the transition states of these reactions are now possible with a measure of precision. These studies constitute the subject matter of Chapter 6.

5.4 References

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6. Theoretical and Computational Approach

The mechanism of electrocyclic reactions are studied using the Orbital Symmetry Conservation, the Frontier Orbitals Method and the Möbius-Hückel Approach. The molecular orbitals used in these approaches are derived from the HMO (Hückel Molecular Orbital) theory which is the simplest of the molecular orbital theories. However, it is known to give only qualitative results. The above mentioned three approaches provide qualitative predictions regarding the direction of ring opening in electrocyclic reactions. Thus, the elegance and simplicity of the three approaches used cannot be questioned. However, their limitations, as compared to the rigorous theoretical and computational approach, must be recognized. Theoretical and computational studies on pericyclic reactions were initiated in the early seventies and are being carried out, to date. Tools of computational chemistry are used to predict the geometries, energies and electronic characteristics of the reactants, products and the transition states. Although the geometries of the reactants and the products are obtained from experimental spectroscopic techniques, the details of transition state geometries and energetics can only be obtained using quantum mechanical calculations. These calculations provide a detailed picture of the shape and bonding present in transition structures of pericyclic reactions.

The *energy of activation* (i.e. the energy difference between the ground state and the transition state) is another important parameter which is obtained from theoretical calculations, as well as from experimental data. However, the reaction profile, which illustrates the energy variation as the reaction proceeds, may only be studied in detail using quantum mechanical calculations. Interpretation of quite a number of phenomenae becomes possible by following the reaction paths. The stereoselectivity of electrocyclic reactions is one such example which cannot be explained on the basis of steric arguments. The phenomenon is explained by studying the reaction paths using different sophisticated theoretical methods (Appendix A). A few basic concepts related to the reaction paths are discussed.

A reaction profile, or an energy profile, is the simplest representation of a reaction pathway and is illustrated in Figure 6.1. This reaction profile illustrates the way in which the energy of the reacting system changes as a function of the reaction coordinate. The *reaction coordinate* is a general term that represents the nuclear reorganization, i.e. the geometric change in the position of the atoms that take place, as the reactant is converted into a product.

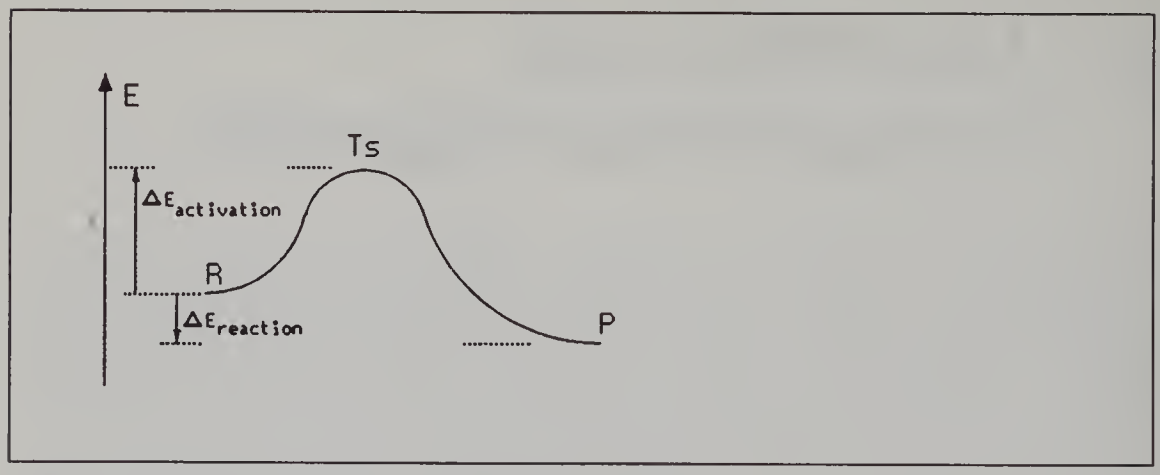


Figure 6.1: *Reaction profile of a concerted reaction.*

The energy changes during the conversion of a reactant into a product are not linear, the system goes rather through at least one high energy structure, which is the point of maximum energy along the reaction coordinate. This specific point is termed as the *transition state*. The term *transition structure* is commonly used for the geometrical structure of the transforming species at this point of maximum energy. Roughly speaking, the terms *transition state* and *transition structure* are considered to be synonymous.

The energy difference between the energy of the transition state and that of the reactant is known as E_a , the *activation energy*. This difference in energy is also known as the activation energy barrier. Another parameter is the *heat of reaction*, i.e. the difference in energy between the product and the reactant. The heat of reaction is a measure of the amount of heat evolved (exothermic), or absorbed (endothermic), during a reaction.

An interesting observation is: that for an exothermic reaction the transition structure resembles the reactant, whereas for an endothermic reaction it resembles the product. When the transition state resembles the reactant, it is formed early along the reaction coordinate and is termed as the *early transition state*. On the other hand, when a transition state resembling the product is formed, the reaction is obviously near completion, and is termed as a *late transition state* (Figure 6.2).

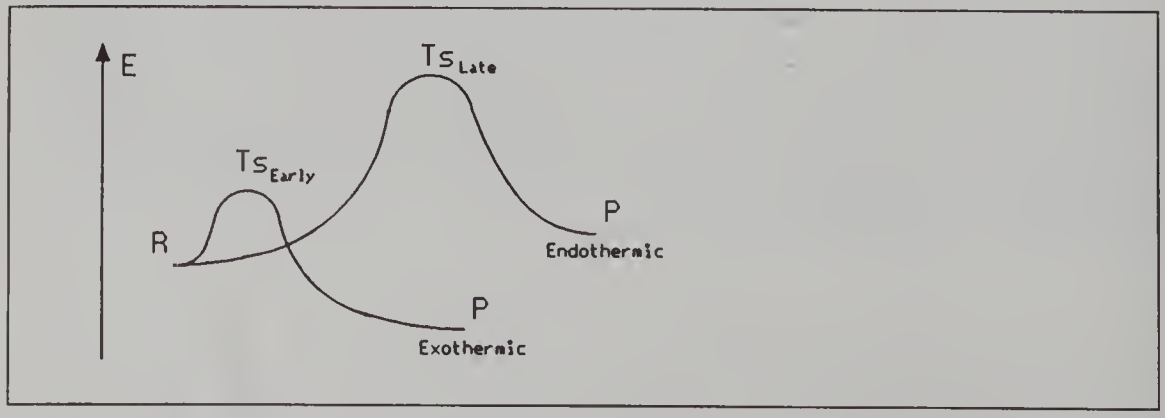


Figure 6.2: *Early and late transition states.*

6.1 Study of Reaction Paths

In this section the reaction paths for electrocyclic reactions of simple polyenes are discussed. A simple polyene may have an even, or an odd number of π electrons. As discussed earlier, the Woodward Hoffman rules can generally predict the direction of the ring opening in polyenes with an even number of electrons. For odd-electron systems, there are no specific rules. The two systems are discussed separately.

6.1.1 Even-Electron Systems

Polyenes with an even number of sp^2 hybridized carbon atoms form an even-electron system, e.g. butadiene, hexatriene or octatetraene. The cations or anions of polyenes with an odd number of sp^2 hybridized carbon atoms may also form an even-electron system, eg. allyl cation or anion, pentadienyl cation or anion.

Theoretical studies on the reaction paths for even-electron systems are now discussed. Some of the simpler systems, e.g. allyl cation, allyl anion and butadiene are discussed in greater detail, so as to provide a better understanding of the use of theoretical methods. As mentioned earlier in Chapter 2, electrocyclic reactions are classified according to the numbering of the carbon atoms involved in the breaking, or formation, of the σ-bond. The allyl anion (or cation), for example, is termed as a [1,3]-system, butadiene as a [1,4]-system, pentadienyl anion (or cation) as a [1,5]-system, and so on. While discussing the theoretical reaction paths for even-electron systems, the above mentioned classification is used.

6.1.1.1 [1,3] Electrocyclic Reactions

The reaction paths for the ring openings of cyclopropyl cation (2-electron system) and cyclopropyl anion (4-electron system) are studied to ascertain whether the reactions followed a disrotatory, or a conrotatory, path [1]. The theoretical method used is MNDO (Modified Neglect of Differential Overlap) MO calculations (Appendix A).

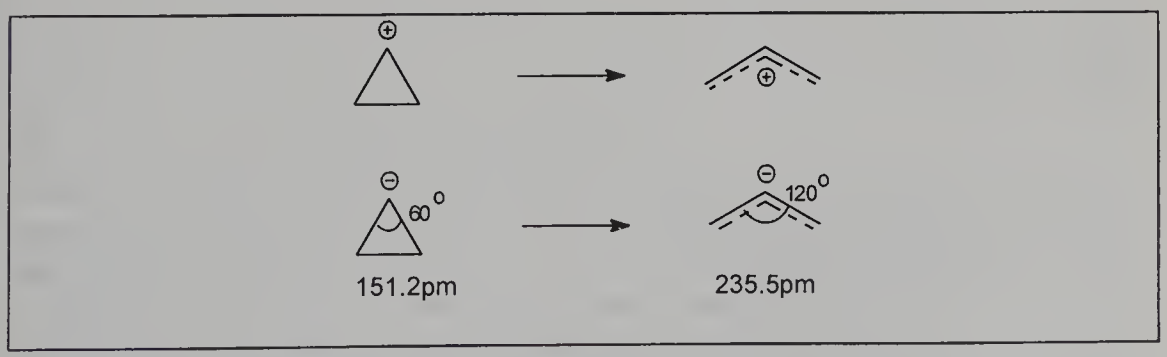


Figure 6.3: *Ring opening of cyclopropyl cation and anion.*

The angle θ is 60° in the cyclopropyl species (cation or anion) and 120° in the allyl species (cation or anion), i.e. the angle gradually opens up from 60° to 120° as the reactants change into products. This angle is taken as the reaction coordinate. The reaction coordinate is defined as any parameter (a bond angle, a bond length or any

physical property) which varies as the reaction proceeds. It simply is a measure of the extent of the reaction. For example, in the above mentioned case, an angle of 62° implies that the ring opening has just started and that the reaction is in its initial stages, whereas, an angle of 110° implies that the reaction is almost complete.

Problem 6.1:

The interatomic distance R changes from 151.2pm to 235.5pm in the ring opening of cyclopropyl anion (Figure 6.3). Could R be considered as a reaction coordinate? Would R depend upon θ ?

R = 168pm implies that the reaction

i) has just begun ii) is in the final stages iii) is somewhere in the middle

The energies of the following species are now calculated using MNDO calculations;

i) cyclopropyl cation, or anion, with $\theta = 60^\circ$

ii) allyl cation, or anion, with $\theta = 120^\circ$

iii) intermediary species with $60^\circ < \theta < 120^\circ$

Using MNDO calculations, the energies are calculated with an initial angle $\theta = 60^\circ$, and with 5° increments, the energies of the corresponding intermediate structures are also found. Two sets of energies are calculated; the first set is for the disrotatory ring opening and the second set for conrotatory. These energies are then plotted versus the reaction coordinate (Figure 6.5). It is seen that the energy of the product formed does not depend upon the reaction path, i.e. both disrotatory and conrotatory paths give the same product. This is expected for unsubstituted systems. However, the energies of the intermediate forms differ. This is because the geometry, as related to the position of the hydrogen atoms, differs (Figure 6.4).

Figure 6.4: *Geometry of the intermediate forms during the ring opening of cyclopropyl cation or anion.*

For the cyclopropyl cation the activation barrier for disrotation is lower than that for conrotation (Figure 6.5). This implies that the reaction for a 2-electron system proceeds through disrotation. On the other hand, for a cyclopropyl anion, the energy barrier for conrotation is lower than that for disrotation. This shows that the ring opening of the 4-electron system prefers a conrotatory mode. These theoretically plotted energy profiles confirm that systems with (4n+2) electrons undergo ring opening through a disrotatory mode, whereas systems with (4n) electrons prefer the conrotatory mode.

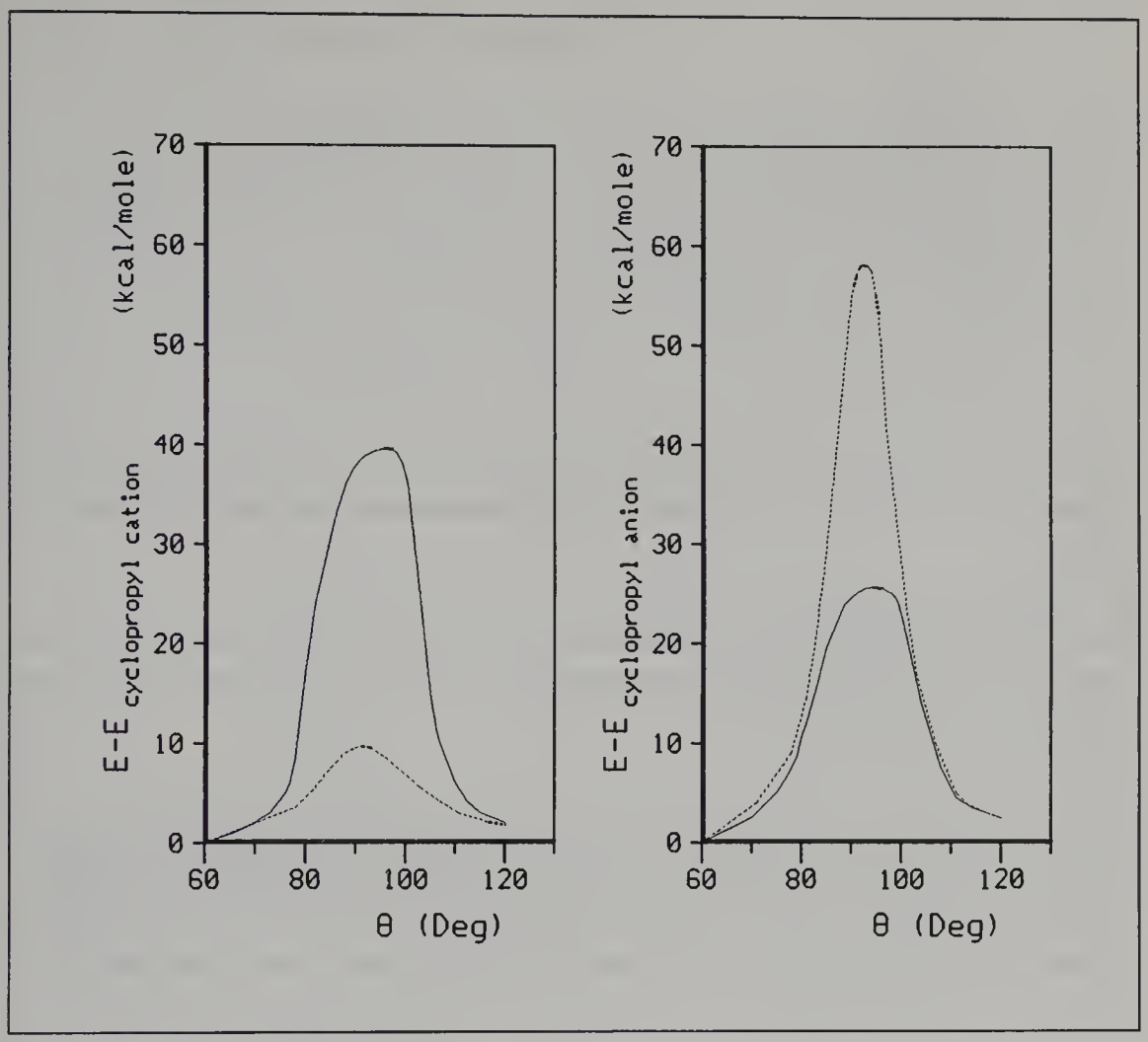


Figure 6.5: *Plot of energy versus θ for rearrangement of cyclopropyl cation and anion to allyl cation and anion (dotted line ..... disrotation, solid line — conrotation).*

The same conclusion was drawn earlier on the basis of orbital symmetry conservation (Chapter 3), the frontier orbitals method (Chapter 4) and the Möbius-Hückel method (Chapter 5). The confirmation of this conclusion, using the theoretical method, establishes the validity of the theoretical approach.

This picture, however, is oversimplified. The energies of the transforming species are calculated by varying the interatomic distance R, and the bond angle θ. These two are interdependent parameters (i.e. if R is known then θ can be calculated, and vice versa). Any one of these parameters is plotted along the reaction coordinate (x-axis) versus energy (y-axis) and a two dimensional graph is obtained.

In addition to the interdependent parameters θ and R, there exists an independent parameter ϕ, which is the angle of twist of the terminal methylene groups. This twist angle is 90° in the reactant and 0° in the product.

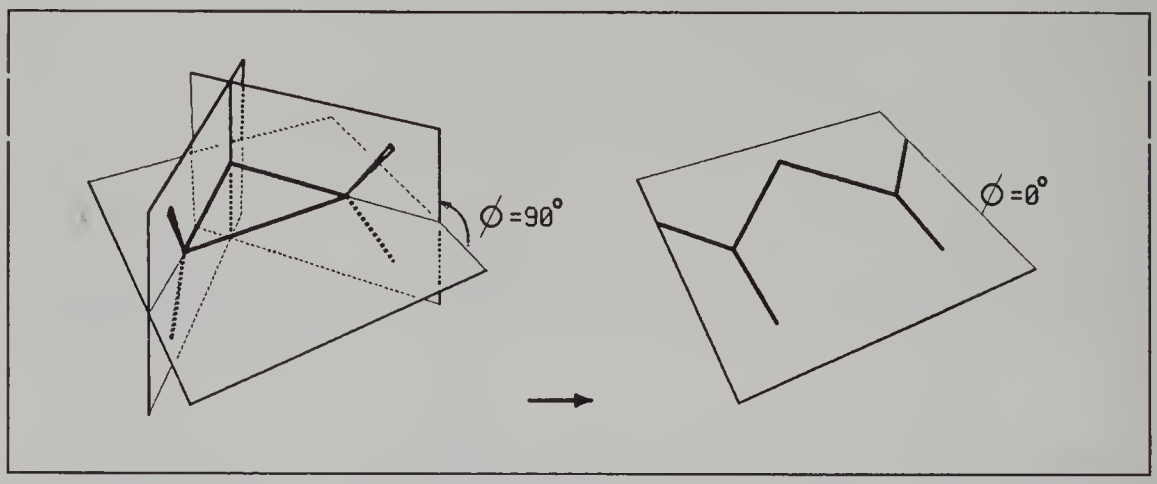


Figure 6.6: *Angle of twist $\phi = 90^o$ and $\phi = 0^o$. during the ring opening of a cyclopropyl system.*

In the energy profiles shown in Figure 6.5 it is assumed that the reaction follows a linear path, i.e. the angle of twist ϕ gradually increases. This is known as *synchronous rotation*. However, this may not be necessarily so, and the methylene group may rotate independently of the bond angle θ or bond length R. This would then be called *non-synchronous rotation* [2].

To get a better picture of the ring opening, a set of two independent parameters, θ and ϕ (or R and ϕ), are plotted along the *x*- and *y*- coordinates. The corresponding energy E is then plotted along the *z*-coordinate. The plot obtained is a three dimensional graph, where the potential energy is plotted along one of the axis and is known as the *potential energy surface*. Figure 6.7 illustrates a simple potential energy surface.

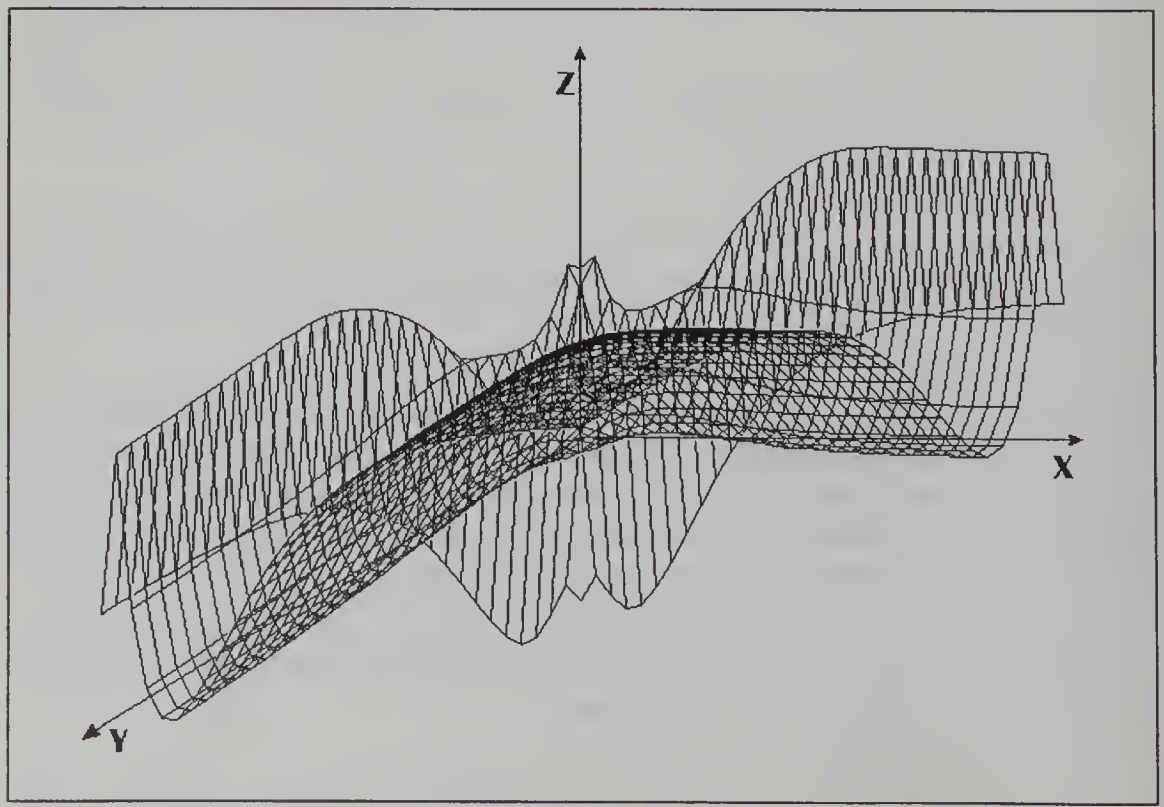


Figure 6.7: *Three dimensional graphic representation of a potential energy surface.*

6.1.1.2 [1,4] Electrocyclic Reactions

The interconversion of cyclobutene and butadiene is the simplest electrocyclic reaction for a closed-shell neutral system. This transformation is considered to be a classic example of electrocyclic transformations, and its mechanism is interpreted extensively using different approaches, namely Orbital Symmetry Conservation, Frontier Orbitals, Möbius-Hückel and Theoretical cum Computational. All the four approaches predict a preference for the conrotatory process in agreement with the experimental observation. However, the theoretical and computational studies provide many details about the reaction path and intermediary states which cannot be obtained otherwise. Extensive theoretical and computational treatments [3] [4 a-c] are found in contemporary literature for this classic example of an electrocyclic reaction. The simplest possible theoretical treatment is that of Woodward and Hoffman [3] using EHMO (Extended Hückel Molecular Orbital) calculations (Appendix A).

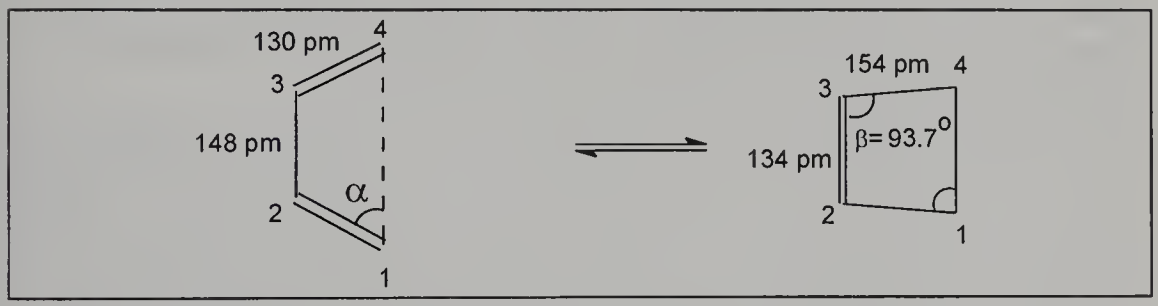


Figure 6.8: *Electrocyclization of cis-butadiene.*

In EHMO calculations, the initial conformation of the planar *s-cis* form of butadiene was taken as

C1—C2 = C3—C4 = 130pm.,
C2—C3 = 148pm,
all the carbon —hydrogen bond lengths = 110pm
and a range of values for the internal angle α.

The dotted line in butadiene depicts the 1,4-bond, which is yet to be formed. The angle between the dotted line and the 3,4-bond (or 1,2) is known as the internal angle α (Figure 6.8). As cyclization proceeds, α increases, and the 1,4-bond order changes from zero to some positive value. EHMO calculations show that the 1,4-bond order gradually changes to a positive value for a conrotatory process, while a negative bond order develops for a disrotatory process. This implies the energetic preference for a conrotatory process.

The same transition state may also be approached from the cyclic form, i.e. the ring opening reaction. A model of cyclobutene is chosen with geometry

C2—C3 = 134pm (C—C double bond),

C3—C4 = C1—C4 = C1—C2 = 154pm (C—C single bond)

and $\beta = 93.7^{\circ}$

The carbon atoms C1and C4 are sp^3 hybridized and the two C—H and C—C bonds form a tetrahedral structure. As the ring opening proceeds, β increases, and the

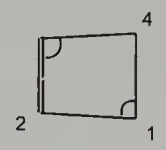
1,4-bond order changes from a positive value to zero. According to EHMO calculations the 1,4 bond order decreases more rapidly for a conrotatory process than for a disrotatory process. The EHMO calculations also reveal an energetic preference for the conrotatory path, i.e. the activation energy for the conrotatory process is lower than that of the disrotatory process. The EHMO calculations provide the simplest possible quantitative quantum mechanical treatment for the ring opening of cyclobutene. Calculations at higher levels of theory were also carried out for this system. The optimized geometries and the reaction energetics (i.e. activation energies and heat of reactions) are obtained from these calculations.

The *optimized geometry* is the geometry which has the minimum energy. For example, a certain geometry for a molecule is first assumed; the bond lengths, bond angles and tetrahedral angles are repeatedly changed by small increments and the energy calculated. The geometry which finally gives the minimum energy is the optimized geometry. Different levels of theory give different optimized geometries, however, it is observed that the optimized geometries obtained from theoretical calculations are in reasonable agreement with the experimental geometries [4a].

All theoretical treatments predict the favourability of the conrotatory process. It is observed that the calculated activation energies vary and cover a range of 36 to 88 Kcal $mole^{-1}$. The experimental activation energy has a value of 32.9 ± 0.5 Kcal $mole^{-1}$ Accurate activation parameters can only be calculated at high levels of theory.

In Table 6.1 the optimized geometries of cyclobutene are compared with the experimental geometries. These optimized geometries were calculated using *ab initio* and a semiempirical molecular orbital method. The *ab initio* MO calculations are MO calculations with rigorous mathematical formulations without any approximation or simplifying assumption. The *ab initio* method used here is RHF (Restricted Hartree Fock) with STO-3G orbitals. The semiempirical method used was Austin model or AM1 model (Appendix A).

Table 6.1: *Theoretical and experimental geometries of cyclobutene .*



	Bond Lengths (pm)		
	C1—C4	C3—C4, C1—C2	C2—C3
RHF/STO-3G	156.5 pm	152.6	131.42
AM1	156.7	152.19	135.4
Experimental	156.6	151.7	134.2
	Bond Angles		
	∠C2-C3-C4	∠C3-C4-C1	∠C2-C3-C4-H *
RHF/STO-3G	94.7°	85.3°	115.3° *
AM1	94.0°	86.0°	114.8° *
Experimental	94.2°	85.8°	—

* Dihedral angle. A dihedral angle is the angle between two planes. C2C3C4 constitue one plane, while C3C4H constitute the other plane. The bond C3C4 is the line intersecting the two planes.

The optimized geometry of cyclobutene, when calculated using two different theoretical formulations, is similar to the experimental geometry as listed in Table 6.1. The optimized geometry of the transition state is given in Table 6.2. However, for the transition state, a comparison with experimental data is not possible. The credibility of the theoretical method has to be established in cases where experimental data is available, i.e. for the reactant and the product.

Table 6.2: *Theoretical geometry of the conrotatory transition state of cyclobutene.*

	Bond Lengths (pm)		
	C1—C4	C3—C4, C1—C2	C2—C3
RHF/STO-3G	210.22pm	145.5	138.80
AM1	211.96	142.78	138.89
	Bond Angles		
	∠C2-C3-C4	∠C3-C4-C1	∠C2-C3-C4-H *
RHF/STO-3G	102.7°	74.8°	—
AM1	103.8°	74.5°	—

Problem 6.2

i) Complete the following table using the data in Tables 6.1 and 6.2 (use bond lengths and bond angles from RHF STO-3G method).

	Cyclobutene	Transition state (conrotatory)
C2—C3	—	138.8pm
C3—C4	—	145.5pm
C1—C4	—	210.22 pm
C1—C2	152.6pm	—
∠C3-C4-C1	—	74.8°
∠C2-C3-C4	94.7°	—

i) Identify the bond-lengths which are: a) increasing b) decreasing

ii) Identify the bond angles which are: a) increasing b) decreasing

Tables 6.1 and 6.2 show that the breaking single bond C1—C4 stretches from 156.5pm to 210.2pm in the transition structure. In butadiene the C1—C4 interatomic distance is about 290pm. This change is about 40% of the total change. The single bonds flanking the breaking bond (C1—C2) or (C3—C4) contracts from 152.6pm to 145.5pm. In butadiene, this bond length is about 134pm. This change is again about 40% of the total change. Thus, considering both the parameters, i.e. (C1—C4 and (C1—C2) / (C3 —C4), the transition structure shows a 40% change. Since most of the changes have yet to take place, it could be called an early transition state.

Problem 6.3:

The calculated optimized geometries [5] for the ring opening of cyclopropyl are shown below:

The breaking C—C bond in the transition structure = 156.0pm

Total change in C—C bond distance = 235.5-151.2 = 84.3pm

Change in C—C bond distance from the reactant to the transition state = 156 - 151.2 = 4.8pm

% change = 100 x 4.8 / 84.3=_____?

What is the % change in the breaking C—C bond in the transition state? Do these calculations predict an early transition state.

Another example of a [1,4] electrocyclic process is the ring opening of benzocyclobutene to *o*-xylylene (Equation 6.1). This ring opening of

benzocyclobutene is analogous to the ring opening of cyclobutene. The system is considered as a 4-electron, or an 8-electron system.

(6.1)

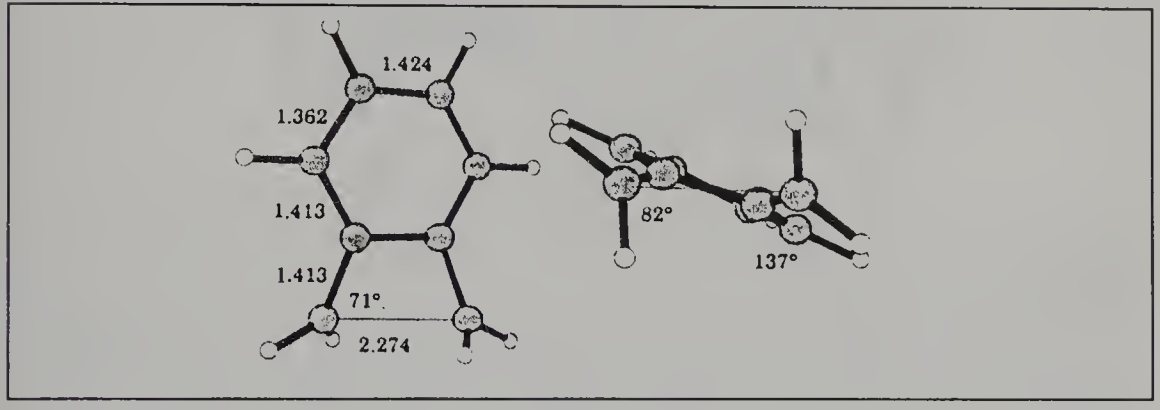


***Figure 6.9**: The transition structure for conrotatory electrocyclic ring opening of benzocyclobutene.*

The theoretically calculated [6] transition structure of benzocyclobutene (Figure 6.9) shows that the breaking C—C single bond (227.4pm) is slightly longer than that in the cyclobutene transition structure (213pm). This 'lateness' of the transition structure is consistent with the experimental observation as the ring opening of benzocyclobutene is found to be endothermic by 15 Kcal $mole^{-1}$ (Endothermic reactions generally have a 'late' transition state). On the contrary, the ring opening of cyclobutene is exothermic by 10 Kcal $mole^{-1}$ and shows a comparatively early transition state.

6.1.1.3 [1,5] Electrocyclic Reactions

The preceeding examples studied the ring openings of cyclic structures. It was observed that the ring opening is preferred over the ring closure, in case the open chain structure is more stable than the cyclic structure. On the other hand, the ring closure is the favoured process when the cyclic structure is more stable.

Pentadienyl cation (4-electron system) and anion (6-electron system) undergo electrocyclic transformations. For the pentadienyl cation the conrotatory ring closure process (Equation 6.2) is the favoured process, because the cyclic structure is the stable structure.

(6.2)

Theoretical calculations [7a,b] predict that in the transition structure the partial C—C bond length is 227pm (Figure 6.10). In the reactants the C—C distance is 295pm and for the products it is equal to 156pm. The calculated bond length of the transition structure indicates an early transition state. Moreover, all partial double bonds have identical bond lengths of 139pm, i.e. the transition structure is similar to the reactants.

The calculated activation energy is nearly zero for this process. The heat of reaction is 27 Kcal mole^{-1} and the reaction is, therefore, highly exothermic.

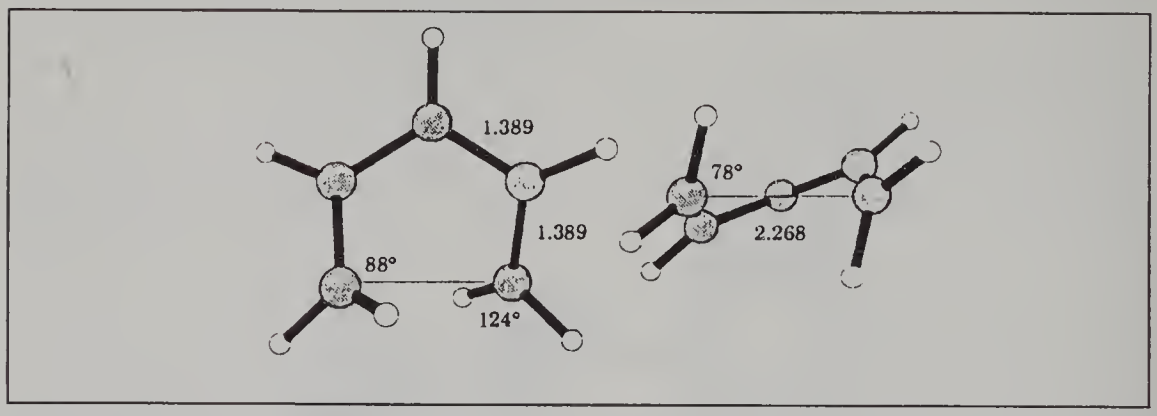


Figure 6.10: *The transition structure for the conrotatory electrocyclization of the pentadienyl cation.*

For the anionic species the disrotatory ring opening (Equation 6.3) is the preferred process as the pentadienyl anion is more stable than the cyclopentenyl anion.

(6.3)

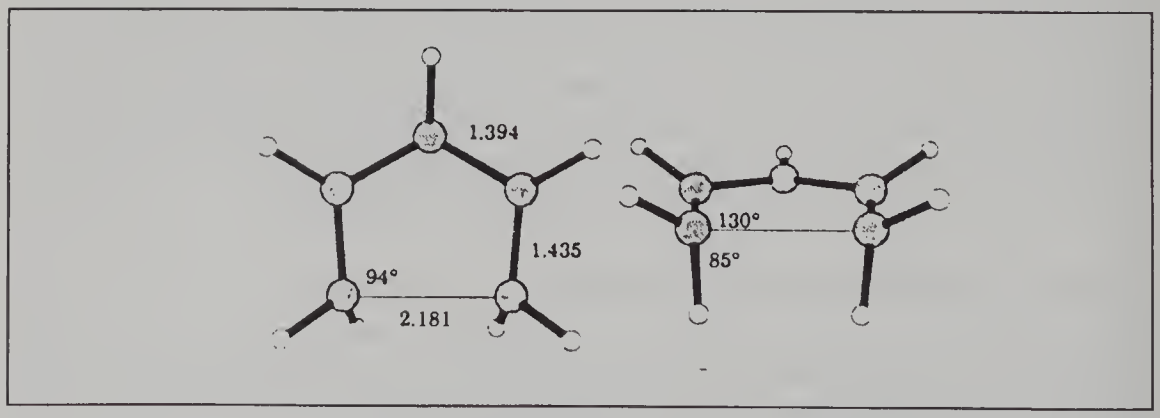


Figure 6.11: *The transition structure for the disrotatory ring opening of the cyclopentenyl anion.*

During the ring opening of cyclopentenyl anion the C—C breaking bond in this transition structure has a length of 218pm, while the partial double bonds vary from 139 to 144pm. The transition structure is again similar to the reactants in this respect. The calculated activation energy barrier is 20 Kcal mole^{-1}.

6.1.1.4 [1,6] Electrocyclic Reactions

Another theoretically studied reaction is the disrotatory ring closure of *cis*-1,3,5-hexatriene to form 1,3-cyclohexadiene (Equation 6.4) [8 a-c]. The transition structure for the ring closure is shown in Figure 6.12. The activation energy of 26 Kcal mole^{-1} for the disrotatory ring closure agrees with the experimental value of 29 Kcal mole^{-1}.

(6.4)

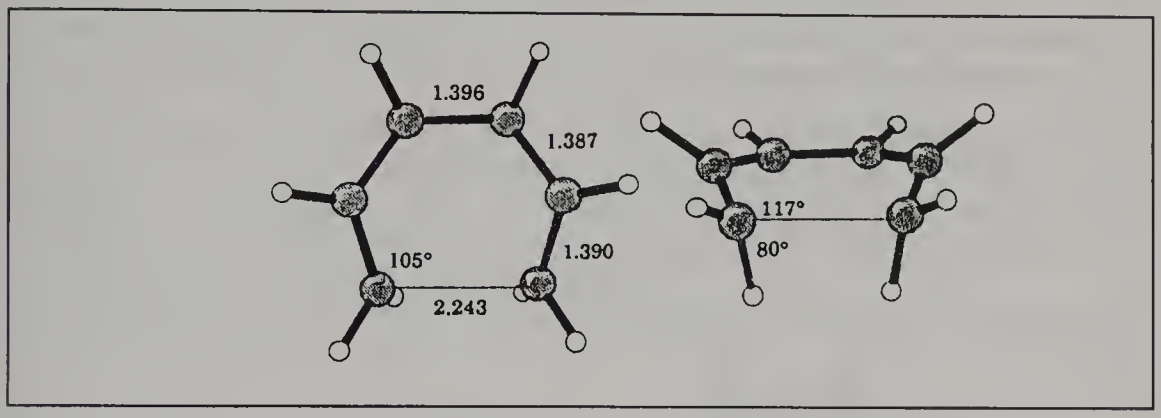
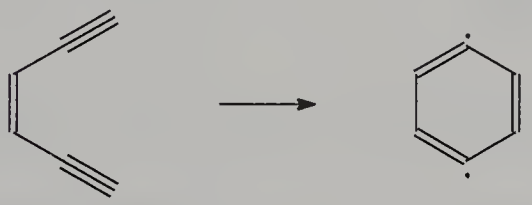


Figure 6.12: *The transition structure for disrotatory electrocyclization of hexatriene.*

Another interesting example of a [1,6] electrocyclic reaction is the disrotatory electrocyclization of hex-3-ene-1,5-diyne, to give benzene-1,4-diyl as shown in Equation 6.5 [9 a,b].



(6.5)

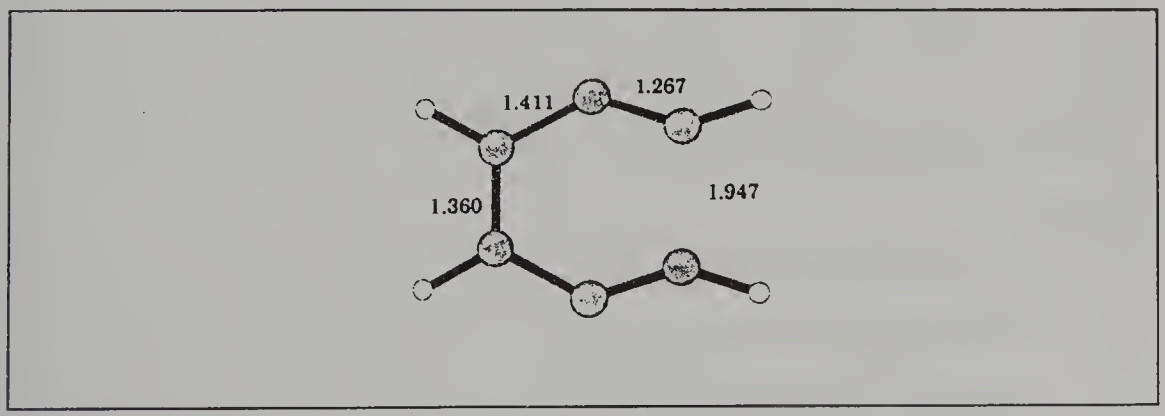


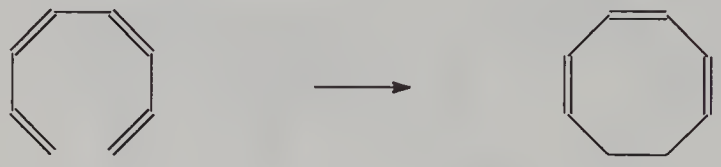
Figure 6.13: *The transition structure for disrotatory electrocyclization of hex-3-ene-1,5- diyne.*

This is an important electrocyclic process, as the naturally occurring antibiotics, esperamicin and calicheamicin [9c], undergo this type of reaction. Both these antibiotics are complex molecules with the active moiety hex-3-ene-1,5-diyne, which undergo electrocyclization to form benzene-1,4-diyl. The benzene diradical thus formed abstracts hydrogen atoms from DNA to cause cleavage of a double strand DNA and subsequent cell death. There is much excitement about this process and simple versions of the reaction are extensively studied, using computational methods [9 d,e].

The calculated activation energy barrier is found to be low. It is also experimentally observed that cyclization readily occurs at room temperature.

6.1.1.5 [1,8] Electrocyclic Reactions

Another system studied theoretically is the electrocyclization of 1,3,5,7-octatetraene to 1,3,5-cyclooctatriene (Equation 6.6) [10].



(6.6)

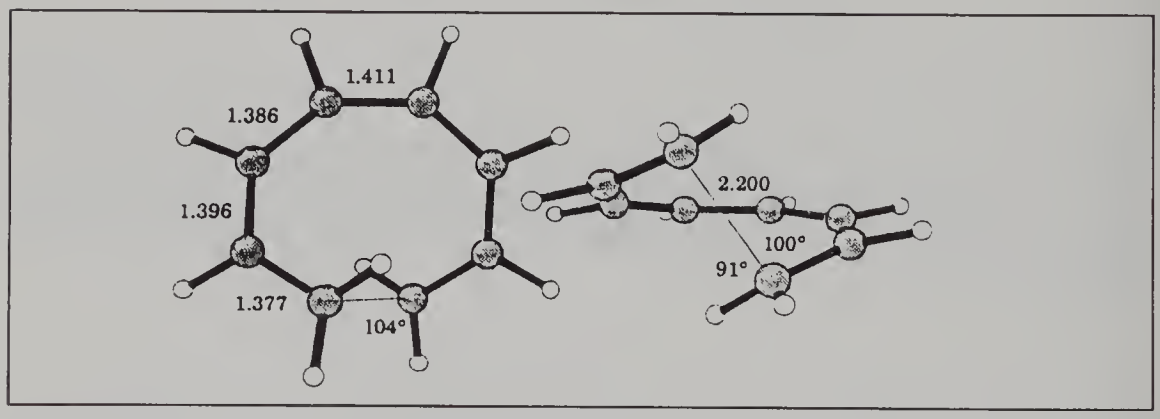


Figure 6.14: The transition structure for conrotatory electrocyclic ring closure of octatetraene.

During the conrotatory ring closure of the 8-electron system (Equation 6.6), the two termini of the C—C bond are almost perfectly aligned and not twisted as in the butadiene and cyclobutene interconversion [11]. The coiled arrangement of the eight carbon atoms allows an excellent overlap throughout the molecule. The calculated activation energy is 8 Kcal $mole^{-1}$.

Problem 6.4:

List two electrocyclic processes where the:

i) ring opening is the favoured process.

ii) ring closure is the favoured process.

The electrocyclization, or ring opening, of even-electron systems is discussed above. The mechanism referring to the disrotatory, or conrotatory mode, is easily predicted for these systems.

6.1.2 Odd-Electron Systems

Regarding the electrocyclic ring opening, or ring closure, of a radical with (4n+1) or (4n-1) electrons, no conclusion can be drawn from the Woodward Hoffman rules, nor from the energy level, nor symmetry state, correlation diagrams. It needs to be seen

whether theoretical calculations could be of any use in predicting the preferred mode of an electrocyclic reaction.

6.1.2.1 Ring Opening of Cyclopropyl Radical

The ring opening of a cyclopropyl radical is an example of a (4n-1) electrons system, which was studied theoretically in detail [12].

The ground states of cyclopropyl radical and allyl radical belong to different symmetry point groups; the allyl radical belongs to the point group C_{2v} , while cyclopropyl belongs to C_s (Appendix B). On the basis of energy level correlation analysis (Figure 6.15), it is predicted that the thermal interconversion would be forbidden, both through conrotation and disrotation (Chapter 3).

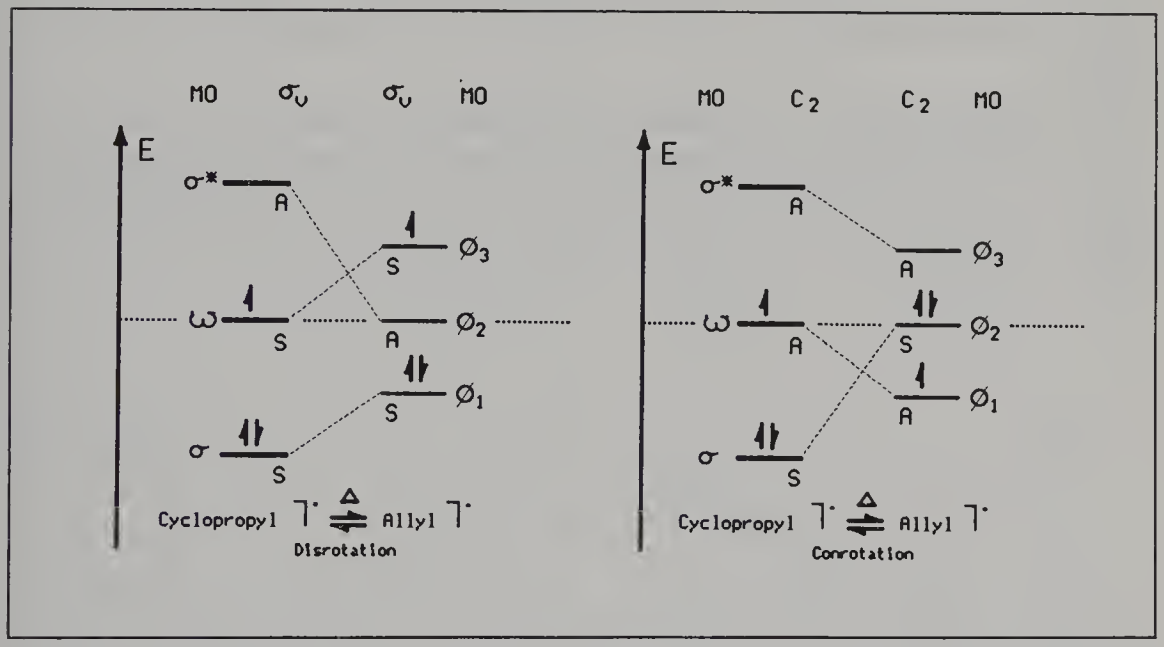


Figure 6.15: *Energy level correlation diagrams for thermal interconversion of cyclopropyl radical to allyl radical through disrotation and conrotation.*

However, experimentally it was observed that the cyclopropyl radical opens up to form an allyl radical with an activation barrier of 22±2 Kcal $mole^{-1}$ [12].

Several theoretical methods, both semi-empirical and *ab initio,* are therefore devoted to this system to study the ring opening mechanism [12].

Some details of the calculations performed, and their predictions, are now discussed. By starting at the equilibrium geometry of cyclopropyl radicals, and using the length of the breaking C—C bond as the reaction coordinate, the energy of the system was calculated. The energy was minimized without imposing any symmetry restriction. There was no rotation of the methylene groups, i.e. they remained perpendicular to the molecular plane (Figure 6.16).

The energy profile for this reaction path is represented by curve I (Figure 6.17).

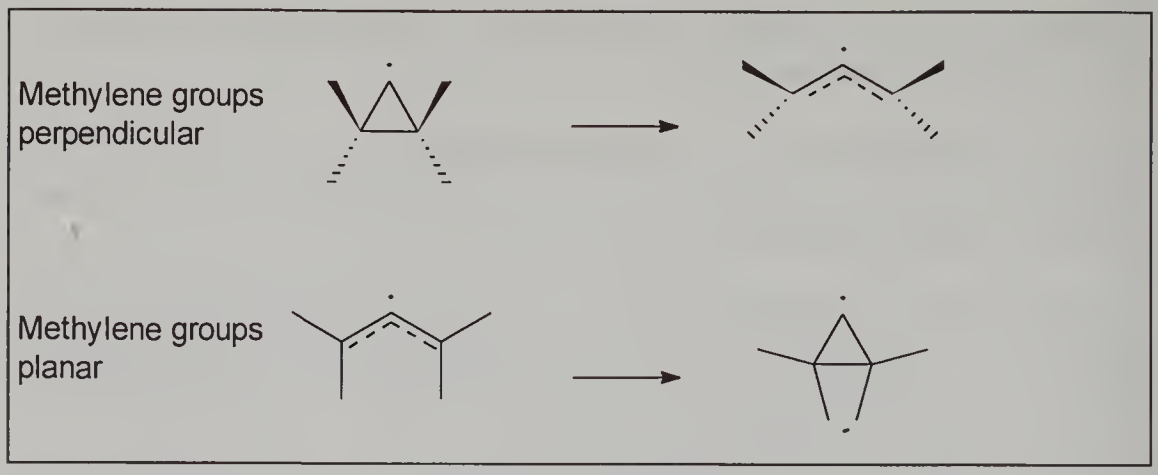


Figure 6.16: *Hypothetical intermediate structure for the ring opening of cyclopropyl radical.*

The equilibrium geometry of the planar allyl radical is now taken as the starting point (Figure 6.16). The length of the forming C—C bond is the reaction coordinate. The energy is calculated as this interatomic distance varies. The methylene groups remain planar along this path. The curve II in Figure 6.17 depicts the energy profile for this path.

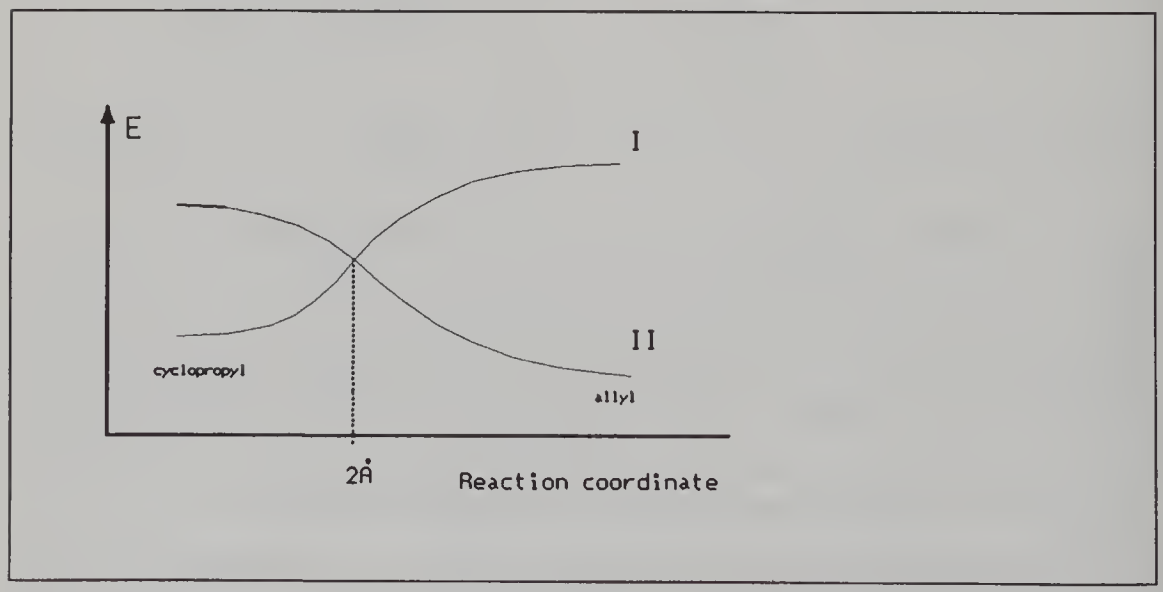
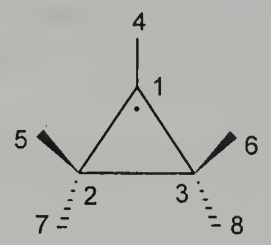


Figure 6.17: *Energy profiles for a hypothetical ring opening, or closure, of the cyclopropyl radical.*

At the crossing point of the two curves, the C—C distance equals 200pm. The geometry optimization for the cyclopropyl-like structure with the above mentioned C—C interatomic bond distance was carried out. The optimized structure obtained was totally non-symmetric. Initially, these calculations were carried out using semiempirical SCF MO methods. Later on, sophisticated *ab initio* theoretical treatments of the system also predicted an unsymmetric transition state.

The optimized structures for cyclopropyl radical, allyl radical and transition state are given in Table 6.3. The symmetry point groups of cyclopropyl, transition state and allyl radical are C_s ,C_1 and C_{2v}, respectively (Appendix B).

Table 6.3: *Some geometrical parameters for the UHF/3-21G optimized structure of a cyclopropyl radical.*



	cyclopropyl	Ts	allyl
Bond length (pm)			
C1—C2	148.5	142.4	138.8
C1—C3	148.5	148.5	138.8
C2—C3	157.5	206.6	245.0 *
Bond angles			
∠C2-C1-C3	64.1°	90.5°	124.3°
∠H5-C2-H7	115.4°	117.3°	117.4°
∠H6-C3-H8	115.4°	119.2°	117.4°
Plane-plane angles			
∠(C1-C2-C3)(H5-C2-H7)	89.7°	66.0°	0.0°
∠(C1-C2-C3)(H6-C3-H8)	89.7°	86.1°	0.0°

* In an alyll radical, no bond exists between atoms 2and 3. However, in this case the length mentioned is the interatomic distance.

Problem 6.5: Fill in the blanks:

In cyclopropyl C1-C2 = C1-C3 = _____ pm

In allyl C1-C2 = C1-C3 = _____ pm

In the transition structure C1-C2 ≠ C1-C3

C1-C2 = _____ pm C1-C3 = _____ pm

The unequal bond lengths and plane-plane angles indicate that an unsymmetric transition state is formed. Thus, in this ring opening, symmetry is not conserved.

Further sophisticated calculations reveal a non-synchronous rotation of the methylene groups, i.e. only one methylene group rotates initially. The second methylene group rotates in the last phase of the ring opening process, i.e. when the C2—C3 bond is completely broken.

This implies that this electrocyclic conversion takes place via a transition state, which is common to both disrotatory and conrotatory modes of reaction. Sophisticated CASSCF (Complete Active Space SCF) calculations confirm the existence of a common non-symmetric transition state for conrotatory, and disrotatory, thermal interconversion of cyclopropyl and allyl radical.

Thus, theoretical calculations predict an equal probability for both the disrotatory and the conrotatory ring openings. Another prediction is that the symmetry is not conserved in this reaction.

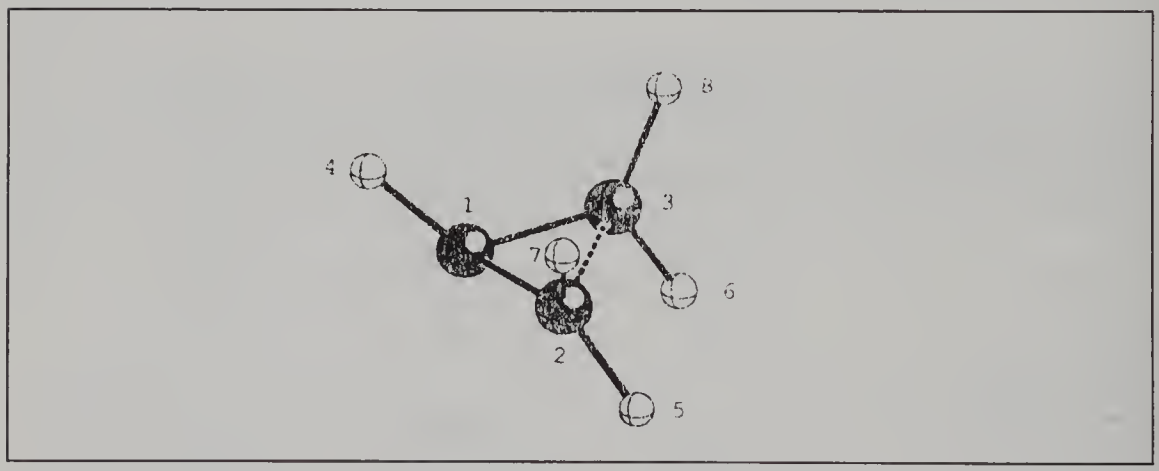


Figure 6.18: *Optimized structure of the transition state in the interconversion of the cyclopropyl and allyl radical.*

The experimental, and theoretical, activation energies (E_a) and heats of reaction (E_{rxn}) are given below.

E_a(theoretical) = 19.2 Kcal mole^{-1} E_{rxn}(theoretical.) = -19.8 Kcal mole^{-1}

E_a(expt.) = 19.1 to 22 Kcal mole^{-1} E_{rxn}(expt.) = -22.8±4.9Kcal mole^{-1}

The experimental and theoretical energies are in reasonably good agreement.

6.1.2.2 Electrocyclic Reactions of Bicycloalkyl Radicals

Besides the cyclopropyl radical, the ring opening of some other radical systems (including bicycloalkyl radicals) were studied theoretically [13]. A few examples are illustrated and discussed below.

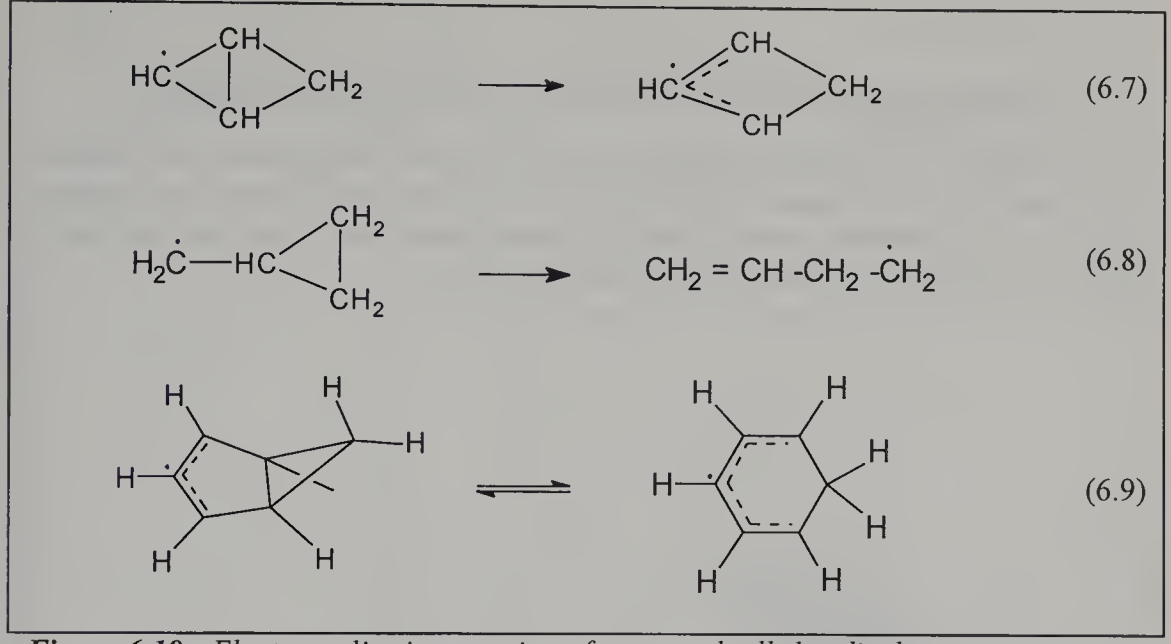


Figure 6.19: *Electrocyclic ring opening of some cycloalkyl radicals.*

The geometries of the transition structures, activation energies and the lengths of the breaking C—C bonds were calculated [13]. Theoretical calculations predict a non-symmetric change of geometrical parameters, in passing from the reactant to the product, i.e. the existence of a non-symmetric transition state was indicated for electrocyclic reactions of radicals.

For cyclopropylmethyl radical (Equation 6.8) *ab initio* calculations predicted two equilibrium geometries; a bisected form and an eclipsed form. These results were in agreement with the experimental ESR studies. Detailed theoretical calculations were carried out to establish the reaction mechanism and the intermediates involved in the ring opening of bicyclo[3.1.0]hex-3-ene-2-yl radical (Equation 6.9). In mechanistic investigations some hypothetical reaction paths and mechanisms were proposed. Theoretical calculations were then carried out for all the proposed reaction paths and the path with the lowest activation energy was predicted to be the favourable reaction path [13].

6.2 Stereoselectivity in Electrocyclic Reactions

Stereoselectivity of pericyclic reactions is a phenomenon which cannot be explained on the basis of steric arguments. Electrocyclic ring openings of mono substituted and disubstituted cyclobutenes were studied in detail, theoretically and experimentally. Distinct stereospecific products were formed in each case.

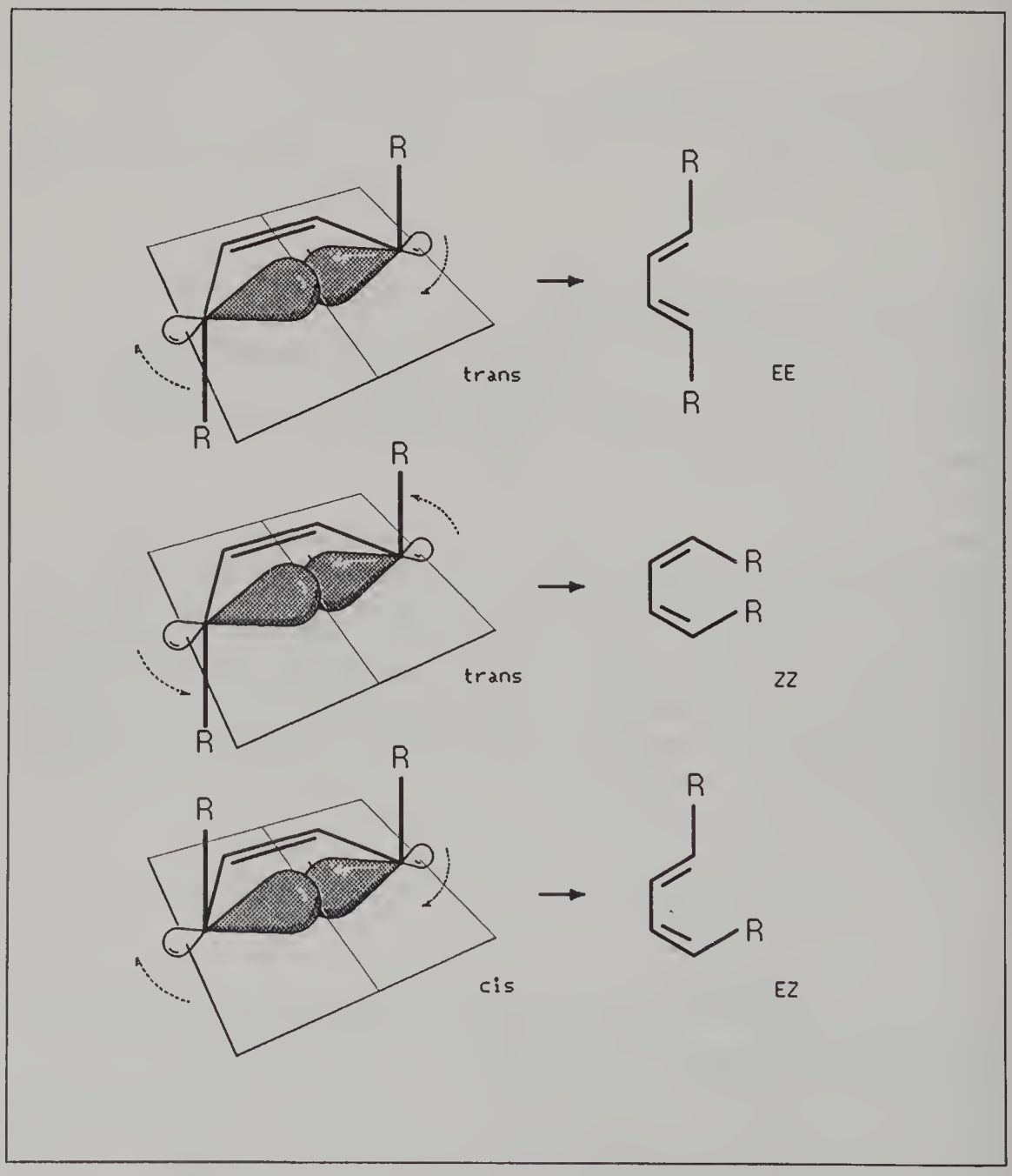


Figure 6.20: *Possibilities for conrotatory ring opening of cyclobutene.*

Consider a specific example of the thermal ring opening of cyclobutene or the reverse process. The reaction proceeds in a conrotatory manner; both orbitals involved in the

breaking, or formation, of σ bond rotate either clockwise or anticlockwise. This is depicted graphically in Figure 6.20.

Obviously for an unsubstituted system (R=H), or for a symmetrically substituted system, the product of the two processes is the same. Theoretical possibilities for the ring opening of mono- and disubstituted cyclobutenes are shown (Figure 6.21).

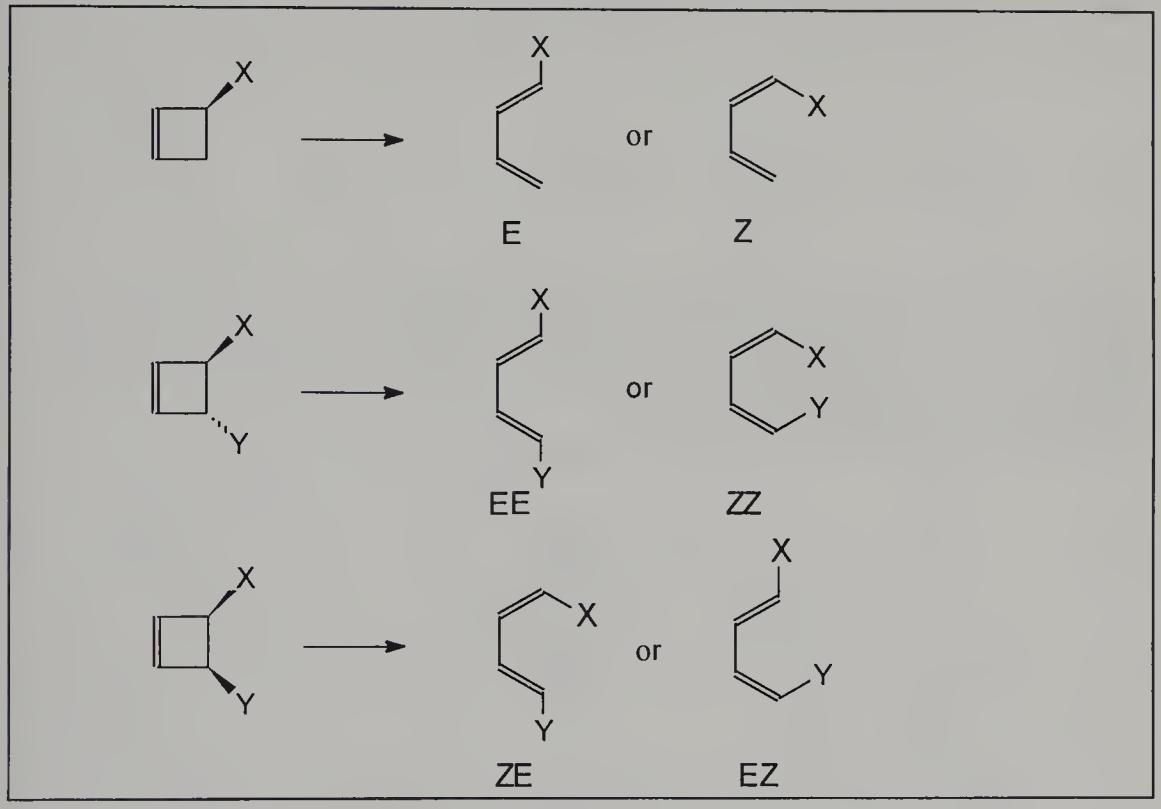


Figure 6.21: *Theoretical possibilities of conrotatory ring opening of substituted cyclobutenes.*

It is evident from Figure 6.21 that for monosubstituted cyclobutene there is an equal probability of formation of Z- and E- isomers. Thus, a substituent may either rotate "inwards" leading to the formation of Z-diene, or "outwards" to give the E-diene. The ring opening of *trans*-disubstituted cyclobutene through conrotation may give rise to two products, EE and ZZ isomers, whereas the *cis*- isomer opens up to form only one product .

6.2.1 Experimental Aspect

6.2.1.1 Experimental Observations

Extensive experimental studies were carried out for the ring opening of mono-, and disubstituted, cyclobutenes. It was observed that in both the cases only one isomer was obtained. The monosubstituted cyclobutene opened up to form an E-diene and the *trans*- disubstituted cyclobutene opened up to form an EE-diene. Initially these, and the related results, were rationalized on the basis of steric arguments. That is, although the inward rotation of the substituent is allowed by orbital symmetry, the steric

repulsion destabilizes the corresponding transition states. Consequently only the product resulting from an outward rotation is observed [14 a,b].

However, other results were reported which were inconsistent with the steric arguments, e.g. the ring opening of 3-ethyl-3-methyl cyclobutene (Figure 6.22). On the basis of the steric effect, the bulkier ethyl group was expected to rotate outwards, however, it was observed to rotate inwards [15 a,b].

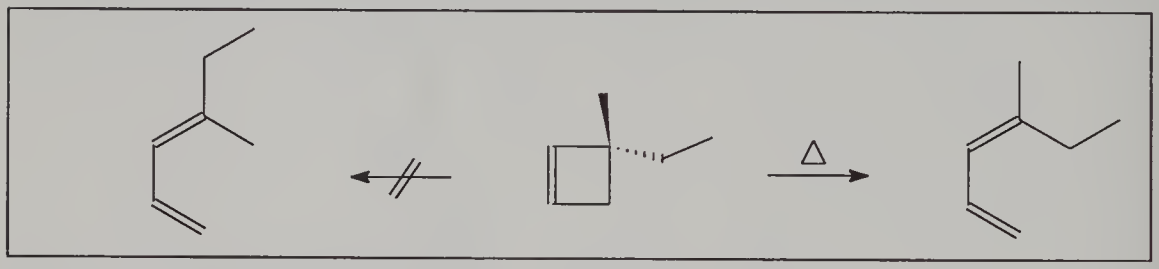


Figure 6.22: *Ring opening of 3-ethyl, 3-methyl cyclobutene.*

Another example which refutes the steric considerations is the ring opening of *trans*-perfluoro-3,4-dimethyl cyclobutene [16].

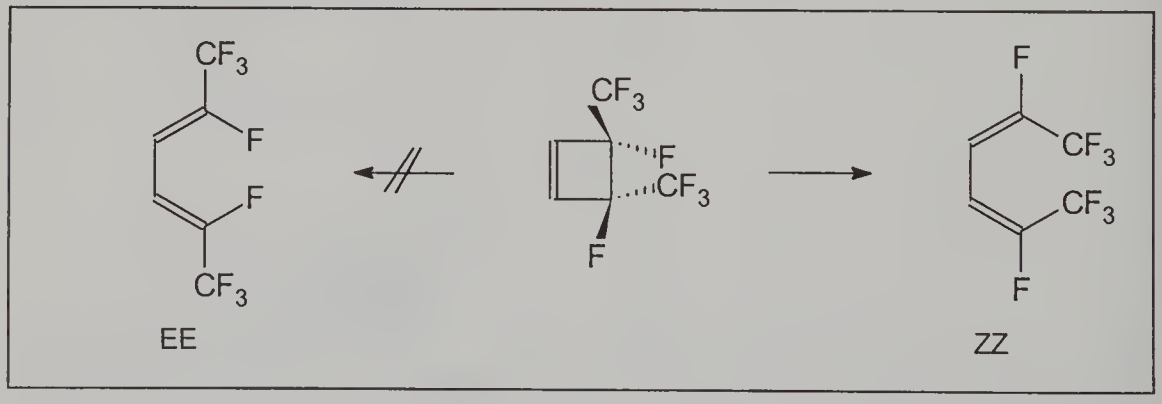


Figure 6.23: *Contrasteric ring opening of trans-perfluoro-3,4-dimethyl cyclobutene.*

Steric considerations favour the formation of the EE-diene, however, the ZZ-diene is formed. In view of these contradictory results there arises the need for a better, and more quantitative, understanding of the factors involved in determining the mode of rotation in electrocyclic reactions. The two approaches used are the determination and study of:

i) experimental parameters such as the activation energy.

ii) the reaction paths using computational methods.

A systematic study of experimental activation energy data gives a very good idea of the relative preference of the substituent to move inwards, or outwards, whereas theoretical calculations reveal that the substituents have a profound effect on the energies and geometries of the transition structures.

6.2.1.2 Interpretation of Experimental Activation Energy Data

Activation energies of a number of substituted and disubstituted cyclobutenes were calculated, analyzed and interpreted.

Consider the activation energies for the ring opening of cyclobutene and some substituted cyclobutenes as shown in Figure 6.24 [17].

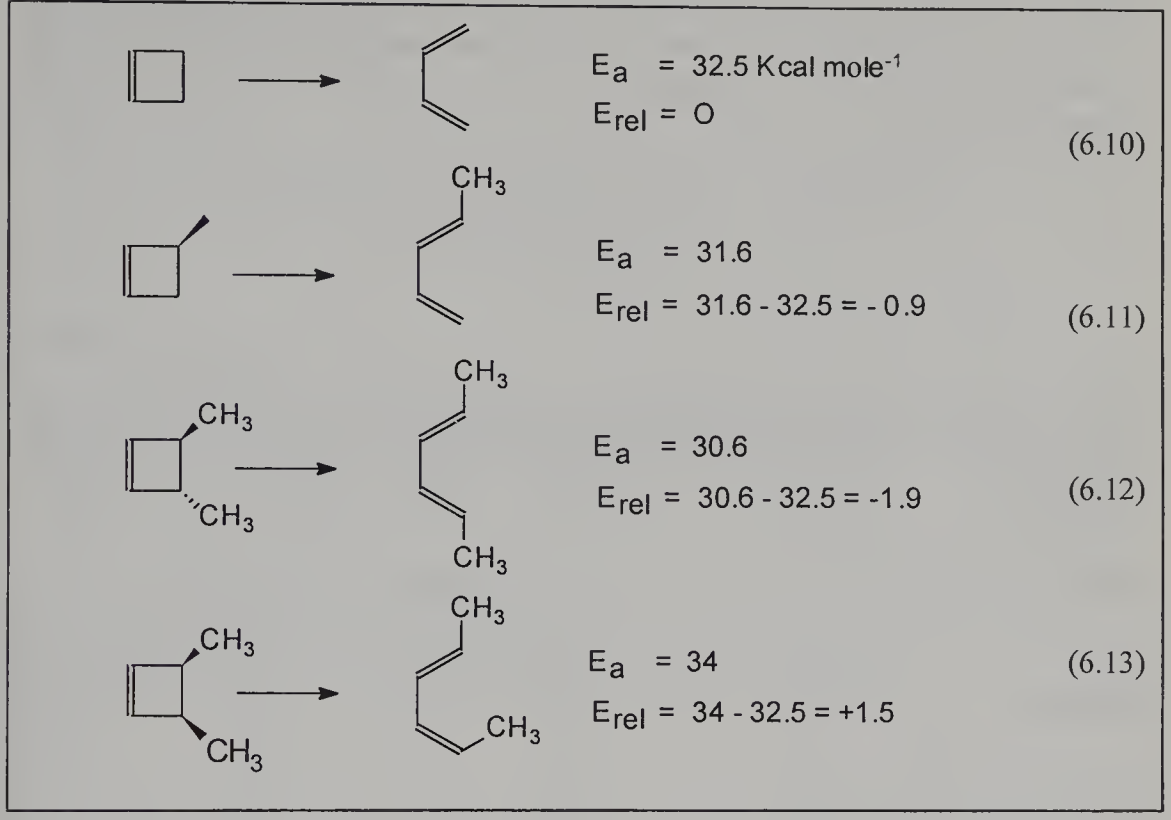


Figure 6.24: *Activation energies for the ring opening of some substituted cyclobutenes.*

E_{rel} is the activation energy relative to the activation energy of cyclobutene, i.e.

$$E_{rel} = E_a - E_a(\text{cyclobutene})$$

The experimental activation energies are given in Table 6.4 and in Figure 6.24. A comparison of E_a and E_{rel} for cyclobutene and 3-methyl cyclobutene (Equations 6.10 and 6.11) shows that an outward rotation of the methyl group lowers the activation energy for the ring opening by 0.9 Kcal mole^{-1}. This lowering of the activation energy of the ring opening is known as the *outward substituent effect* for the methyl group. Thus, the substituent effect for the outward rotation of methyl group is -0.9Kcal mole^{-1} (approximated as -1 Kcal mole^{-1}). A negative substituent effect indicates a lowering in the activation energy.

The two methyl groups rotate outwards in the ring opening of *trans*-3,4-dimethyl cyclobutene (Equation 6.12), and an EE diene is formed. From the E_{rel} value it can be seen that the activation energy of ring opening for the outward rotation of the two methyl groups is lowered by 1.9 Kcal mole^{-1} (approximated as 2 Kcal mole^{-1}). This shows that the substituent effect is additive, i.e. the outward rotation of one methyl group lowers the activation energy by 1 Kcal mole^{-1} whereas the outward rotation of two methyl groups lowers the activation energy by 2 Kcal mole^{-1}.

It is clear from the above examples that the methyl substituent(s) prefer to move outwards to form an E- or EE- diene. However, in *cis*- disubstituted dimethyl cyclobutenes, one of the methyl groups is forced to move inwards. A comparison of

the activation energies of cyclobutene and of the disubstituted system (Equations 6.10 and 6.13) shows that the activation energy is raised by 1.5 Kcal $mole^{-1}$. However, in the case of *cis*-disubstituted systems, the outward rotation of one methyl group lowers the energy, whereas an inward rotation of the other methyl group raises it. Thus 1.5 Kcal $mole^{-1}$ is the net change in activation energy (Figure 6.24). As these energy changes are additive

$$\text{net change in } E_a = \text{change in } E_a \text{ (outward)} + \text{change in } E_a \text{ (inward)}$$

$$1.5 = -1 + \text{change in } E_a \text{ (inward)}$$

$$\therefore \quad \text{change in } E_a\text{(inward)} = 2.5 \text{ Kcal mole}^{-1}$$

thus the substituent effect for the methyl group going inwards is 2.5 Kcal $mole^{-1}$.

Table 6.4 lists the experimental activation parameters for the thermal ring opening of 3,4-disubstituted cyclobutenes with methyl-, chloro-, acetoxy- and ethoxy-substituents.

Table 6.4: *Activation energies for conrotatory ring opening of cyclobutenes.*

	E_a Kcal $mole^{-1}$	E_{rel}^{*} Kcal $mole^{-1}$
cyclobutene	**32.5**	**0.0**
3-methyl cyclobutene	31.6	-0.9
cis-3,4-dimethyl cyclobutene	34.0	1.5
trans-3,4-dimethyl cyclobutene	30.0	-1.9
3-chloro cyclobutene	29.4	-3.1
cis-3,4-dichloro cyclobutene	35.6	+3.1
trans-3,4-dichloro cyclobutene	25.7	-6.8
cis-3-chloro, 4-methyl cyclobutene	31.6	-0.9
3-ethoxy cyclobutene	23.5	-9.0
cis-3,4-diethoxy cyclobutene	27.8	-4.7
cis-3,4-dimethoxy cyclobutene	28.6	-3.9
cis-3-chloro-4-methoxy cyclobutene	29.1	-3.4
cis-3- methoxy-4-methyl cyclobutene	25.5	-7.0
3-acetoxy cyclobutene	27.8	-4.8

* $E_{rel} = E_a - E_a$ (cyclobutene)

Problem 6.6:

What would be the substituent effect for the outward rotation of chloro-, ethoxy-, and acetoxy-substituent?

A comparison of the activation energy data for the ring opening of cyclobutene, 3-chloro cyclobutene (where one chloro moves outwards) and *trans*-3,4-dichloro cyclobutene (both chloro groups move outwards) shows that the substituent effects are only approximately additive, i.e. the outward rotation of one chloro- group lowers the activation energy by 3.1 Kcal $mole^{-1}$, whereas the outward rotation of two chloro-groups lowers the activation energy by 6.8 Kcal $mole^{-1}$.

Problem 6.7:

Calculate the substituent effect for the inward rotation of the chloro substituent.

Substituent effect on the activation energies for conrotatory electrocyclic reactions of substituted cyclobutenes are given in Table 6.5.

Table 6.5: *Influence of 3- or 4- substituents upon activation energies for conrotatory electrocyclic reactions of cyclobutenes.*

Substituent	Outward*	Inward*
-CH3	-1	+3
-Cl	-3	+6
-OR	-9	+5
-OAC	-5	+5

*Estimated to be additive within +1 Kcal $mole^{-1}$ for each substituent.

Another conclusion drawn from this activation energy data is that the lowering in activation energy for outward rotation increases as the donor nature of the substituent increases, e.g. E_{rel} for CH_3 group is -1, whereas for the -OR group it is -9. This is because the -OR group is a much better electron donor than the $-CH_3$ group. On the other hand, the increase in activation energy for inward rotation is directly proportional to the donor nature of the substituent. The substituent effect for inward rotation of CH_3 group is +3, while that of the - OR group is +5.

Problem 6.8:

Using the data given in Table 6.5 predict which of the two would be a better electron donor?

i) -OR (alkoxy)
ii) -OAc (acetoxy)

The experimental activation energy data was analyzed and discussed. Theoretical calculations were also carried out to study the reaction path of these substituted cyclobutenes. Some details of the applications of the theoretical computational methods are discussed:

6.2.2 Theoretical Aspect

Quantum mechanical calculations are used to calculate the energies and geometries of the reactant, the product and the transition state. Activation energy, E_a. (i.e. the energy difference between the transition state and the reactant) and heat of reaction (i.e. the energy difference between the product and the reactant) can be calculated. The energies and geometries of the reactant and the product are compared with the experimentally obtained values. Theoretical activation energy and heat of reaction can also be compared with the available experimental data.

Theoretical calculations can be carried out for any structure, even if it does not exist. On the other hand, the experimental work can only be carried out on species which do exist and for reactions which actually do take place. For example, in the ring opening of *trans*-3,4-dimethyl cyclobutene, the theoretical activation energies for both EE- and ZZ-diene can be calculated. On the other hand, the experimental activation energy for the formation of only ZZ-diene can be measured because EE-diene is never formed.

6.2.2.1 Interpretation of Theoretical Activation Energy Data

The theoretical activation energies for the ring opening of cyclobutenes differed quantitatively from the experimental activation energies. As mentioned earlier, accurate activation parameters are not easy to calculate. Sophisticated theoretical calculations may give activation parameters which are consistent with the experimental data to a certain extent. However, the direction of ring opening predicted by both theoretical and experimental activation energy data is the same. The examples of *trans*-3,4-dimethyl cyclobutene and *trans*-3,4-dihydroxy cyclobutene are discussed in some detail. Theoretical activation energies [18] for inward and outward rotation are given in Table 6.6.

Table 6.6: *Theoretical activation energies (Kcal mole^{-1}) of some disubstituted cyclobutenes.*

cyclobutene	*trans*-3,4-dimethylcyclobutene		*trans*-3,4-dihydroxycyclobutene	
	methyl		hydroxy	
	Inward	Outward	Inward	Outward
41.6	53.4	<u>40.4</u>	55	<u>23.4</u>

Underlined values are the lower activation energies.

It may be recalled that in *trans*-disubstituted cyclobutenes both the substituents might rotate inwards or outwards. Theoretical results clearly predict a preference for the outward rotation of methyl- or hydroxy- groups as the activation energy decreases for the outward rotation and increases for the inward rotation. Obviously, the lower energy reaction path is preferred.

Problem 6.9:

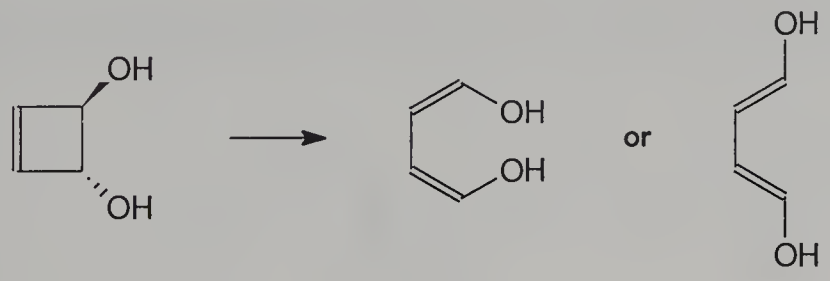
Find E_{rel} for two modes of conrotatory ring openings of *trans*-3,4-dimethyl cyclobutene from Table 6.6. Also calculate the theoretical substituent effect for the outward, and inward, rotation of the methyl group. Compare these values with the substituent effect obtained from the experimental data in Table 6.5.

The theoretical substituent effect for the outward and inward rotation of methyl group is calculated and found to be -0.6 and 5.9 Kcal $mole^{-1}$ respectively. Comparing these values with the experimental values of -1 and +3, it is deduced that a qualitative agreement exists between the theoretical and experimental substituent effects.

Thus, the theoretical approach provides an understanding of experimental data and facilitates the prediction of the direction of rotation for substituents not yet studied. Although experimental E_a values for 3,4-dihydroxy cyclobutene were not known, the direction of rotation is predicted from the calculated activation energies given in Table 6.6.

Problem 6.10:

i) Which product would you expect during the conrotatory ring opening of *trans*-3,4-dihydroxy cyclobutene?



ii) What would be the value of E_{rel} for the expected product? Also calculate the substituent effect for the hydroxy group (use Table 6.6).

iii) During the ring opening of *cis*-3-methyl-4-hydroxycyclobutene two products are possible. Use substituent effects to predict the expected product.

Steric preference for ring opening of substituted cyclobutenes, where the substituents are electron donors, are discussed in detail from the experimental, and the theoretical, point of view and it is concluded that *electron donating substituents prefer to rotate outwards during conrotatory ring openings.*

For electron accepting substituents, e.g. the formyl-, nitro- or borohydryl groups, the experimental activation energy data for quantitative analysis was not available. Some experimental observations did prove that the *electron accepting substituents preferred an inward rotation.* This effect is opposite to the steric effect and shows that the electrocyclic reactions are not just sterically controlled. There are other electronic factors involved which determine the direction of rotation.

Theoretical calculations on substituted cyclobutenes, with electron accepting substituents, also predicted an inward rotation for the electron accepting groups [19]. Theoretical data for 3-formyl cyclobutene is given in Table 6.7.

Table 6.7: *Theoretical activation energies (Kcal mole^{-1}) for inward and outward rotation of 3-formyl group.*

cyclobutene	3-formyl cyclobutene			
	*syn**		*anti**	
	Inward	Outward	Inward	Outward
41.6	40.9	<u>39.9</u>	<u>34.7</u>	39.2

Underlined values are the lower activation energies.

* *syn* indicates that oxygen is pointing towards the ring.

* *anti* indicates that oxygen is pointing away from the ring.

These calculations indicate that an inward rotation of the formyl group is preferred for the ring opening of the *anti* form of 3-formyl cyclobutene by 4.5 Kcal mole^{-1}, whereas for the *syn* form an outward rotation was preferred by 1 Kcal mole^{-1}. These predictions were verified experimentally. Thus, in this case, the direction of rotation was theoretically predicted and then experimentally verified.

An interesting aspect is that the less stable Z-isomer is formed in preference to the more stable E-isomer for the ring opening of the *anti* form of 3-formyl cyclobutene.

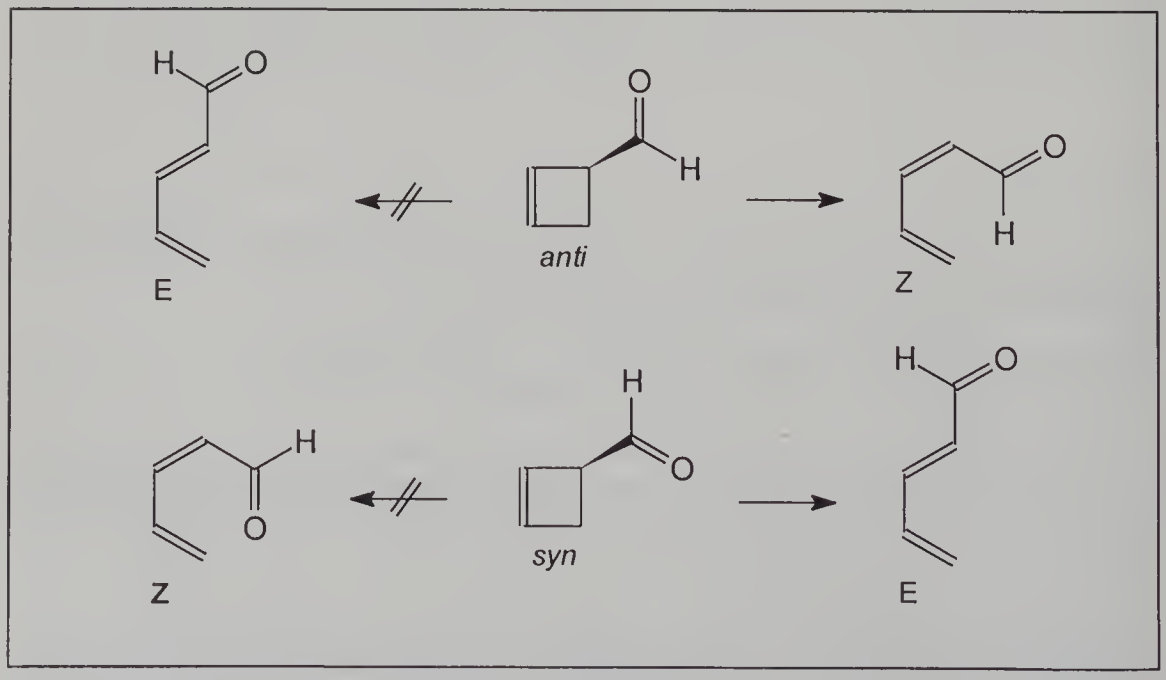


Figure 6.25 : *Ring opening of 3- formyl cyclobutene.*

This shows that the preference for inward rotation does not arise from product stability.

Another example of an electron accepting substituent is that of the –NO substituent. Theoretical calculations show that the inward rotation of the –NO group lowers the

activation energy by 4.1 Kcal mole^{-1}, whereas for the outward rotation, this lowering is 1 Kcal mole^{-1} [20]. Obviously the inward rotation causes a greater lowering of activation energy and is preferred. Similar studies on ring opening of cyclobutenes with electron accepting substituents predicted an inward rotation of this substituent. However, for weak electron acceptors, e.g. the cyano- or carboxylic group, an outward rotation is predicted. The credibility of theoretical predictions being established, the calculations on cyclobutene-3-carboxylic acid (A), its deprotonated form (B) and protonated form (C) were carried out [21].

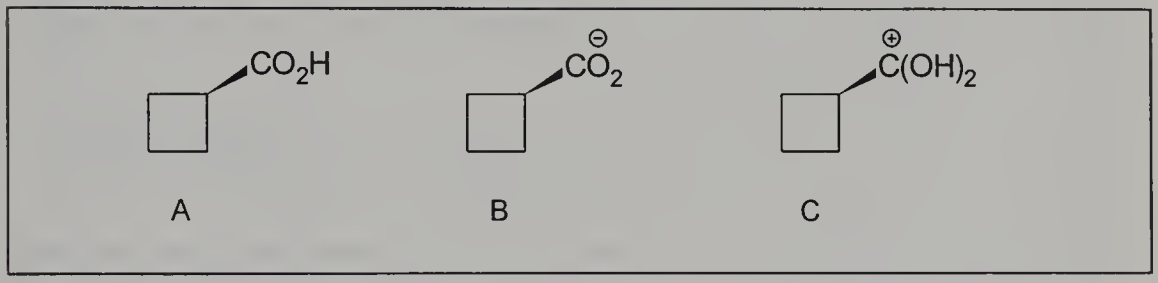


Figure 6.26: *Cyclobutene carboxylic acid, its deprotonated and protonated forms.*

In the three species, the steric effects are similar but the electronic effects are different. It is interesting to see what the theoretical calculations can predict.

Table 6.8: *Theoretical activation energies for the inward and outward rotation of the substituent in cyclobutene carboxylic acid, its deprotonated and protonated forms.*

	A ($-CO_2H$)		B $(-CO_2)^-$		C $C-(OH)_2^+$	
	Inward	Outward	Inward	Outward	Inward	Outward
syn	40.0	<u>38.5</u>	—	—	<u>23.3</u>	29.6
anti	40.9	<u>39.1</u>	42.1	<u>37.2</u>	<u>28.1</u>	31.8

Underlined values are the lower activation energies.
syn indicates that oxygen is pointing towards the ring.
anti indicates that oxygen is pointing away from the ring.

Problem 6.11:

Fill in the blanks with *inward* or *outward* (use Table 6. 8).

The *syn* and *anti* forms of A would prefer an_____ rotation of the carboxylic group.

The *anti* form of B would prefer an_____ rotation of the carboxylic group.

The *syn* and *anti* forms of C would prefer an_____ rotation of the carboxylic group.

Theoretical calculations predict an outward rotation of the substituent in butene-3-carboxylic acid (A) and its deprotonated form (B). However, an inward rotation of the substituent is predicted in the protonated form (C). This is because carboxylic acid group being a weak electron acceptor and its deprotonated form being an electron donor favour outward rotation of the substituent. On the other hand, the protonated

form of the carboxylic acid group, being a strong electron acceptor, favours inward rotation.

Thus, without appreciably changing the geometry or steric effects, the outward rotation has changed into inward rotation by changing the electronic factor.

This phenomenon, where the electronic factors control the outward or inward rotation of a substituent in electrocyclic reactions is termed as torquoselectivity.

Although extensive theoretical and computational studies were carried out for substituted cyclobutenes the criteria for torquoselectivity was found to be equally applicable to other electrocyclic reactions.

The electrocyclization (reverse of ring opening) of the pentadienyl cation was investigated using *ab initio* computational methods [22]. The substituent effects of hydroxyl-, formyl-, boryl-, fluoro- and amino groups were examined.

The electrocyclization of pentadienyl cation was studied, instead of ring opening, as it is the energetically preferred process. Its activation energy was small (1→10 Kcal $mole^{-1}$) and the reaction was highly exothermic (heat of reaction = -27 Kcal $mole^{-1}$).

In a substituted pentadienyl cation (Figure 6.27) the substituent is substituted either on the outer side (E-) or on the inner side (Z-). In conrotatory electrocyclization, the E-diene forms an outward transition state whereas Z-diene forms an inward transition state. Theoretical activation energies for the electrocyclization of E- and Z-dienes with different substituents were calculated using *ab initio* calculations [22].

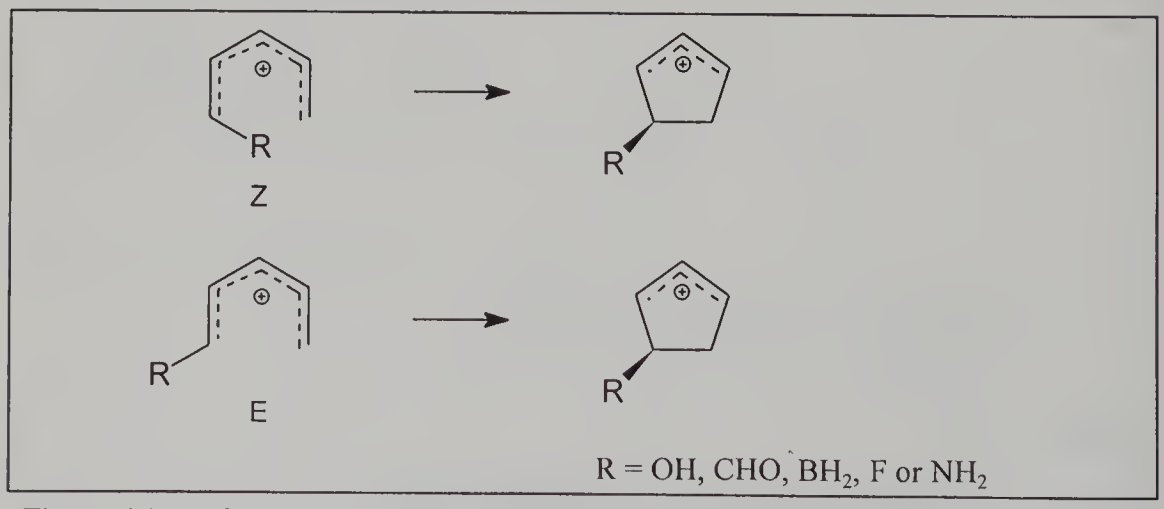


Figure 6.27: *Electrocyclization of some substituted pentadienyl cations.*

Table 6.9: *Theoretical activation energies (Kcal mole^{-1}) for the electrocyclization of substituted pentadienyl cations.*

R	-H		$-NH_2$		$-BH_2$	
	Inward	Outward	Inward	Outward	Inward	Outward
	10.0	10.0	37.5	<u>28.2</u>	<u>44.6</u>	51.0

Underlined values are the lower activation energies.

From Table 6.9 it is observed that the outward transition state is preferred for the NH_2 substituent and an inward transition state for the $-BH_2$ substituent. These theoretical calculations predict that the electron donors (-OH,-F,$-NH_2$) stabilize the transition state, when substituted on the outside, while the electron acceptors ($-BH_2$, -CHO) stabilize the transition state, when placed on the inside. The stereoelectronic effect of the substituents found for substituted cyclobutenes is also predicted to operate during the conrotatory interconversion of pentadienyl cations and cyclopentenyl cations. It can be generalized that similar substituent effects exist in all electrocyclic reactions.

Recent theoretical calculations predict the phenomenon of torquoselectivity for hexatriene-cyclohexadiene and octatetraene-cyclooctatriene interconversions as well as for electrocyclic ring openings of azetines, oxetenes, thietenes, cyclopropenes, aziridines, oxirenes and cyclobutenones [23].

The substituent effects obtained from theoretical or experimental activation energy measures the increase, or decrease, in activation energies for a particular substituent. Another parameter, obtained from theoretical activation energies, is the difference between activation energies for inward and outward rotation of a particular substituent. This parameter is termed as $\Delta E_{a\,(in,out)}$, where

$$\Delta E_{a\,(in,out)} = E_{a\,(inward)} - E_{a\,(outward)}$$

The Taft substituent constant σ_R° is a frequently used experimental parameter, which measures the ability of a π-substituent to donate, or accept, electrons. For electron accepting substituents σ_R° has a +ve value, conversely for an electron donating substituent it is -ve. A plot of $E_{a\,(inward)} - E_{a\,(outward)}$ versus Taft substituent constant gives a linear relationship as shown in Figure 6.28. This shows a quantitative agreement between the theoretical and the experimental parameters [23].

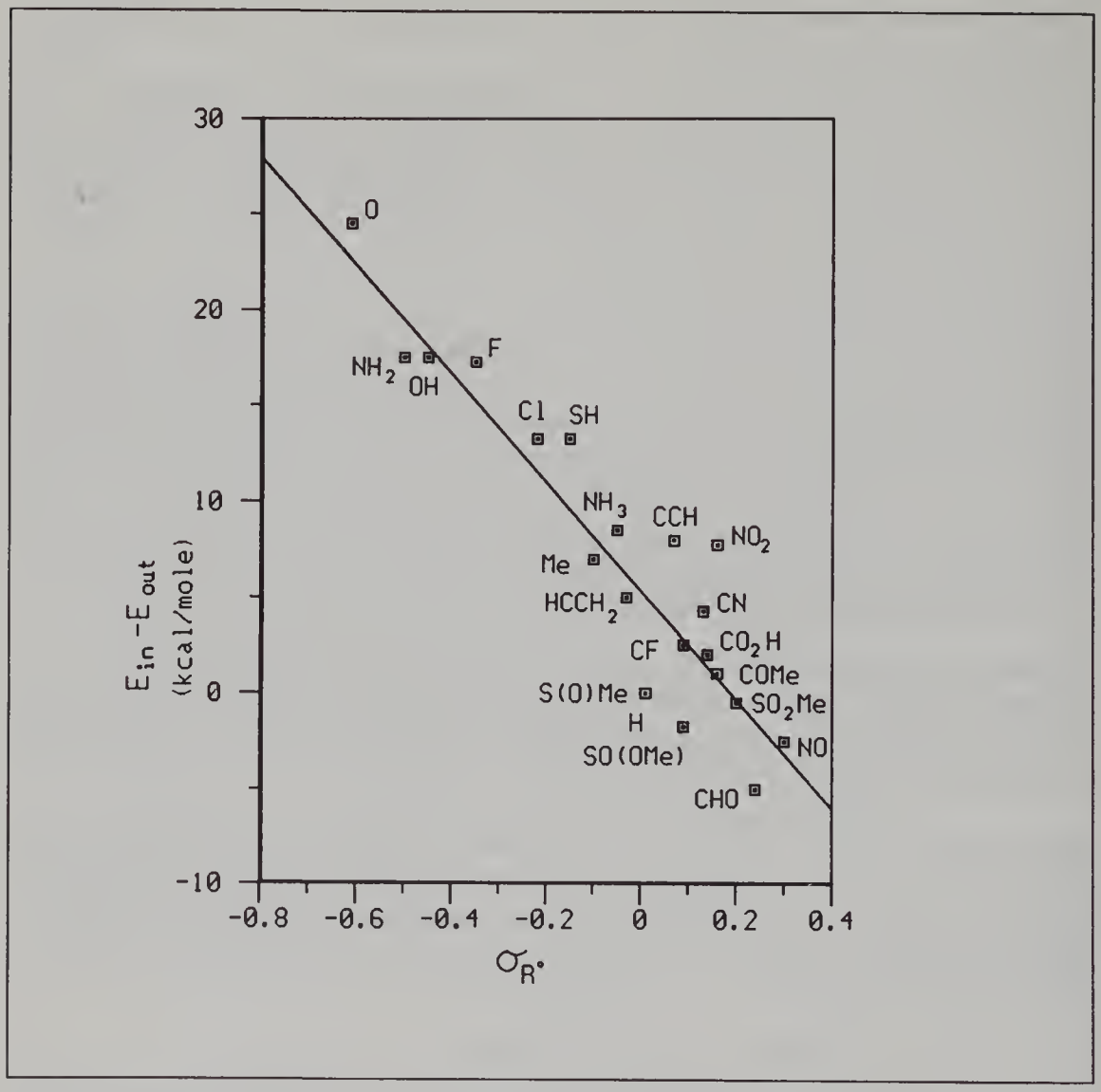


Figure 6.28: *Theoretical activation energy differences plotted against Taft* σ_R° *values.*

6.2.2.2 Theoretical Explanation of Stereoselectivity

A number of theories are developed to explain the torquoselectivity or stereoselective substituent effects in electrocyclic reactions.

Two of these theories relate the phenomenon of torquoselectivity to the stability of the transition state formed. The criterion used to establish the stability of the transition state are the *aromatic interactions* present in the transition state and the *HOMO-LUMO gap* present in the MOs of the transition state. These two criterion are related to the Möbius-Hückel Approach and the Frontier Orbitals Approach, respectively. Another theory explains torquoselectivity on the basis of Symmetry State Correlation diagrams with the inclusion of the MOs of the transition state. These theories are discussed in detail with particular reference to the electrocyclic ring opening of cyclobutenes.

- ***Möbius-Hückel Approach***

As the reaction proceeds during the ring opening of cyclobutene, the σ-bond is stretched and twisted and weakly interacts with the cyclobutene π–bond. A lone pair or a *p*–orbital from an outwardly rotating substituent overlaps with the σ– or σ*-orbital of the partially broken C—C bond. This overlap results in the stabilization of the transition state. Upon inward rotation, the substituent orbital overlaps not only with the σ- or σ* - at the terminal, to which the substituent is attached, but also with the orbital of the other terminal. The inward rotating *p*-orbital of the substituent and the orbitals of the breaking σ–bond form a cyclic transition state as shown in Figure 6.29. This transition state, with no sign inversion, is a Hückel state. A Hückel state is aromatic with (4n+2) electrons and antiaromatic with (4n) electrons (Chapter 5).

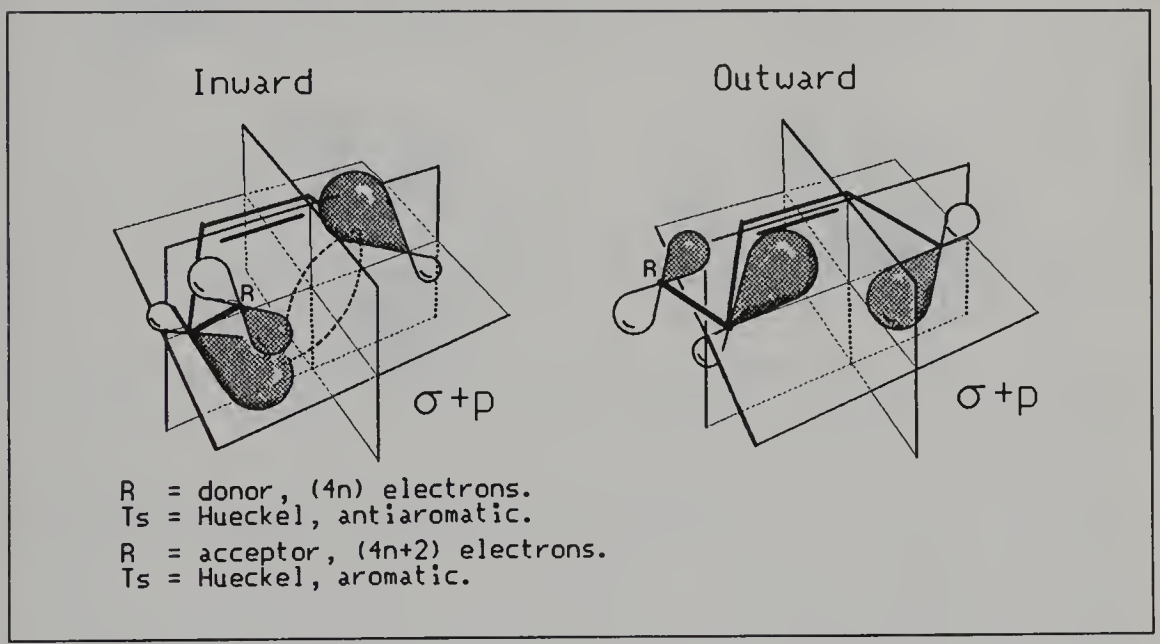


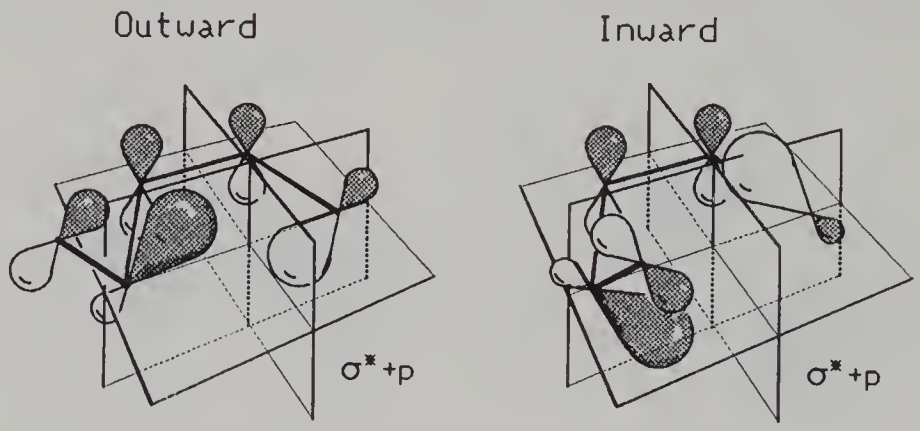
Figure 6.29: *Transition states formed upon inward and outward rotation of the substituent.*

If the substituent is an electron donor then it has a lone pair. In the transition state, a cyclic four-electron interaction (two electrons of the σ bond and two of the substituent) takes place. A four electron cyclic interaction is antiaromatic and the system is destabilized. Hence, an inward rotation of an electron donor destabilizes the system. On the other hand, if the substituent orbital is an electron acceptor (with an empty *p*-orbital) then a two-electron cyclic interaction occurs in the transition state. This interaction is aromatic and it stabilizes the system. Hence, inward rotation of an electron acceptor stabilizes the system. It is evident that the stabilization of the transition structure depends upon the interaction of the orbital of the breaking σ–bond, and the orbital of the inwardly or outwardly rotating substituents. Thus, torquoselectivity is explained on the basis of the aromaticity, or anti-aromaticity, of the cyclic interactions in the transition states during an inward rotation of the substituent [24].

Problem 6.12:

The interactions between the orbitals of the breaking σ* bond and the *p*-orbital of the substituent, both for the inward, and outward, rotation are shown. A cyclic transition state is formed for the inward rotation of the substituent. The substituent could be an electron acceptor or donor. Specify the substituent that forms a cyclic, aromatic transition state.

Hint: The transition state formed is Möbius, where (4n) electrons lead to an aromatic transition state.



- ***Frontier Orbitals Approach***

Reactants have a set of MOs (σ, π , σ*, π*), whereas products also have their own set of MOs. Similarly, a set of MOs can also be associated with the transition structure. The MOs of the transition structure are formed by the mixing together of the orbitals of the reactants. Conceptually this is visualized by considering the ring opening of cyclobutene. The stretching of the C3—C4 σ-bond of cyclobutene is accompanied by a rapid increase in energy. As the reaction proceeds, the σ-orbital undergoing a conrotatory motion starts overlapping the π–orbital. This σ-π overlap is significant in the transition state.

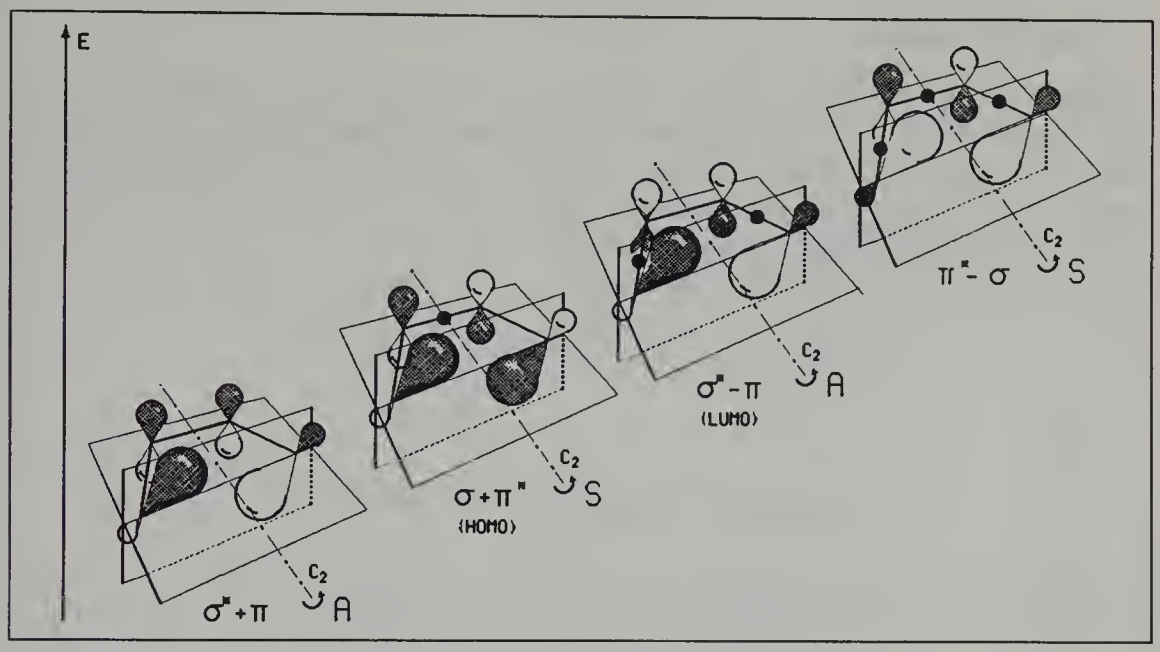


Figure 6.30: *Molecular orbitals of the transition state.*

Thus, the MOs associated with the transition state are σ*+π, σ+π*, σ*–π and π*–σ (Figure 6.30). Energies of these MOs are also calculated using the MO calculations.

Molecular orbital energies of the transition states of different *trans*-3,4 disubstituted cyclobutenes are calculated using computational methods [25]. MO calculations are carried out for an inward, as well as for an outward, rotation of the substituent. The calculated energies of the frontier orbitals, i.e. HOMO and LUMO, and the differences of their energies, are listed in Table 6.10. It seems logical to assume that the greater the HOMO-LUMO energy gap, the more stable the transition state. When the HOMO-LUMO gap is greater for the outward transition state, an outward rotation of the substituent is predicted. Contrarily, when the HOMO-LUMO gap is greater for the inward transition state, an inward rotation for the transition state is predicted. From the theoretical results of the three examples tabulated in Table 6.10 the methyl and hydroxy groups are predicted to rotate outwards, and the boryl group is predicted to rotate inwards. These results are consistent with earlier results. Thus, the stability of the transition state is associated with the magnitude of the HOMO-LUMO energy gap. This is another way of explaining the phenomenon of torquoselectivity.

Table 6.10: *HOMO-LUMO energies (eV) of transition structures in electrocyclic reactions of trans 3,4 disubstituted cyclobutenes.*

		E_{HOMO}	E_{LUMO}	E_{LUMO}-E_{HOMO}
3,4-dimethyl	Outward	-8.26	4.27	12.96
	Inward	-7.79	3.75	11.5
3,4-dihydroxy	Outward	-8.20	4.31	12.5
	Inward	-7.26	3.11	10.37
3,4-diboryl	Outward	-9.47	0.49	9.96
	Inward	-9.80	2.30	12.1

- ***Orbital Symmetry Conservation***

Energy level correlation diagrams are also used to explain the phenomenon of stereoselectivity. A correlation diagram which connects orbitals of the same symmetry with each other shows that the reactant orbitals correlate smoothly with those of the product for a thermally allowed reaction (Figure 6.31). However, this diagram can be considered as an oversimplified energy profile.

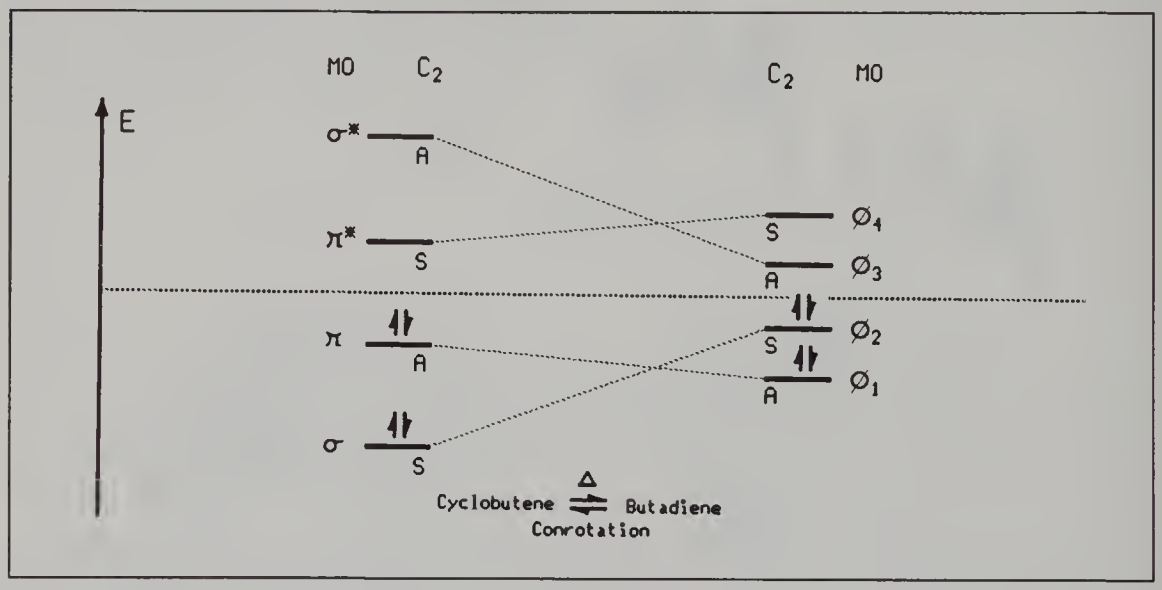


Figure 6.31: *Energy level correlation diagram for the ring opening of cyclobutene.*

In this diagram the energy changes are shown to be linear with no activation barrier which is not true. Even thermally allowed reactions have substantial energy barriers. The energy changes along the reaction pathway are depicted in Figure 6.32. The MOs of the reactants correlate with the MOs of the product via the MOs of the transition state[25].

It is observed that even in this correlation symmetry is conserved, i.e., the reactant MO, the transition state MO and the product MO can only correlate if they have the same symmetry. Figure 6.32 shows that the activation energy barrier depends upon the E_{HOMO} of the transition state. A smaller, or more negative, value of E_{HOMO} leads to a smaller value of activation energy and a greater ease of reaction.

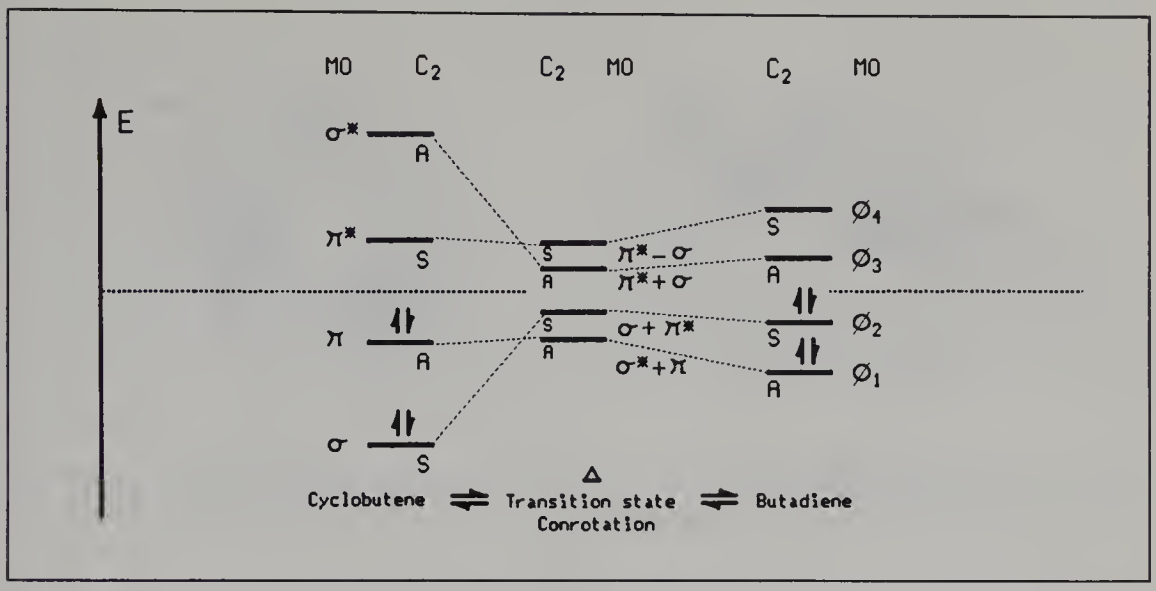


Figure 6.32: *Modified energy level correlation diagram for the ring opening of cyclobutene.*

Table 6.10 shows that for *trans*-3,4-dimethylcyclobutene

$$E_{HOMO}(\text{outwards}) < E_{HOMO}(\text{inwards})$$

Thus the activation barrier of the methyl groups rotating outwards is lower, and is the preferred process. For trans-3,4-dihydroxycyclobutene, outward rotation of the hydroxy group is preferred for similar reasons.

On the other hand, for trans-3,4-diborylcyclobutene,

$$E_{HOMO}(\text{outwards}) > E_{HOMO}(\text{inwards})$$

In this case, the inward rotation of the electron accepting group is the preferred process. Once again, the results obtained from theoretical calculations are consistent with the earlier theoretical and experimental results.

Theoretical explanations for stereospecificity of the ring opening of the disubstituted cyclobutenes are discussed in this section.

An example of a disubstituted cyclobutene, which can hypothetically undergo four different electrocyclic ring openings, summarizes the phenomenon of stereospecificity as shown in Figure 6.33. Orbital symmetry rules out the two disrotatory processes. The stereoselective principle of torquoselectivity favours an inward rotation of the acceptor (A), and an outward rotation of the donor (D). This process thus occurs faster than the others and is virtually the only observable process.

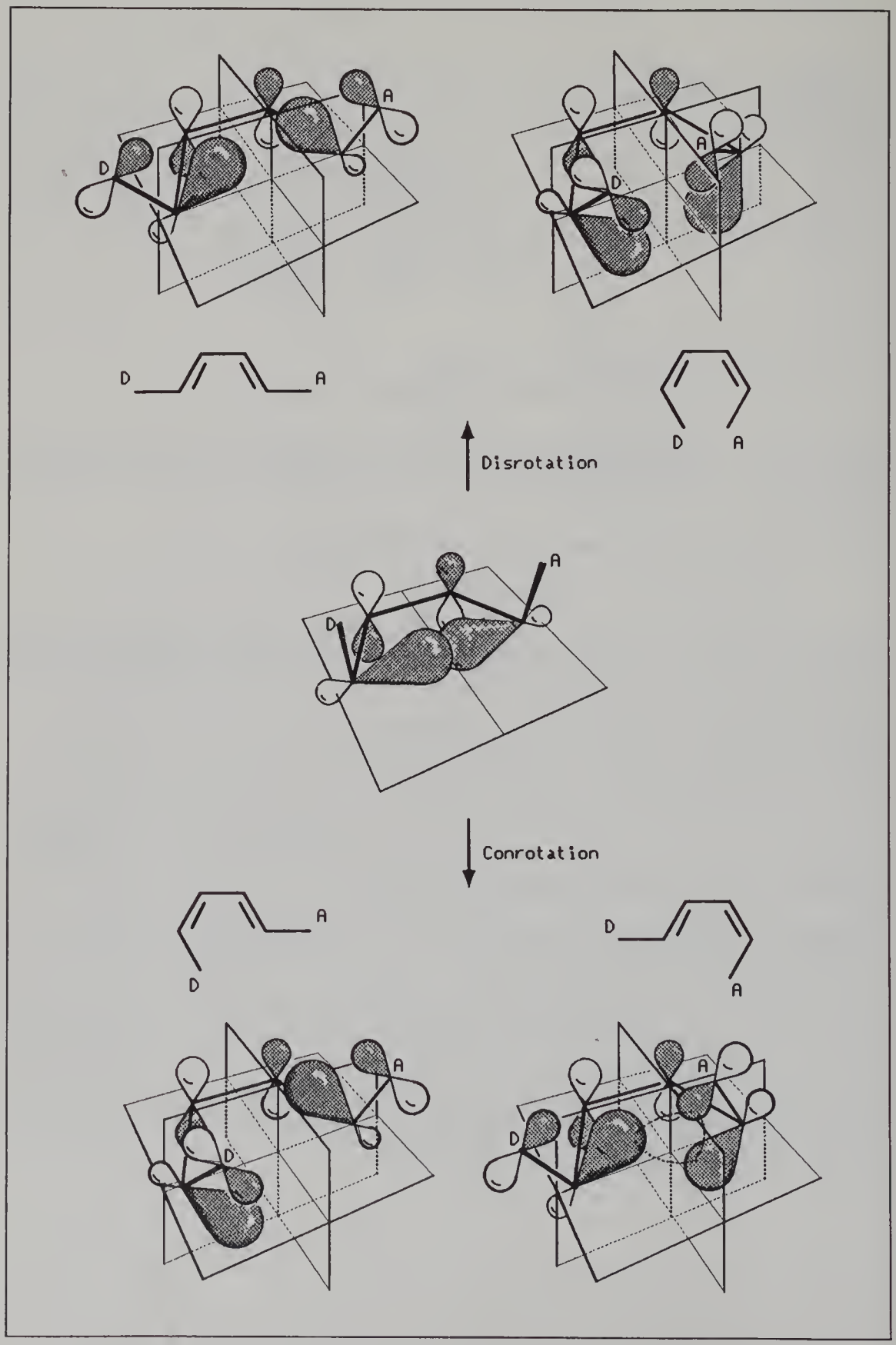


Figure 6.33: *Four possible products from electrocyclic ring opening of cis-3-donor-4-acceptor cyclobutene, where* D *and* A *represent donor and acceptor substituents,*

It was discussed how computational methods are used to study the reaction pathways of electrocyclic reactions. The transition state and the region around it is generally not amenable to experimental observations and is referred to as the 'gray area' of the reaction path. Quantum mechanical calculations provide a method to study the probable events occurring in this gray area. Some experimental techniques are now being developed to study this gray area, for example, kinetic isotope effects are used to determine the vibrational frequencies of the transition states [26], whereas Raman spectroscopic techniques are used to study the reaction pathways of photochemical reactions [27]. The development of these techniques is a very active field of research and the experimental results obtained from these techniques are used as valuable starting points for theoretical investigations.

Chemistry, once a purely experimental science, now encompasses methods of study where theoretical calculations and experimental techniques complement each other.

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Appendix A

Molecular Orbital Theory

The two major approaches, which give a theoretical description of structure and bonding in chemistry, are the VB (Valence Bond) theory and the MO (Molecular Orbital) theory. A comparison of the two methods shows that each has its own advantage. However, molecular orbital theory, in its approximate form, is mathematically simpler and easier to apply to organic systems. The behaviour of atoms and molecules, i.e. the basis of chemical theory, is governed by quantum mechanics.

Before the MO theory is discussed in detail, some basic concepts of quantum mechanics are discussed.

A.1. Basic Concepts of Quantum Mechanics

A.1.1 The Schrödinger Equation

One of the fundamental postulates of quantum mechanics is that the different properties of a system, termed *observables*, may be determined by solving an equation of the general form

$$\mathbf{G}\Psi = \gamma\Psi \qquad \text{(A.1)}$$

where

γ is the particular observable that is to be calculated. Some examples of observables in an atomic or a molecular system are energy, dipole moment, angular momentum, etc. In the language of quantum mechanics γ is termed as an *eigen value*.

Ψ is a mathematical expression which defines the system in a given state and is termed as the *state function* or the *wave function*.

G is a mathematical *operator* whose nature depends upon the nature of the observable. An operator defines a mathematical operation which is to be performed on a mathematical expression, e.g. $\sqrt{\ }$, taking a square, integration, etc., are all mathematical operations.

Equation A.1 can be worded as: *When a certain mathematical operation is carried out on the state function, the result is a product of the state function itself and the observable* γ.

The Schrödinger wave equation is a specific form of equation A.1, where the observable is the energy E of a chemical system.

$$\mathbf{H}\Psi = E\Psi \qquad (A.2)$$

where

H is known as the Hamiltonian and is the energy operator that considers all the kinetic and potential energy contributions to the electronic energy.

Ψ is the electronic wave function of the system. and is a function of the spatial coordinates (x,y,z) or (r,θ,φ) which describe the electronic motion.

The solution of the Schrödinger equation leads to a set of electronic wave functions Ψ_i of energy E_i. The wave functions are known as *eigen functions* and the energies as *eigen values*. Each eigen function has an eigen value associated with it.

Mathematically, the solution of this equation is beyond the scope of this book. This is due to the mathematical complexity of the Hamiltonian **H** and the wave function Ψ.

The exact solution of the Schrödinger equation can only be obtained for a one-electron system, such as the H atom or the H_2^+ molecular ion. Hence, approximate methods, which make the solution more tractable, must be followed.

A.1.2 Atomic Orbitals

Atomic orbitals (AOs) are the conceptual building blocks from which all the concepts of structure and reactivity are derived. When solving the Schrödinger equation for a hydrogen atom, a set of wave functions are obtained, i.e. the *s*-, *p*- and *d*-orbitals (Figure A.1). Shaded areas indicate regions of the orbital where the value of the wave function is positive, while unshaded areas indicate regions in space where the value is negative.

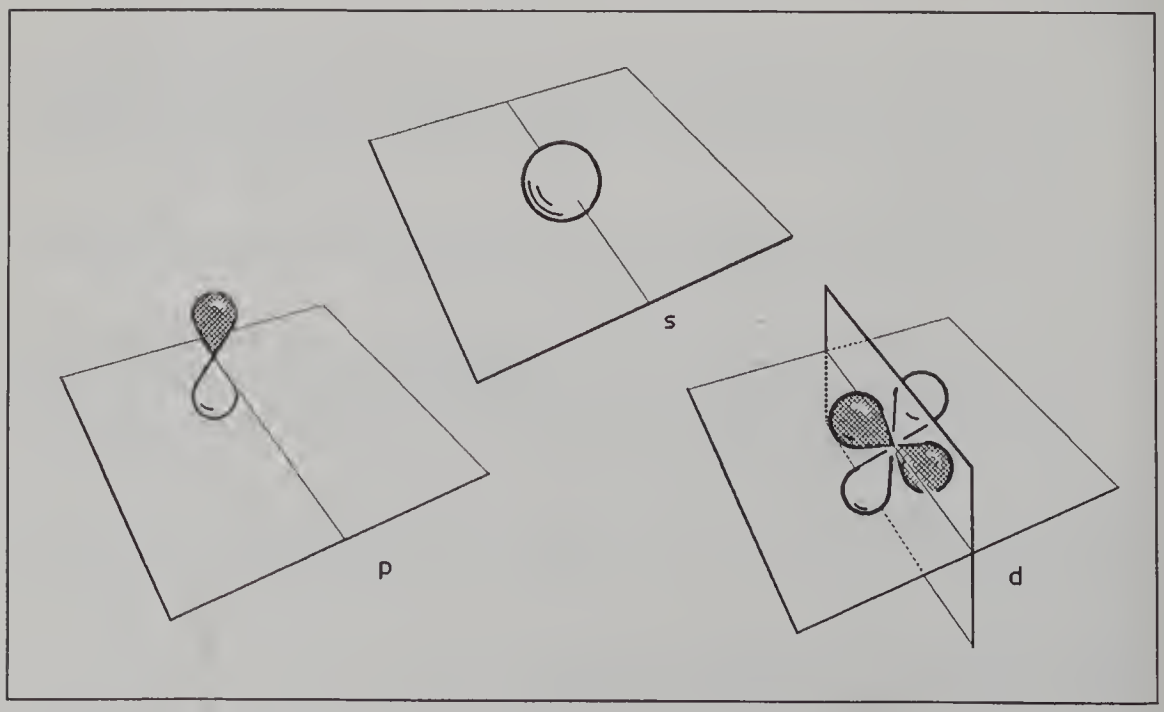


***Figure A.1**: Nodal planes of p- and d-orbitals.*

A plane separating +ve from -ve regions is termed as a nodal plane. The value of the wave function in the nodal plane is always zero. It can be seen that *s*-, *p*- and *d*- atomic orbitals possess 0, 1 and 2 nodes, respectively. This set of AOs form the building blocks in MO and VB theory.

A.2. Difference Between MO and VB Theories

According to the VB theory molecules are composed of atoms that are bonded together by valence electrons through the overlap of atomic orbitals. For example, a H_2 molecule is formed by the overlap of the two 1*s*-orbitals.

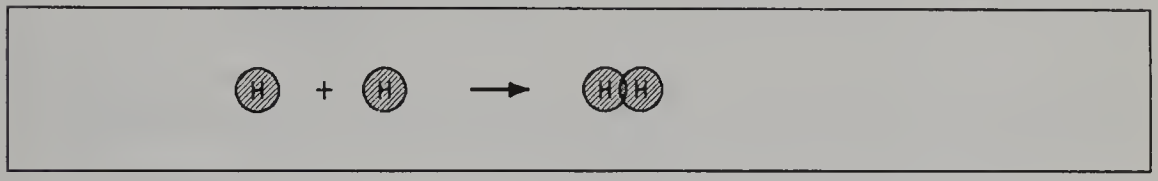


***Figure A.2**: Formation of a hydrogen molecule in valence orbital approach.*

The properties of the molecule are considered to be the sum of the properties of the constituent atoms and of the individual bonds that bind them together.

The basic assumption in the MO theory is that the atomic orbitals on different atoms in a molecule combine to form molecular orbitals. These molecular orbitals formed are simultaneously associated with all the nuclei in a molecule. The electrons within a molecule occupy MOs rather than AOs.

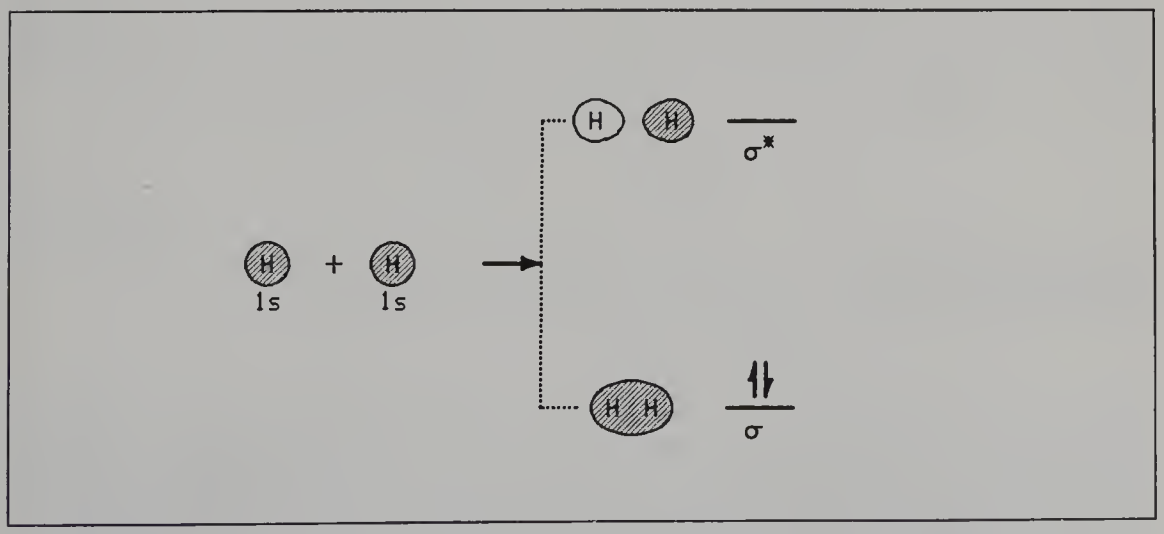


***Figure A.3**: Formation of a hydrogen molecule in molecular orbital approach.*

The basic difference between the molecular orbital theory and the valence orbital theory is that the electrons in a molecular orbital are associated with all the nuclei in a molecule, whereas, in the valence bond theory, the bonding electron is associated with only two nuclei at a time.

A.3. Mathematical Formulation of Molecular Orbital Theory

As mentioned earlier, the basic postulate of the molecular orbital theory is that an *n* number of atomic orbitals combine to form an *n* number of molecular orbitals. The orbitals, which combine to form the molecular orbitals, are known as the *basis orbitals*. Recollecting the example of the H_2 molecule, the two 1*s* AOs combine to form two MOs.

The energy and shape of the molecular orbitals formed are different from those of the initial component atomic orbitals. The two electrons, initially belonging to the two 1*s*-orbitals, would occupy the MO of the lower energy (Figure A.3).

In order to calculate the energy and determine the shape of the molecular orbitals formed, the energies and shapes of the combining atomic orbitals are considered as well as the manner in which they combine.

A.3.1 LCAO Approach

An important approximation used to form these molecular orbitals is the LCAO (Linear Combination of Atomic Orbitals) approach. In this approach it is assumed that molecular orbitals are formed by the linear combination of atomic orbitals. Thus, the wave function for a MO may be obtained by adding the wave functions of the AOs. The wave function of the AO is first multiplied by a coefficient C_i before it is added (C*i* may have a +ve or -ve value).

Diatomic systems, for example H_2 and LiH, are discussed to illustrate the formation of MOs. If ϕ_1 and ϕ_2 are the two AOs which combine to form the MOs σ and σ^* then

$$\sigma = C_1\phi_1 + C_2\phi_2$$
$$\sigma^* = C_1'\phi_1 + C_2'\phi_2 \qquad \text{(A.3)}$$

In the H_2 molecule ϕ_1 and ϕ_2 are the 1*s* atomic orbitals. The values of C_1, C_2, C_1', C_2' can be calculated. Thus, the MOs for the H_2 molecule are

$$\sigma = 0.707\phi_1 + 0.707\phi_2$$
$$\sigma^* = 0.707\phi_1 - 0.707\phi_2 \qquad \text{(A.4)}$$

The σ-orbital is formed from an in-phase mixing of the two AOs, while the σ^*-orbital is formed from the out-of-phase mixing of the two orbitals. As the σ-orbital is stabilized relative to the two 1*s* orbitals, the two available electrons are placed in this lower energy orbital, thus, leading to a reduction in electronic energy (Figure A.3).

For the LiH system, the combining AOs can be represented as 1*s* orbital of hydrogen and 2*s* orbital of lithium. The lithium 1*s* orbital is the core orbital, i.e. it belongs to a shell which is fully occupied in the isolated atom and hence does not take part in bonding. The nucleus, along with the fully occupied shell, is known as the frozen core as it is not involved in bonding. It is assumed that the frozen core does not participate in the formation of the molecular orbitals. This approximation is known as the frozen

core or the valence orbital approximation. Thus, the 1*s*-orbital of hydrogen and the 2*s*-orbital of lithium combine to form two MOs as shown in Figure A.4 (Equation A.5). It may be noted that in this Appendix the symbol for MOs is ψ, while in the rest of the book the symbol for MOs was ϕ.

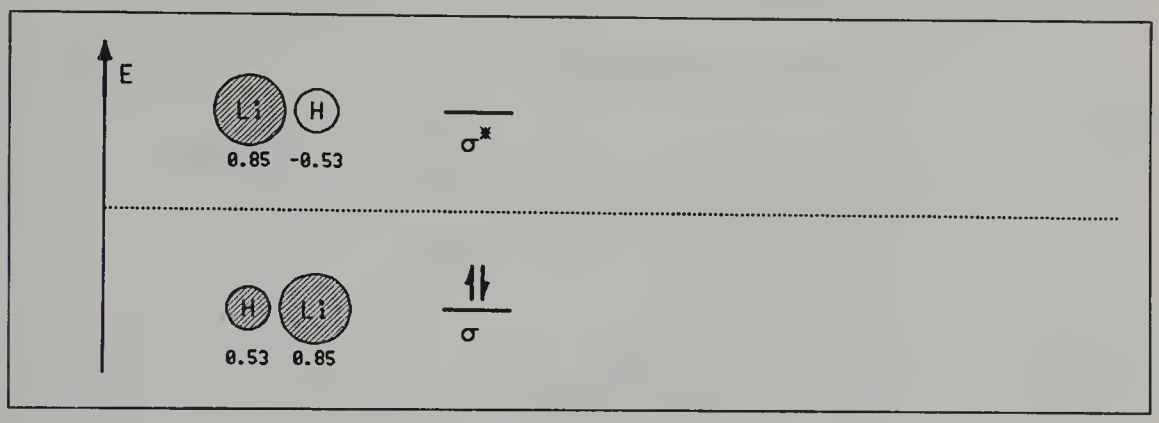


***Figure A.4**: Molecular orbitals of lithium hydride.*

The coefficients C_1, C_2 and C_1', C_2' are calculated numerically and the MOs are

$$\sigma^* = -0.53\phi_1 + 0.85\phi_2$$
$$\sigma = 0.53\phi_1 + 0.85\phi_2 \qquad \text{(A.5)}$$

In this case ϕ_1 is the 1*s* hydrogen orbital and ϕ_2 is the 2*s* lithium atomic orbital.

In general terms, it is considered that the nucleii of a molecule are enveloped by a set of MOs, some occupied by electrons and others unoccupied.

If $\phi_1, \phi_2 \ldots \phi_N$ represent the component orbitals and $\psi_1, \psi_2 \ldots \psi_N$ are the MOs then

$$\psi_1 = C_{11}\phi_1 + C_{12}\phi_2 \ldots . C_{1N}\phi_N$$
$$\psi_2 = C_{21}\phi_1 + C_{22}\phi_2 \ldots . C_{2N}\phi_N$$
$$\psi_N = C_{N1}\phi_1 + C_{N2}\phi_2 \ldots . C_{NN}\phi_N$$

or concisely

$$\psi_i = \sum_{j=1}^{N} C_{ij}\phi_i \qquad \text{(A.6)}$$

Thus, if the AOs are known, then the equation for the MOs can be set up. The molecular orbitals formed should belong to the same symmetry point group as the initial component atomic orbitals (Appendix B). Another important point is that the higher the number of nodes in a molecular orbital, the higher the energy of the orbital, i.e. an MO with no nodes is lowest in energy, an MO with one node is higher and so on. Thus, a σ molecular orbital in H_2 and LiH has zero node and is lower in energy, whereas a σ^* molecular orbital with one node is higher in energy.

The wave function for the AOs is determined by solving the Schrödinger equation for the hydrogen atom. The solution gives a set of wavefunctions and the energies associated with these wavefunctions. These wavefunctions define the motion of the

electrons in the $1s$, $2s$, $2p_x$, $2p_y$, ... orbitals. The mathematical expressions for some of these wavefunctions are

$$\phi_{1s} = (\alpha^3/\pi)^{1/2} e^{-\alpha r}$$

$$\phi_{2s} = (\alpha^5/\pi)^{1/2} e^{-\alpha r}$$

$$\phi_{2px} = (\alpha^5/\pi)^{1/2} r \sin\theta \cos\phi\, e^{-\alpha r} \qquad \text{(A.7)}$$

where

r, θ and ϕ are the polar coordinates which can be expressed in terms of Cartesian coordinates *x, y* and *z*.

α is dependent upon z, σ* and n* where

z is the nuclear charge

σ* is the shielding constant

n* is the principal quantum number.

A.3.2 Shapes and Energies of MOs

The Schrödinger wave equation, along with the variation principle, is used to calculate

i) the energies $E_1, E_2, \ldots, E_n$ of the MOs.

ii) the coefficients $C_{11}, C_{21}, \ldots, C_{N1}$ upto $C_{N1}, C_{N2}, \ldots, C_{NN}$ of the MOs. The coefficients determine the shape of the MOs $\psi_1, \psi_2, \ldots, \psi_N$.

Multiplying both sides of the Schrödinger equation by Ψ gives

$$\Psi \mathbf{H} \Psi = \Psi E \Psi$$

$$\Psi \mathbf{H} \Psi = E \Psi^2$$

$$E = \frac{\Psi \mathbf{H} \Psi}{\Psi^2} \qquad \text{(A.8)}$$

Substituting the value of Ψ in terms of AOs (i.e., $\Psi = \sum C_{ij}\phi_1$) and minimizing the energy by substituting $dE/dC_{ij} = 0$, a set of an N number of equations are obtained

$$\begin{aligned}
&C_{11}(H_{11}-ES_{11}) + C_{12}(H_{12}-ES_{12}) \ldots . C_{1N}(H_{1N}-ES_{1N}) = 0\\
&C_{21}(H_{21}-ES_{21}) + C_{22}(H_{22}-ES_{22}) \ldots . C_{2N}(H_{2N}-ES_{2N}) = 0\\
&\ldots . \qquad\qquad\qquad\qquad\qquad \ldots .\\
&C_{N1}(H_{N1}-ES_{N1}) + C_{N2}(H_{N2}-ES_{N2}) \ldots C_{NN}(H_{NN}-ES_{NN}) = 0
\end{aligned} \qquad \text{(A.9)}$$

where $H_{ij} = \int \phi_i \mathbf{H} \phi_j d\tau$ and $S_{ij} = \int \phi_i \phi_j d\tau$

ϕ_i and ϕ_j are the AOs.

H is the energy operator.

H_{ij} is the extent of overlap as well as the energy of interaction between the ith and the jth atomic orbitals and is known as the *resonance integral.*

If i = j then $H_{ij} = \int \phi_i H \phi_i d\tau$

H_{ii} represents the energy of an electron in the i^{th} atomic orbital and is known as the *Coulomb integral.*

The set of Equations A.9 are solved by first solving the *secular determinant* below.

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \ldots\ldots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \ldots\ldots & H_{2n}-ES_{2n} \\ \ldots\ldots & & & \ldots\ldots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \ldots\ldots & H_{nn}-ES_{nn} \end{vmatrix} = 0 \qquad \text{(A.10)}$$

A set of values for the energy E_i (eigen values) for different MOs are obtained by solving the secular determinant. They are rearranged in an ascending order of energy, and electrons filled in. Substituting the energy values in the set of Equations A.9, the values of the coefficients (eigen vectors) can be obtained. These coefficients C_{ij} determine the shape of the MOs. The charge density on each atom as well as between every two atoms is calculated using these coefficients and a *density matrix* is formed. The charge density between two atoms is known as the bond order.

A.3.3 Different MO Methods

In order to solve the secular determinant (Equation A.10), the magnitudes of the matrix elements H_{ij} and S_{ij} need to be calculated.

The method of calculation of the elements H_{ij} and S_{ij} using different formulations lead to different MO methods. These methods are classified as *ab initio*, semi-empirical and empirical.

1. *ab initio* calculations calculate these elements with no assumptions. *ab initio* means "from the beginning". *ab initio* calculations are quite tedious and complicated, as they do not use any simplifying approximations or assumptions.

2. Semi-empirical methods simplify the mathematical procedure by assuming certain integrals to be zero and use empirical data to avoid having to calculate others. There are different ways of incorporating these simplifications. Different semi-empirical procedures were developed, e.g. CNDO (Complete Neglect of Differential Overlap), MNDO (Modified Neglect of Differential Overlap), INDO (Intermediate Neglect of Differential Overlap) and others.

Differential overlap is the overlap of the AO basis function. The CNDO method assumes that AOs do not overlap. This is a very drastic assumption. However, other methods such as MNDO and INDO use less drastic assumptions and do not neglect the differential overlap so completely. The simplest method used is the HMO method, which would be described in detail later on.

The secular determinant can be solved by using any one of the above mentioned methods. Each method has its own merits and demerits, which are discussed in standard textbooks.

A.4. Hückel Molecular Orbital Method

HMO (Hückel Molecular Orbital) calculations are the simplest molecular orbital calculations. This method is specially applicable to planar hydrocarbons with conjugated double bonds (i.e. systems with alternate double and single bonds). In a conjugated system it is assumed that three sp^2 hybrid orbitals on each carbon atom are involved in the formation of σ-bonds, whereas a 2*p*-orbital perpendicular to the σ-framework is present on each carbon atom. This set of 2*p*-orbitals on each carbon atom forms the basis set for the formation of MOs. If there are an *n* number of carbon atoms, then there are an *n* number of 2*p*-orbitals in the basis set and an *n* number of MOs are formed. The π systems of molecules, such as benzene, butadiene, allyl cation and anion are some of the electronic systems that can be analyzed using the Hückel method.

A.4.1 Limitations and Assumptions of HMO Method

As mentioned earlier, simplifying assumptions are used to reduce the mathematical complexity in the evaluation of the elements H_{ij} and S_{ij}. The Hückel method takes this method to the extreme and incorporates H_{ij} and S_{ij} as parameters, that is, H_{ij} and S_{ij} are not mathematically evaluated. The above simplification of this procedure does limit its utility as a quantitative method, however, inspite of this limitation this method provides an excellent insight into the chemistry of π systems. The limitations and assumptions used in the Hückel method are:

i) The basis set of AOs used to build up the Hückel MOs are the set of 2*p*-orbitals on each of the carbon atoms of the conjugated system.

ii) The energy integral

$$H_{ij} = \int \phi_i \mathbf{H} \phi_j d\tau$$

is the energy of interaction of two atomic orbitals ϕ_i and ϕ_j. When i = j, the integral H_{ii} is the energy of the electron in the 2*p*-orbital of the carbon atom. It is assumed to be the same for all the carbon atoms that contribute to the conjugated system and is named α (that is $H_{ii} = \alpha$). The sign of α is negative since the energy of an electron in any AO is lower than that of a free electron whose energy is defined as zero. The parameter α is commonly termed as the *Coulomb integral* since its magnitude is governed by the Coulomb forces, i.e. nucleus-electron and electron-electron forces.

The value of H_{ij} (where i < > j) depends on whether the two carbon atoms i and j are directly bonded to one another or not. If the two carbon atoms are bonded to one another, then H_{ij} has the value of β and is assumed to be the same for any two neighbouring carbon atoms. Thus $H_{ij}=\beta$, where H_{ij} may be thought of as the energy of the electron in the overlap region of the AOs. The parameter β is commonly termed as the resonance integral and its sign, like α,

is negative. β is the energy of interaction between the AOs of two directly bonded atoms.

If the two carbon atoms are not bonded directly to one another, then H_{ij} is presumed equal to zero.

iii) The overlap integral

$$S_{ij} = \int \phi_i \phi_j d\tau$$

is assumed to be 0, even for the neighbouring carbon atoms. This is a very drastic assumption as, without overlap, no bonding is possible.

A.4.2 Applications of HMO Method

Examples of the application of the HMO method to some simple systems would be useful here.

A.4.2.1 Ethylene

For the π system the secular determinant is

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} \\ H_{21}-ES_{21} & H_{22}-ES_{22} \end{vmatrix} = 0$$

Put $H_{11} = \alpha$

$H_{12} = \beta$

$S_{11} = S_{22} = 1$

$S_{12} = S_{21} = 0$

$$\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} = 0$$

This determinant can be simplified by dividing throughout by β

$$\begin{vmatrix} (\alpha-E)/\beta & 1 \\ 1 & (\alpha-E)/\beta \end{vmatrix} = 0$$

substituting $(\alpha-E)/\beta$ with x

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

This gives $x^2-1=0$

$x^2 = 1$

$x = \pm 1$ i.e. x can have two values

since $x = (\alpha-E)/\beta$

$$\pm 1 = (\alpha - E)/\beta$$

There are two energy values corresponding to the two values of x

$$E_1 = \alpha + \beta \qquad \text{(lower energy orbital)}$$

$$E_2 = \alpha - \beta \qquad \text{(higher energy orbital)}$$

Solving the secular Equation A.9 the values of C_1 and C_2 are also obtained. For ethylene these values are

$$C_1(\alpha - E) + C_2\beta = 0$$

$$C_1\beta + C_2(\alpha - E) = 0$$

$$C_1 = C_2 = 1/\sqrt{2} = 0.707$$

The MOs of ethylene are

$$\psi_2 = 0.707\phi_1 - 0.707\phi_2$$

$$\psi_1 = 0.707\phi_1 + 0.707\phi_2$$

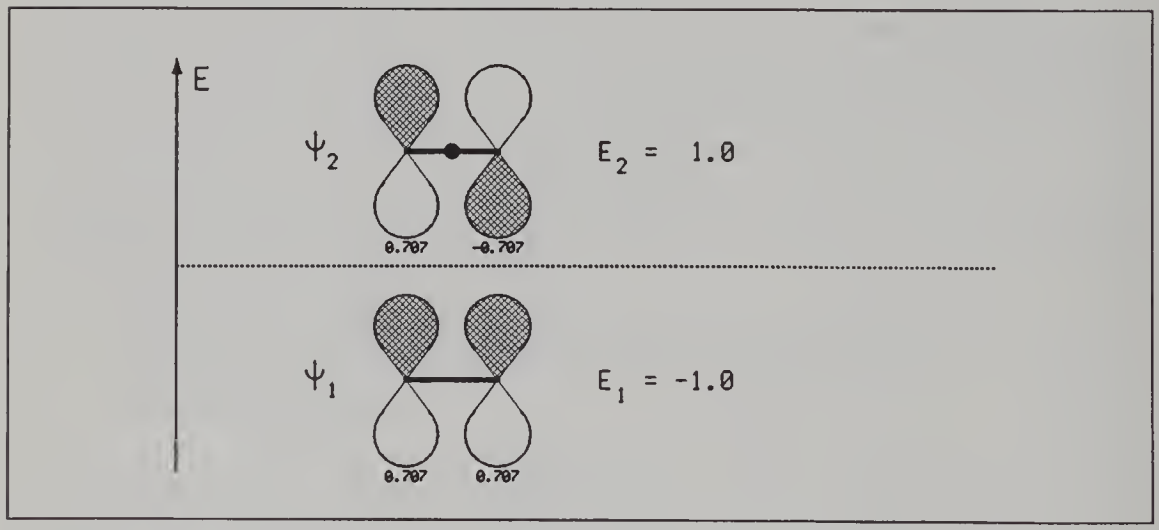


***Figure A.5**: Molecular orbitals of ethylene.*

It can be seen that the lower energy orbital has zero nodes, whereas the higher energy orbital has one node.

A.4.2.2 Allyl System

The allyl system is built up from three 2*p* AOs. Solving the secular determinant and secular equation, the values for the coefficients and energies of the MOs are obtained.

$$\psi_3 = 0.500\phi_1 - 0.707\phi_2 + 0.500\phi_3$$

$$\psi_2 = 0.707\phi_1 + 0.000\phi_2 - 0.707\phi_3$$

$$\psi_1 = 0.500\phi_1 + 0.707\phi_2 + 0.500\phi_3$$

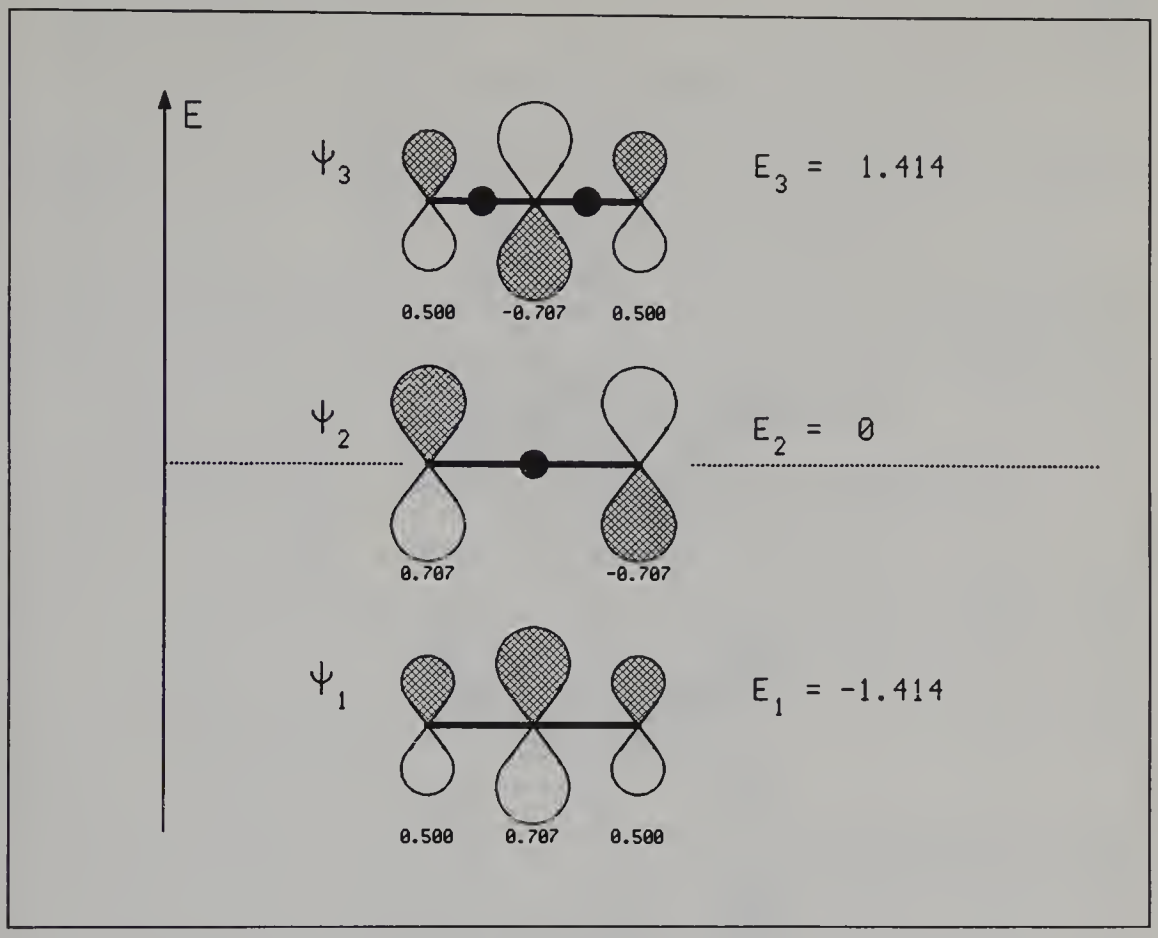


***Figure A.6**: Molecular orbitals of allyl system*

It can be seen that the orbitals have 0, 1 and 2 nodes (node is the point where the phase of the wave function changes, i.e. the coefficient changes from a positive to negative value, or vice versa). The energy values obtained are

$$E_1 = \alpha + 1.414\beta$$

$$E_2 = \alpha$$

and $$E_3 = \alpha - 1.414\beta$$

ψ_1 is called the bonding MO, as the energy of this MO is lower than the energy of the component AO. ψ_2 is the non-bonding MO as its energy is the same as are the energies of the component AOs (α is the energy of the electron in the 2*p*-atomic orbital of carbon). ψ_2 is the anti-bonding MO, as its energy is less negative than that of the starting AOs.

A.4.2.3 Butadiene

For butadiene the solution of the secular determinants and secular equation gives

$$E_4 = \alpha - 1.612\beta$$

$$E_3 = \alpha - 0.618\beta$$

$$E_2 = \alpha + 0.618\beta$$

$$E_1 = \alpha + 1.618\beta$$

and

$$\psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 + 0.602\phi_4$$
$$\psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$
$$\psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$
$$\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$

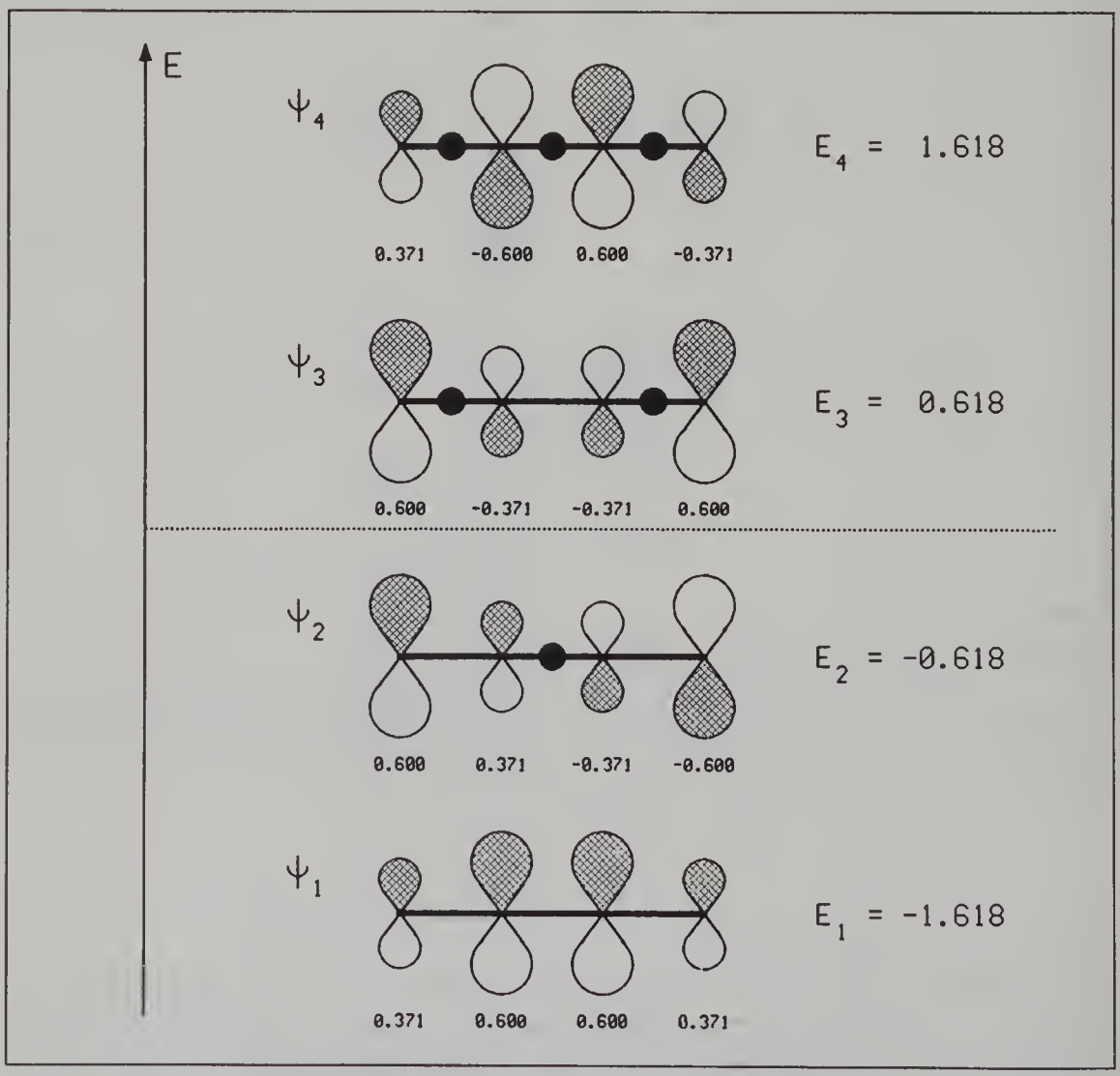


***Figure A.7**: Molecular orbitals of butadiene.*

It can be seen that the MOs have 0, 1, 2 and 3 nodes, respectively.

It can be generalized that in a conjugated system of n number of electrons, an n number of MOs are formed. The lowest MO has zero node, the next MO one node and so on. The nth. MO has n-1 nodes.

It was also observed that the contribution of the different AOs in the formation of MOs was different, i.e. in the ψ_1 of butadiene, the contribution of different AOs were 0.372 and 0.602. However, in qualitative predictions, especially the predictions concerning

the direction of rotation, it is only the phase of the wave function which is important. As for the coefficient, it is the sign, and not the magnitude, which matters.

The MOs are sometimes illustrated by drawing all the AOs of the same size (Figure A.8). This is not the real picture, but is usually good enough to serve the required purpose.

This illustration of the MOs is obtained by following a certain set of rules based on symmetry principles as detailed below.

An advantage of this representation is that without solving the secular determinant, or equations, a set of MOs for the conjugated system can be obtained.

A.4.3 Rules for Construction of Molecular Orbitals

Some simple rules which can be used for the construction of MOs are:

i) The number of MOs formed is equal to the number of the combining basis orbitals.

ii) The lowest energy orbital has 0 node, the next lowest energy orbital has one node and so on. The *n*th. MO has *n*-1 nodes.

iii) The nodes in a MO are equidistant from each other.

iv) The MOs formed are Symmetric or Antisymmetric with respect to the mirror plane or the C_2 -axis passing through the central atom, i.e. the mirror plane or the C_2 -axis are the symmetry elements.

v) The nodes must always be symmetrically located with respect to the central mirror plane. In chains with an odd-number of atoms (e.g. the allyl system), the central atom lies in the mirror plane. In these antisymmetric MOs, the central atom has zero contribution. As shown in Figure A.6, the central atom is forming a node.

vi) In an odd number of chains, there is a non-bonding level to which alternate *p*-orbitals make no contribution.

The qualitative MOs can be constructed by using these rules. Some of these MOs are constructed using this method, as given in Figure A.8.

The energies of the MOs can be calculated by solving the secular determinant. A simpler method for calculating the energies is by applying the mathematical expression given in Chapter 5. Even if the energies of the MOs are not calculated the relative energies can be determined form the number of nodes.

The greatest drawback of the HMO method is that it is not applicable to systems which are not conjugated e.g. ethane, cyclobutene, etc. For such systems the EHMO (Extended Hückel Molecular Orbital) method can be used.

In the Hückel MOs shown in Figure A.8, the symmetry labelling is with respect to the mirror plane.

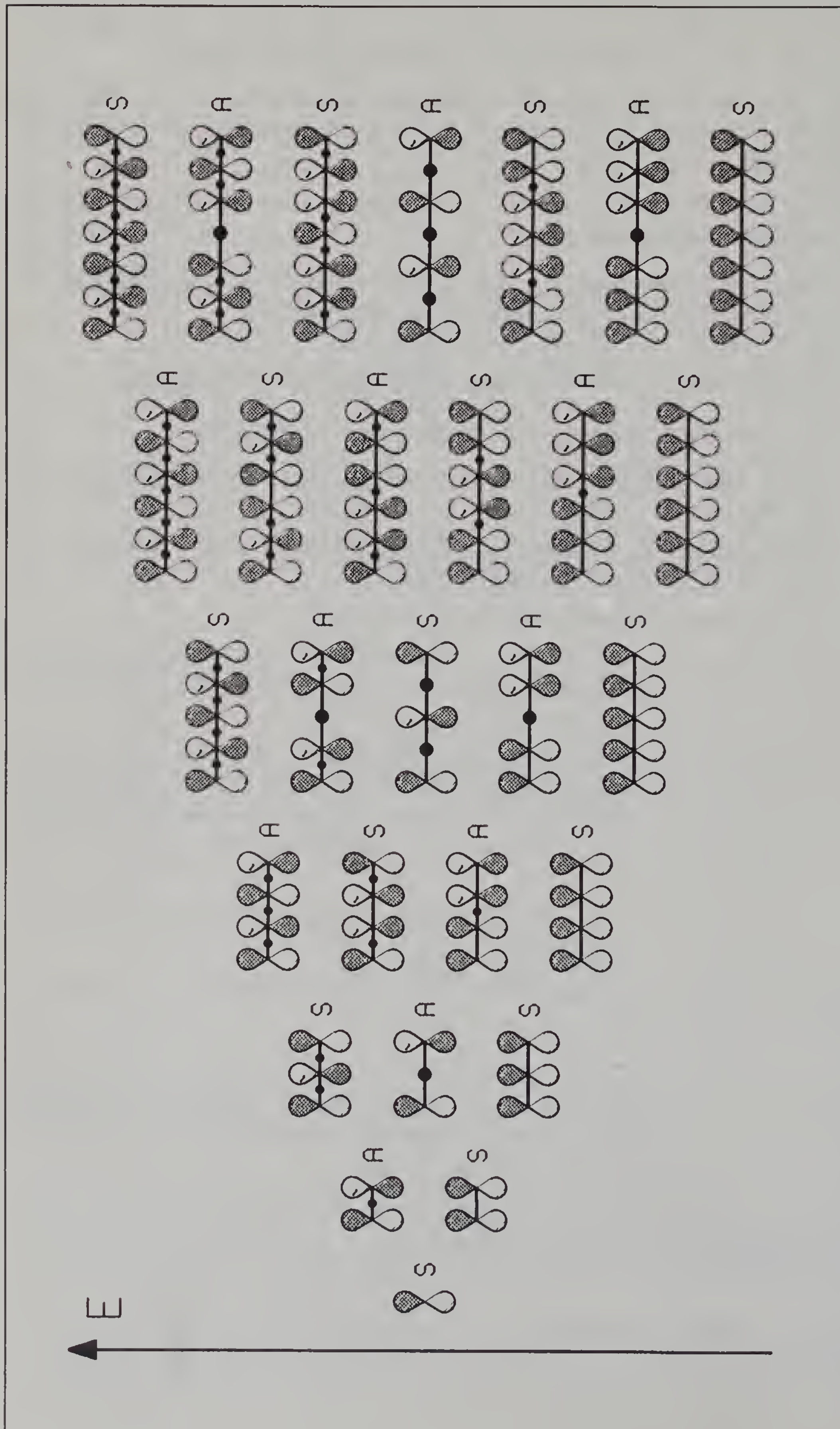


***Figure A.8**: Qualitative Hückel Molecular Orbitals for linear conjugated polyenes.*

A.4.4 EHMO Method

This method is a useful extension of the simple Hückel molecular approach. The basic approach used in the EHMO method is as follows:

i) All atoms in the molecular system are taken into account.

ii) The set of basis orbitals in the HMO method is formed by the $2p$-orbitals, whereas, in the EHMO method all valence orbitals on each atom form the basis set. For example, in a methane (CH_4) molecule, four $1s$-orbitals of hydrogen atoms and four valence orbitals of carbon, i.e. $2s$, $2p_x$, $2p_y$ and $2p_z$ form the basis set. These eight basis orbitals combine to form eight molecular orbitals.

iii) The wave function ϕ for the basis orbitals is given by the Slater Type atomic Orbitals that are hydrogen like AOs (Equation A.5).

iv) The secular determinant is set up as before. None of the matrix elements is assumed zero in the EHMO method as was assumed in the HMO method.

v) Overlap integrals S_{ij} are calculated using Slater type orbitals. Coulomb integrals H_{ii} are considered equal to the experimental valence state ionization potential and are available in literature.

Thus EHMO method is less approximate and more widely applicable than the HMO method. However, both HMO and EHMO are *one-electron* treatments of LCAO-MO calculations. In this case *one-electron* means an assumption that the electron does not interact with other electrons in the molecule. Initially the energy levels are calculated and then the electrons are inserted in the MOs. The number of electrons do not affect the energy levels, i.e. the allyl radical, its cation and anion all have the same orbital energies. This is not a realistic picture because any one electron in an allyl anion is repelled by two more electrons than an electron is in an allyl cation. This would obviously affect the electronic energy levels.

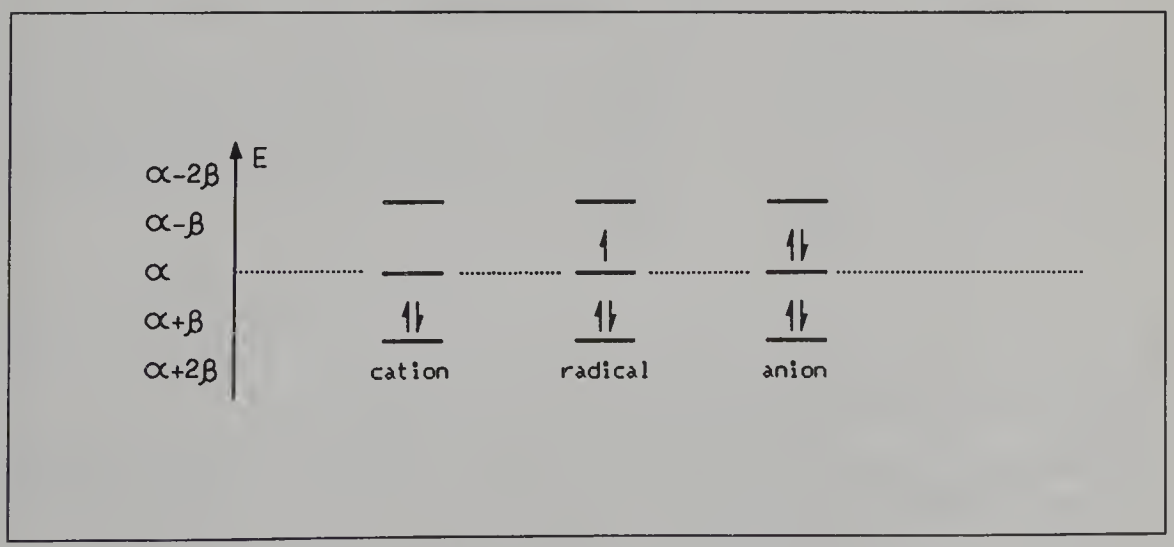


Figure A.9: *Electronic configuration for the allyl systems.*

A.5. SCF Methods

There are other methods which take electron-electron repulsion into account, by considering the interaction between an electron in a given orbital and the average field of the other electrons in the molecule. This approach is known as the SCF (Self Consistent Field) method and involves an iterative process in which the orbitals are improved from cycle to cycle until the electronic energy reaches a minimum constant value and the orbitals no longer change. The SCF method is also known as the Hartree-Fock theory.

A.5.1 RHF Method

One of the major problems in applying the SCF-MO method lies in the consistent treatment of both open- and closed-shell systems. An allyl radical (with an unpaired electron) and an allyl cation or anion (with no unpaired electrons) can be taken as examples of open- and closed-shell systems. Closed-shell systems are calculated using the RHF (Restricted Hartree Fock) method. In closed-shell systems a set of molecular orbitals is calculated. These orbitals may either be empty or occupied by an electron pair with opposite spins. The problem of electron spin does not arise because all spins are paired.

A.5.2 UHF Method

For open shell systems the UHF (Unrestricted Hartree Fock) method is used. UHF calculations determine two sets of molecular orbitals, one for each type of spin. These two sets of MOs, namely alpha and beta, are similar but not identical.

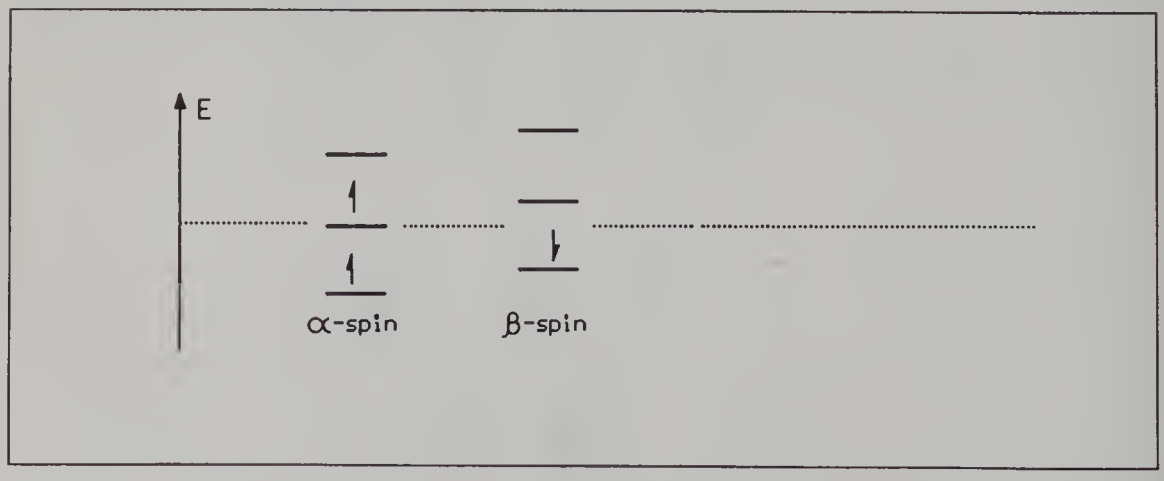


***Figure A.10**: Unrestricted Hartree Fock orbitals for an allyl radical.*

Electrons of the same spin occupy one set of orbitals, whereas the electrons of opposite spin occupy the other set of orbitals.

A.6. *ab initio* Methods

The term *ab initio* means a rigorous molecular orbital treatment derived from first principles. As mentioned earlier, in *ab initio* methods, the matrix elements for solving the secular determinant are solved without any simplifying assumptions or approximations. In order to evaluate the matrix elements, H_{ij} and S_{ij} should be known. These can only be evaluated if the exact mathematical expression for the Hamiltonian H and the basis orbitals ϕ_i are known. The expression for the Hamiltonian can be written as the sum of kinetic and potential energy operators. For the mathematical expression of the wave function of the combining AOs, one option is the use of STOs (Slater Type atomic Orbitals). Unfortunately if STOs are used as basis functions then the solution of the Schrödinger Equation becomes tedious. Thus this problem is solved by using some other mathematical function which shows the same behaviour as the STOs and is easier to solve. Such functions are Gaussian type functions. Almost all modern *ab initio* calculations employ GTOs (Gaussian Type Orbitals) basis sets. To mimic each STO, a number of Gaussian functions have to be combined. A number of optional basis sets are available, the simplest of them is the STO-3G basis set. As the name implies, three Gaussian type orbitals are combined to form a mathematical function, which show the same behaviour as the Slater type atomic orbitals.

In general, STO-*n*G is an abbreviation used for Slater Type atomic Orbitals simulated by adding an *n* number of Gaussian functions.

A.7. Configuration Interaction

Before discussing the CI (Configuration Interaction), two terms must first be defined. They are the *electronic configuration* and the *electronic state*.

A.7.1 Electronic Configuration and Electronic States

When electrons within a molecule are allocated to specific orbitals (MOs), an electronic configuration is obtained. An example of an electronic configuration for a hydrogen molecule is shown below.

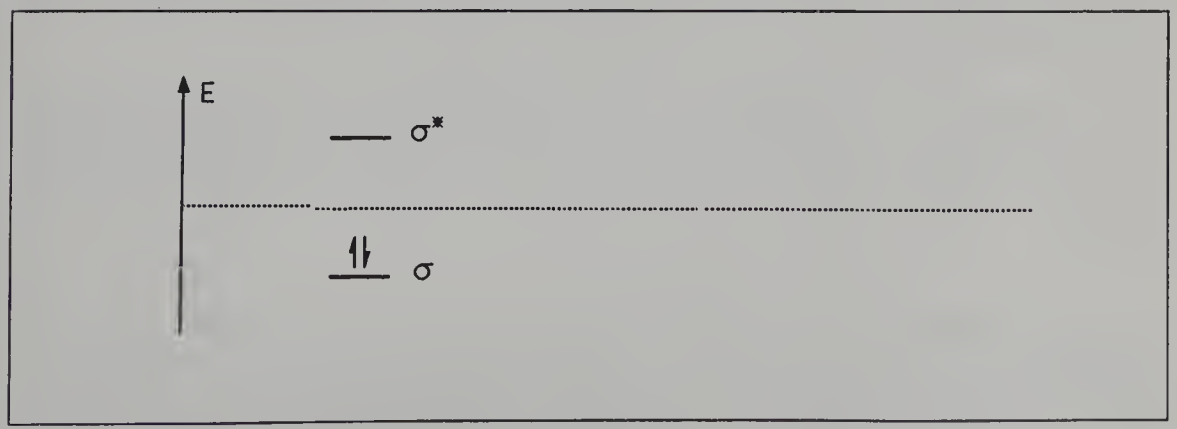


Figure A.11: *Ground state electronic configuration of hydrogen molecule.*

This is the ground state electronic configuration of H_2 molecule and can also be written as σ^2, where the superscript 2 symbolizes the number of electrons. However, in addition to the ground state, excited state electronic configurations are also possible. Two other possible electronic arrangements for the H_2 molecule are shown in the figure below.

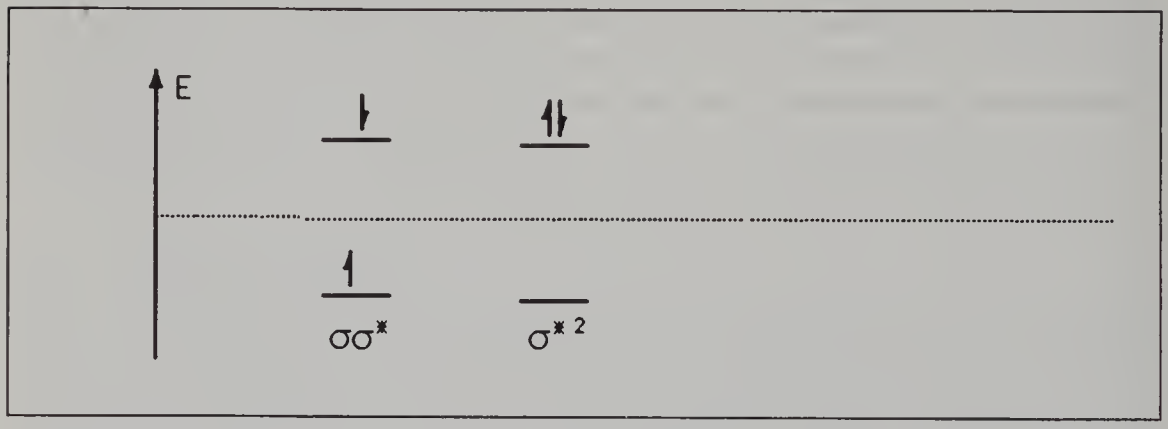


***Figure A.12**: Excited state electronic configurations possible for the hydrogen molecule.*

All these configurations are known as electronic states. An electronic state is just an arrangement of electrons in the molecule that is allowed by the laws of quantum mechanics. The ground state electronic configuration is generally represented by Ψ_0, and the excited state configurations by $\Psi_1, \Psi_2 \ldots \Psi_N$.

In the above example

$$\Psi_0 = (\sigma)^2 \qquad \text{(ground state)}$$

$$\Psi_1 = (\sigma)(\sigma^*) \qquad \text{(excited states . . .)}$$

and $$\Psi_2 = (\sigma^*)^2$$

A particular electronic configuration may be a useful representation of a particular state, it is not an accurate representation of that state. Because of the approximations inherent in the construction of MOs, an individual configuration is only an approximate representation of the molecule in one of these allowed electronic states.

To obtain a better model of an electronic state, two or more configurations are combined together. The process of constructing these combinations is known as *configuration interaction.*

In the example of the H_2 molecule, the CI (Configuration Interaction) method assumes that the actual state of the H_2 molecule is not just represented by Ψ_0, but a mixing of the ground state and the excited states takes place and the state function Ψ is then given by

$$\Psi = C_1\Psi_0 + C_2\Psi_1 + C_3\Psi_2 \qquad \text{(A.11)}$$

The coefficients C_1, C_2, C_3 and the energy of the state can be calculated using the Schrödinger equation. The values of C_1, C_2 and C_3 give the contribution of the various electronic states. In this case Ψ_0 has the major contribution, while Ψ_1 and Ψ_2 have minor contributions. Hence, C_1 has a much larger value than either C_2 or C_3.

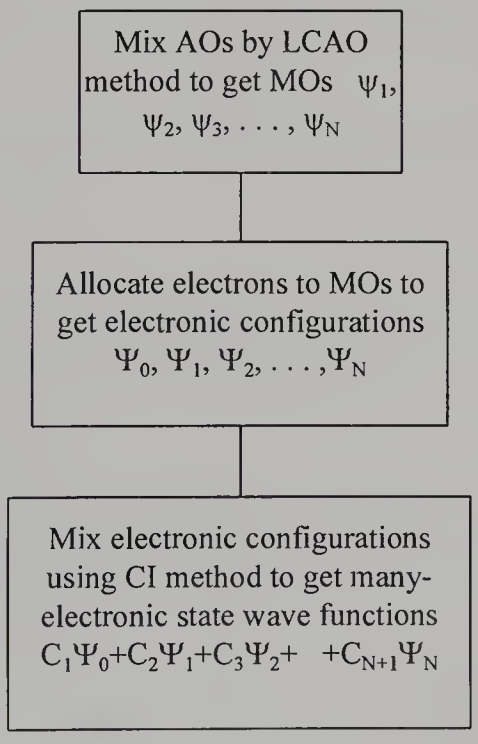
Thus, an electronic state may be represented by a particular configuration, or by a combination of these configurations, the latter representation being more accurate.

A.7.2 Schemes for Configuration Interaction

For a reasonably sized molecule, a large number of electronic states may exist and it is usually impossible to consider them all in a CI calculation. Many schemes have been designated to select the correct states to be used in the CI calculations. The smallest one, and the most commonly used, for a closed-shell molecule is a 3x3 CI, in which the ground state, and the two excited states are obtained by promoting one and two electrons from the HOMO to the LUMO.

Some other complicated mixing schemes are also available. One of these schemes is termed as CAS (Complete Active Space) scheme, which mixes together all configurations involving the *active orbitals*. These are defined as orbitals that undergo significant changes during the reaction. For example, in a breaking σ-bond, σ and σ* orbitals constitute the *active space*.

Ψ is known as the *many-electron state wave function* (Equation A.11), and the procedure for generating the wave function is summarized below.



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Appendix B

Symmetry Classification of Molecules

Symmetry plays an important role in the structure of the molecules. Some are highly symmetrical, some less so and many have no symmetry at all. It is thus reasonable to set up some system whereby molecules could be classified by their symmetry characteristics. The presence or absence of symmetry has consequences on the appearance of spectra, the relative reactivity of groups and many other aspects of chemistry, including the one that makes use of orbitals and their interactions.

It was discussed in various chapters that it is the orbitals which make up the primary description of the electronic structure of molecules, or groups, within a molecule. The orientation of the nuclear framework determines the orientation of the orbitals. The relationships between structural units (groups) of a molecule with each other can often be classified in terms of the symmetry that the molecule possesses as a whole.

The classification of the molecular orbitals of different polyenes, undergoing electrocyclic transformations, was done in order to construct energy level correlation diagrams and symmetry state correlation diagrams, which eventually led to the predictions regarding the favoured mechanism in electrocyclic transformations (Chapter 3). A brief discussion of the symmetry elements, symmetry operations and molecular point groups follows.

i) **Symmetry Elements**

The elements of symmetry of a solid are the geometric elements in relation to which the symmetry operations are carried out. These elements may be a point, an axis or a plane and are called symmetry elements.

ii) **Symmetry Operations**

A symmetry operation is defined as an operation, which when performed on an object, results in a new orientation of the object, which is indistinguishable from the original one. There is then no way of knowing if the object has, or has not, been subjected to a symmetry operation.

iii) **Molecular Point Groups**

A restricted combination of certain symmetry elements is called a point group.

B.1. Symmetry Elements

A molecule may posses the following symmetry elements:

B.1.1 Center of Symmetry

If identical atoms are found on either side of the centre of a molecule, and at an equal distance from the centre, then this centre is called the *centre of symmetry*. A molecule has a center of symmetry *i* if by reflection at the center (inversion) the molecule is transformed into itself. For every atom with *x*, *y*, *z* coordinates from the center there must be an identical atom with -*x*, -*y* and -*z* coordinates. Some examples of molecules possessing a center of symmetry are shown. Benzene also has a center of symmetry, but it does not have an atom located at the center (Figure B.1).

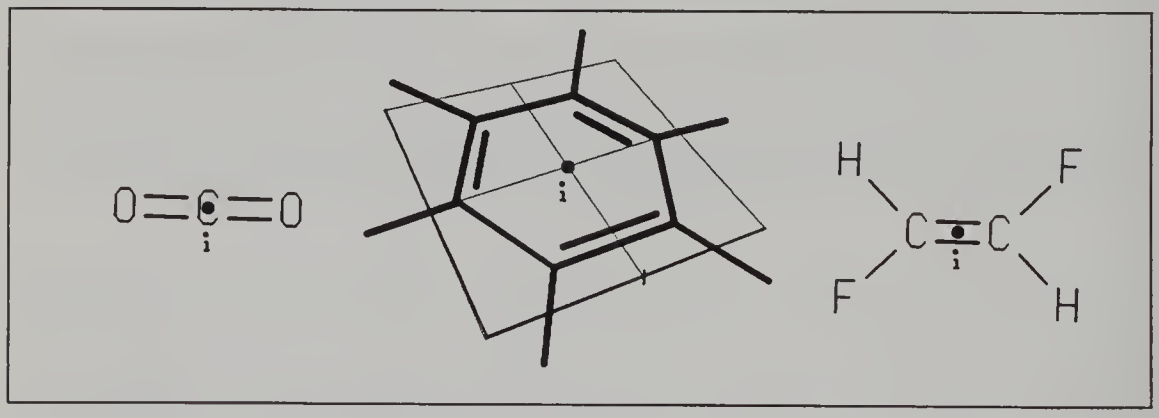

Figure B.1: *Examples of molecules having a center of symmetry i.*

B.1.2 Rotation Axis of Symmetry

A molecule has an *n-fold rotation axis of symmetry* designated as C_n, if rotation through $360°/n$ yields a molecular configuration indistinguishable from the original, where C stands for cyclic and *n* symbolizes the number of axes undergoing inversion.

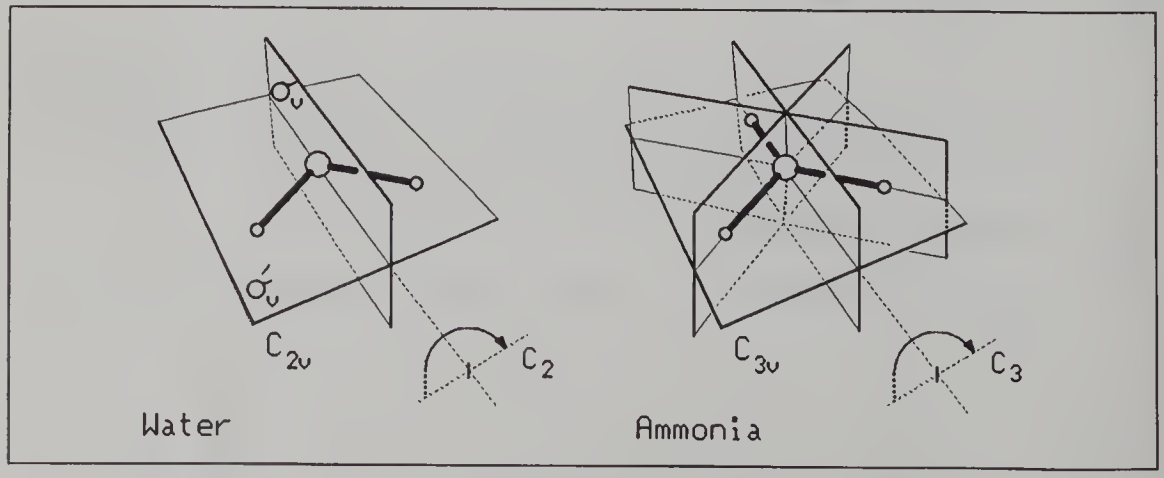

Figure .2: *Symmetry elements of water and ammonia.*

For example, in water, a rotation about the axis shown through 180° yields a water molecule indistinguishable from the molecule upon which the rotation has been performed. In this case n=2 and the axis is designated as C_2 axis and is often spoken of as a two-fold axis (Figure B.2).

In the case of ammonia a rotation through 120° (360°/3) yields a similar result (Figure B.2).

As explained earlier in Chapter 3, both butadiene and cyclobutene have a two-fold rotation axis C_2 and a plane of symmetry σ_v as shown in Figure B.3.

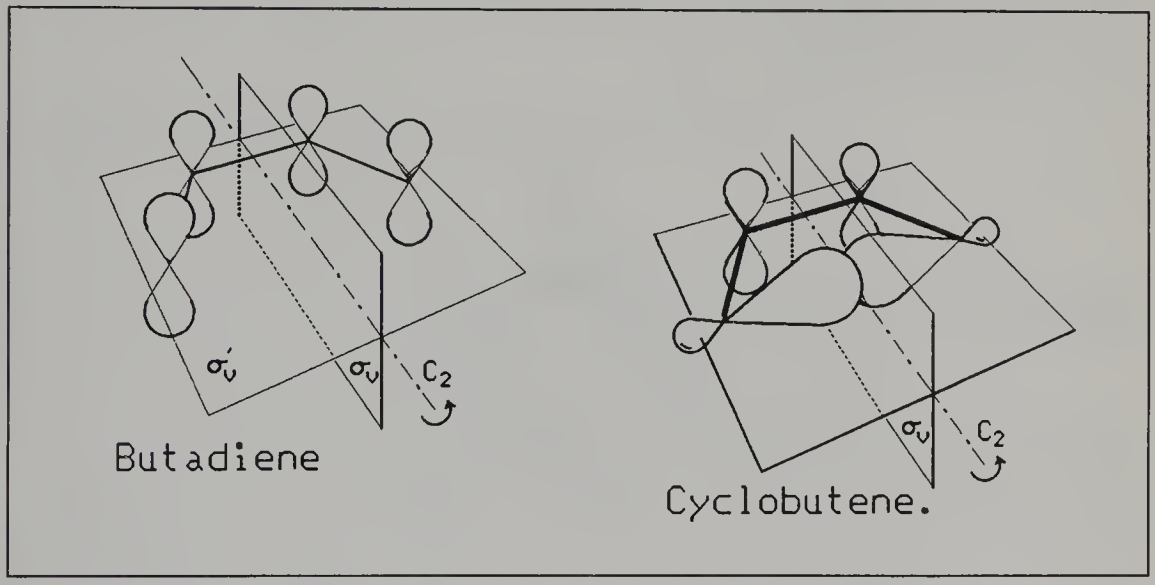

Figure B.3: *Symmetry elements present in butadiene and cyclobutene.*

B.1.3 Plane of Symmetry

A plane of symmetry, usually designated as σ, bisects an object into two symmetrical halves. A molecule has a plane of symmetry σ, if by reflection in the plane the molecule is transformed into itself. In other words, a plane of symmetry bisects the molecule into two equivalent parts, one part being the mirror image of the other. The subscripts *v*, *h* or *d* indicate whether the plane is vertical, horizontal or diagonal.

For example, in the water molecule shown in Figure B.2, a plane σ_v is shown which bisects the HOH angle of (105°). If every portion of the water molecule on the left-hand side of this plane were transposed across the plane to the right-hand side, into a new position equidistant from the plane, and vice versa (i.e. the right-hand portion transposed to the left) the resulting figure would not be distinguishable from the original one. The water molecule, therefore, has a plane of symmetry bisecting the angle HOH. It is evident that this is a special plane in the *yz*-dimension. For any other plane parallel to this particular plane a corresponding operation of reflection, similar to the one just described, would not yield the same water molecule.

It should be noted that each atom (or nucleus) ends up, after the symmetry operation, in the exact original position of its identical atom (or nucleus) and that the resulting total molecule is thus indistinguishable from the original molecule.

It is apparent from Figure B.2 that the plane in which the water molecule lies is also a plane of symmetry in the *xy*-dimensions. Both planes of symmetry are designated as σ_v because they are both vertical to the major symmetry axis, i.e. the C_2 axis shown in the *y* direction. To distinguish the two planes, one is designated as σ'_v.

Likewise, the NH_3 molecule has three planes of symmetry vertical to the three-fold rotation axis C_3 (Figure B.2).

However, in the case of benzene, the plane in which the carbon and hydrogen atoms lie is horizontal to the major symmetry axis, i.e. the C_6 axis. The remaining six planes of symmetry are vertical to the C_6 axis. Hence, benzene has one horizontal plane (σ_h) and six vertical planes of symmetry (σ_v).

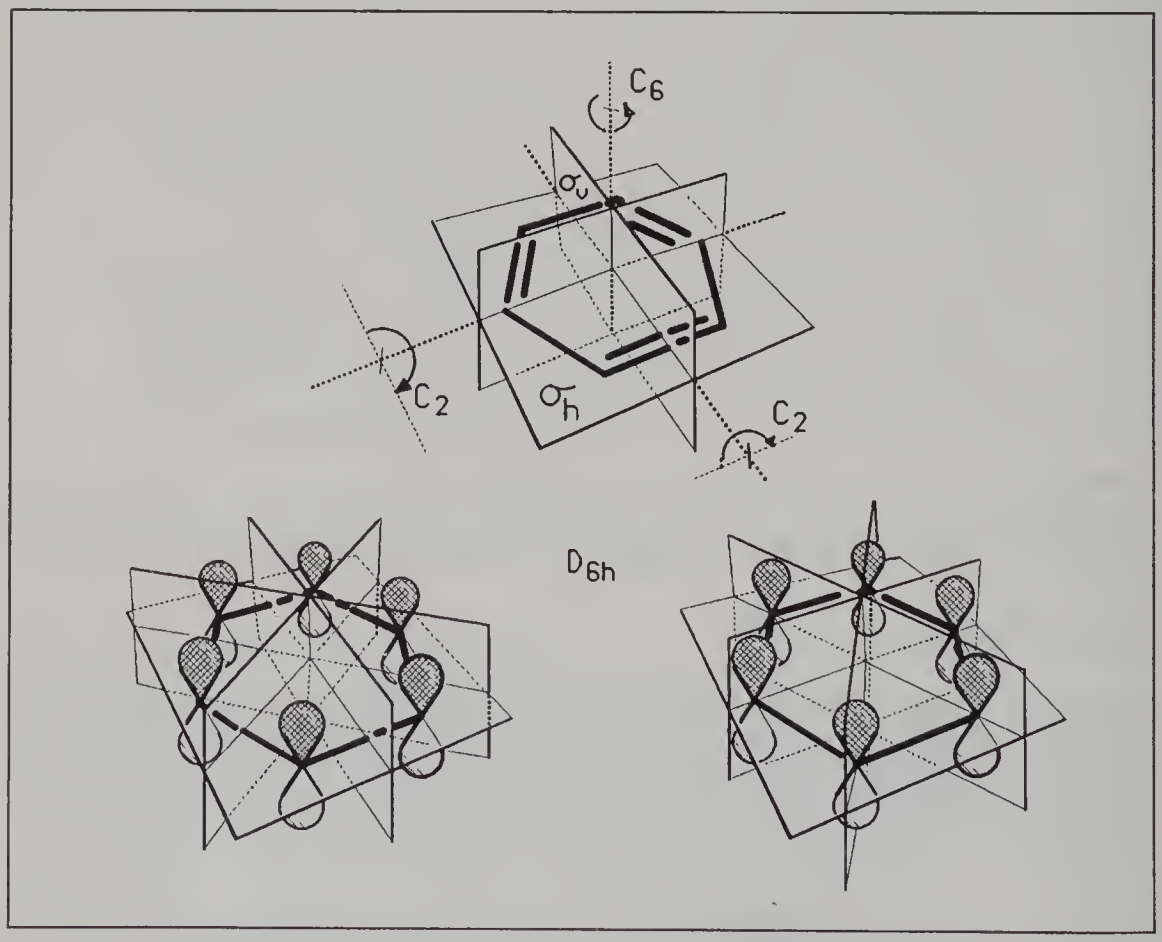

Figure B.4: *Symmetry elements of benzene.*

In benzene, there is a six-fold C_6 axis of rotation passing through the center of symmetry. Perpendicular to this six-fold axis of rotation are six C_2 axes, three of which pass through the carbon atoms and the other three pass through the carbon-carbon bonds. Rotation through 180° about each of these six axes yields an indistinguishable benzene molecule (Figure B.4).

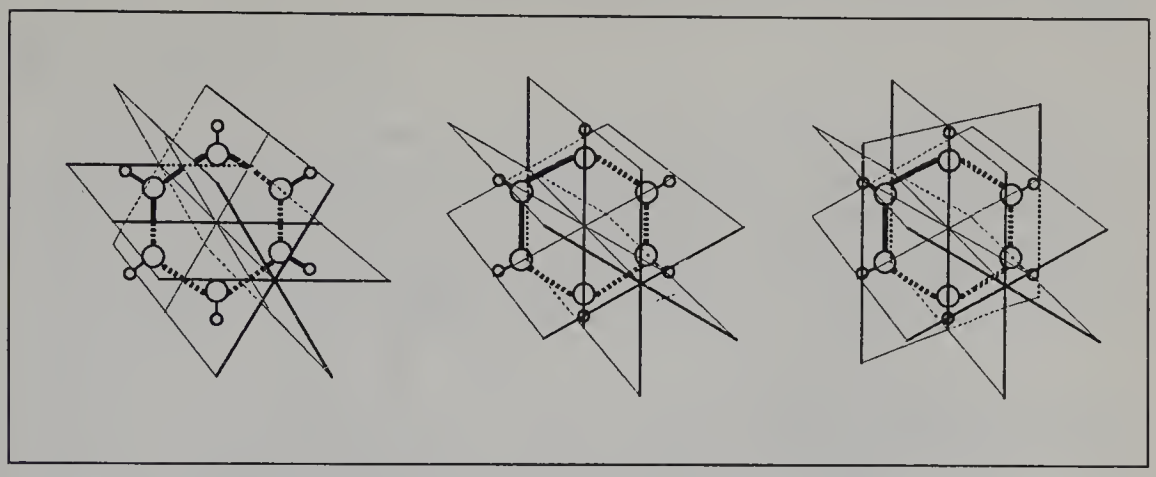

Figure B.5: *Perspective views of benzene showing σ planes.*

B.1.4 Rotation-Reflection Axis of Symmetry

A molecule has a *n*-fold rotation-reflection axis of symmetry S_n, if rotation through $2\pi/n$ (or $360^\circ/n$), followed by reflection in a plane perpendicular to the axis of rotation, yields a configuration indistinguishable from the starting molecule.

In the case of dibromodichloroethane (C) a rotation through 180° does not yield the original configuration (D) as shown in Figure B.6. However, by reflection in a plane perpendicular to the axis of rotation the original structure can be obtained, i.e. the mirror image of $C(M_C)$ and the mirror image of $D(M_D)$ are identical. Such an axis is designated as an S_2 axis.

Likewise the allene molecule (A) has an S_4 rotation-reflection axis. Again the mirror images of A and B (i.e. M_A and M_B) are identical (Figure B.6).

In the case of benzene there is an S_6 axis coincident with the C_6 axis previously discussed.

B.1.5 Identity

The fifth and the last symmetry element is the identity *E*. All molecules possess the identity even if they possess none of the other four symmetry elements. The symmetry operation corresponding to this symmetry element involves leaving the molecule unaltered. Hence, the resulting molecule can not be distinguished from the original.

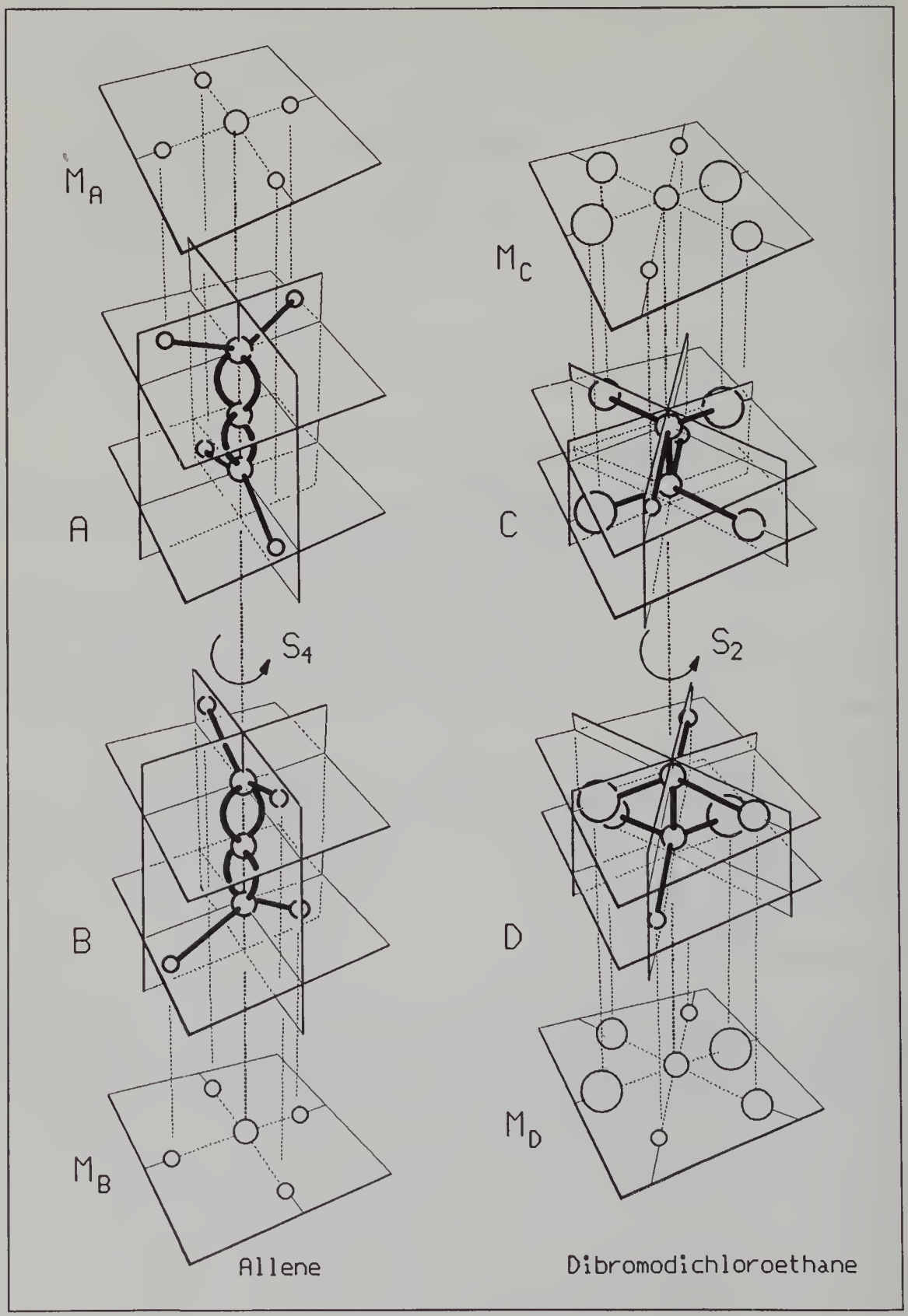

Figure B.6: *Rotation-reflection axis of symmetry S_2 in dibromodichloroethane (A) and S_4 in allene (C).*

B.2. Point Groups

As mentioned earlier, all molecules possess the symmetry element, the identity *E*. It is also shown that a large number of molecules have additional symmetry elements. For example the water molecule has two vertical planes of symmetry and a two-fold rotation axis of symmetry. Any molecule, which has two vertical planes, must out of necessity have a two-fold rotation axis, however, the reverse is not true, since a molecule may possess a two-fold rotation axis and not the two mirror planes of symmetry.

Likewise, in the case of ammonia, the three vertical planes of symmetry require the presence of a three-fold rotation axis of symmetry. Hence, the presence of certain symmetry elements means that others are required out of necessity.

In the case of benzene the symmetry can be adequately described by the following elements:

E	identity.
i	center of symmetry.
σ_v	plane of symmetry perpendicular to rotational axes.
C_2	two-fold rotation axis.
C_3	three-fold rotation axis.
C_6	six -fold rotation axis.
S_2	two-fold rotation-reflection axis.
S_3	three-fold rotation-reflection axis.
S_6	six -fold rotation-reflection axis.

Thus the existence of certain symmetry elements requires the presence of others. It might be assumed that any possible combination of symmetry elements is permitted, however, such an assumption can be misleading. For example, a molecule cannot possess a three-fold and four-fold axis in the same direction. Likewise, it can be shown that only certain combinations of symmetry elements are possible. *A restricted combination of symmetry elements that leaves at least one point unchanged is called a point group.*

A brief description of the classification of the molecules on the basis of their point groups follows:

B.2.1 Schönflies Notations

Shorthand notations are used to describe and classify the distinct point groups by either the Hermann-Mauguin notations or the Schönflies notations.

The widely used Schönflies notations are listed below:

E identity

C_n rotation about an axis through $2\pi/n$ radians (the principal axis is the axis of highest n).

σ_h reflection in a horizontal plane (the plane through the origin perpendicular to the axis of highest n).

σ_v reflection in a vertical plane (the plane containing the axis of highest n).

σ_d reflection in a diagonal plane (the plane containing the axis of highest n and bisecting the angle between the two-fold axes perpendicular to the principal axis). This is a special case of σ_v.

S_n improper rotation through $2\pi/n$ (C_n followed by σ_h.).

i $= S_2 =$ inversion through the center of mass ($r \rightarrow -r$).

Table B.1: *Schönflies notations for specific symmetry elements.*

Number	Notation	Number	Notation
1	C_1	17	S_6
2	C_i	18	C_{3v}
3	C_s	19	D_3
4	C_2	20	D_{3d}
5	C_{2h}	21	C_{3h}
6	C_{2v}	22	C_6
7	D_2	23	C_{6h}
8	D_{2h}	24	D_{3h}
9	C_4	25	C_{6v}
10	S_4	26	D_6
11	C_{4h}	27	D_{6h}
12	C_{4v}	28	T
13	D_{2d}	29	T_h
14	D_4	30	T_d
15	D_{4h}	31	O
16	C_3	32	O_h

The above symmetry elements are interrelated with each other as described below.

i) The intersection of two reflection planes must be a symmetry axis. If the angle ϕ between the planes is π/n, then the axis is n-fold.

If a reflection plane contains an n-fold axis, then there must be an n-1 number of other reflection planes at angles of π/n.

ii) Two 2-fold axes separated by an angle π/n require a perpendicular n-fold axis.

A 2-fold axis and an n-fold axis perpendicular to it require an n-1 number of additional 2-fold axes at angles of π/n.

iii) An even-fold axis, a reflection plane perpendicular to it, and an inversion center are interdependent. Any two of these imply the existence of the third.

The following is a discussion of those particular point groups, where some questions regarding the symmetry elements might arise.

- ***Point Group C_n***

A molecule possessing only a C_n rotation axis of symmetry falls in this group.

The molecules with no symmetry at all, except for the identity E, fall in group C_1.

A molecule with only a two-fold axis of symmetry is a member of the C_2 point group, and so on for C_3 .....C_n.

- ***Point Group S_n***

A molecule having only an n-fold rotation-reflection axis of symmetry belongs to the S_n point group. This point group is also designated as C_i for those molecules with a center of symmetry i and an S_2 axis, for example, *trans*-dibromodichloroethane.

- ***Point Group C_{nv}***

The point group C_{nv} includes those molecules which have a vertical rotation axis of order n where v symbolizes the vertical planes of symmetry containing the rotation axis.

- ***Point Group C_{nh}***

Molecules belonging to this point group have a rotation axis of order n and a horizontal plane of symmetry perpendicular to this axis. As mentioned earlier C_{1h} is equivalent to C_{1v} or C_s .The point group C_{2h} has an S_2 axis coincident with the C_n axis.

- ***Point Group D_n***

D stands for Dihedral. Molecules belonging to this point group have an n-fold axis C_n, and perpendicular to this axis are an n number of two-fold axes at equal angles to each other. Point group D_1 is identical with C_2.

- ***Point Group D_{nd}***

The molecules in this group have an n-fold axis C_n, an n number of two-fold axes perpendicular to this axis and an n number of planes of symmetry (σ_d), passing through the n-fold axis bisecting the angles between the two consecutive two-fold axes. The point group D_{2d} has three mutually perpendicular C_2 axes and one S_4 axis coincident with one of the C_2 axes and two diagonal planes of symmetry passing through the S_4 axis. Allene shown in Figure B.6 belongs to the point group D_{2d}.

- ***Point Group D_{nh}***

Molecules with a n-fold axis and an n number of vertical planes of symmetry containing the rotation axis plus a horizontal plane of symmetry perpendicular to the C_n axis fall in this point group. The D_{1h} group is identical to C_{2v} and is, therefore, not listed as such. Boron trichloride is an example of the D_{3h} point group.

In the point group D_{4h} the S_4 axis is coincident with the C_4 axis. On this same axis there is a coincident C_2 axis and four C_2 axes, which are perpendicular to the C_4 axis.

In the point group D_{6h} the S_6 axis which is coincident with the C_6 axis C_2 and C_3 or S_2 and S_3 axes which are also coincident with the C_6 axis. Benzene is the only known example of this group.

- ***Point Group T_d***

The T stands for Tetrahedral. The classic example of this point group is methane which has four three-fold axes and three mutually perpendicular two-fold axes which are coincident with the S_4 axes.

- ***Point Group O_h***

The O stands for Octahedral. Molecules in this group have three mutually perpendicular four-fold axes, four three-fold axes, a center of symmetry, nine planes of symmetry and three S_4 axes coincident with the three C_4 axes.

Table B.2: *Symmetry point groups and their examples.*

	Symbols	Symmetry elements	Examples
Type 1	C_1, C_s,	C_i	
1	C_1	E	fluorobromochloromethane
2	C_s	E, σ	$SOCl_2$, cyclopropyl system
3		E, i	*trans*-1,2-dibromodichloroethane
Type 2	C_n, S_n,	C_{nv}, C_{nh}	
1	C_n	E, C_n	
	C_2	E, C_2	S_2Cl_2, H_2O_2, cyclohexane
	C_3	E, C_3	triphenylmethane
2	S_n	E, C_n	
	S_2	E, $S_2 \equiv C_2$	*trans*-1,2-dibromodichloroethane
	S_4	E, C_2, S_4, S_4^3	$Si(OMe)_4$
3.	C_{nv}	$C_n\sigma_v$	
	$C_{1v} \equiv C_s$		
	C_{2v}	E, C_2, $2\sigma_v$	butadiene, cyclobutene, H_2O
	C_{3v}	E, $2C_3$, $3\sigma_v$	$CHCl_3$, NH_3, CH_3Cl
	C_{4v}	E, $2C_4$, C_2, $2\sigma_v$, $2\sigma_d$	$SbCl_5$, $Fe(CO)_5$, $XeOF_4$
	$C_{\infty v}$	E, C_∞, $\infty\sigma_v$	HCl, CO, H-C≡C-CN
4	C_{nh}	C_n, σ_h	

	$C_{1h} \equiv C_{1v} \equiv C_s$		
	C_{2h}	E, C_2, i, σ_h	*trans*-1,2-dichloroethane, glyoxal, $CH(CN)_2$
	C_{3h}	$E, 2C_3, \sigma_h, 2S_3$	boric acid, $B(OH)_3$, $B(OMe)_3$
Type 3	D_n, D_{nh}, D_{nd}		
1	D_n	$C_n, nC_2 \perp C_n$	
	$D_1 \equiv C_2$		
	D_2	$E, 3C_2$	ethylene (twisted)
	D_3	$E, 3C_2, 2C_3$	*tris*-ethylenediamine complexes of transition metals
2	D_{nh}	$C_n, nC_2 \perp C_n, n\sigma_v, \sigma_h$	
	D_{2h}	$E, 3C_2, 3\sigma_v, i$	ethylene, naphthalene, diborane
	D_{3h}	$E, 2C_3, 3C_2, 3\sigma_v, \sigma_h, 2S_3$	BF_3, cyclopropane, ethane, PCl_5
	D_{4h}	$E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, \sigma_h, 2\sigma_v, 2\sigma_d$	cyclobutane (planar)
	D_{5h}	$E, 2C_5, 2C_5^2, 5C_2, 2S_5, 2S_5^2, \sigma_h, 2\sigma_v$	cyclopentadienyl anion (cation)
	D_{6h}	$E, 2C_6, 2C_3, C_2, 3C_2', i, 3C_2'', 2S_6, 2S_3, \sigma_h, 3\sigma_v, 3\sigma_d$	benzene
	$D_{\infty h}$	$C_\infty, \infty C_2, \perp C_\infty, \infty\sigma_v, \sigma_h$	CO_2, acetylene
3	D_{nd}	$E, C_n, nC_2 \perp C_n, n\sigma_v$	
	D_{2d}	$E, 3C_2, 2\sigma_d, 2S_4$	allene, cyclobutane (puckered), cyclooctatetraene
	D_{3d}	$E, 2C_3, 3C_2, i, 3\sigma_d, 2S_6$	ethane, cyclohexane, 18-crown-6
	D_{4d}	$E, 2C_4, C_2, 2C_2', 2C_2'', 2S_8, 2S_8^3, 4\sigma_d$	
	D_{5d}	$E, 2C_5, 2C_5^2, 5C_2, i, 2S_{10}, 2S_{10}^3, 5\sigma_d$	ferrocene
Type 4	T_d, O_h		
1	T_d	$E, 4C_3, 3C_2\ 6\sigma_v$	methane, CCl_4, OsO_4
2	O_h		SeF_6, SF_6

B.2.2 Establishing the Molecular Point Group

Figure B.7 shows a possible scheme for establishing the molecular point group. The symmetry of most molecules may be reliably established by this scheme.

An examination is first carried out to ascertain if the molecule belongs to some *special* group. If the molecule is linear, then it may have a symmetry plane perpendicular to C_∞ (point group $D_{\infty h}$), or it may not have one (point group $C_{\infty v}$). Very high symmetries are easy to recognize. Each group T, T_h, T_d, O, and O_h, has four three-fold rotation axes. Both icosahedral I and I_h groups require ten three-fold rotation axes and six five-fold rotation axes. The molecules belonging to these groups have central tetrahedron, octahedron, cube or icosahedron.

If the molecule does not belong to one of these *special* groups, a systematic approach is followed. Firstly, the possible presence of rotational axes in the molecule is checked. If there is no rotational axis, then it is determined whether there is a symmetry plane (C_s). In the absence of rotational axes and mirror planes, there may only be a center of symmetry (C_i), or there may not be any symmetry element at all (C_1). If the molecule has rotation axes, it may have a rotation-reflection axis S_n with an even-number order (S_{2n}), coinciding with the rotation axis (C_2). For S_4 there is a coinciding C_2, for S_6 a coinciding C_3, and for S_8, both C_2 and C_4.

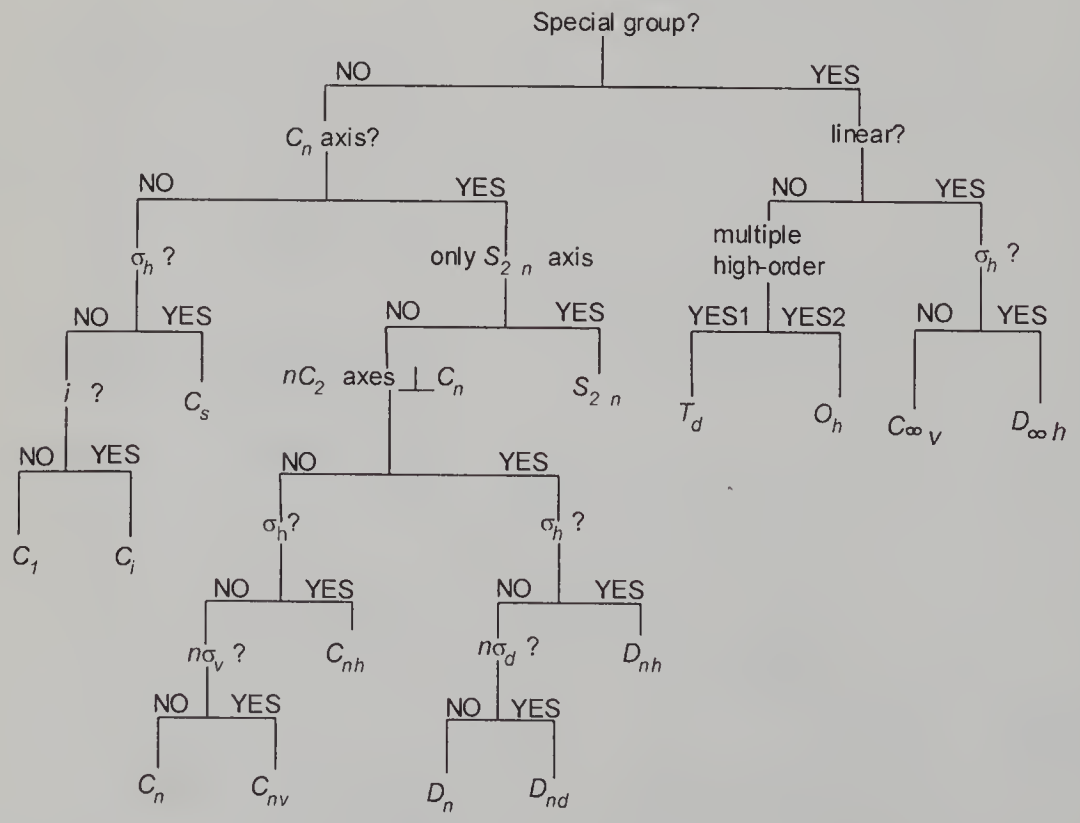

Figure B.7: *Steps involved in establishing a symmetry point group.*

In any case the search is for the highest order C_n axis. It is examined whether there are an n number of C_2 axes present which are perpendicular to the C_n axis. If such axes are

present then there is D symmetry. If in addition to D symmetry there is a σ_n plane then the point group is D_{nh}, while if there are n symmetry planes (σ_d) bisecting the two-fold axes then the point group is D_{nh}. If there are no symmetry planes in a molecule with D symmetry then the point group is D_n.

Finally, if no C_2 axes perpendicular to C_n are present then the lowest symmetry is C_n, if a perpendicular symmetry plane is present then the point group is C_{nh}, and if there are an n number of coinciding symmetry planes then the point group is C_{nv}.

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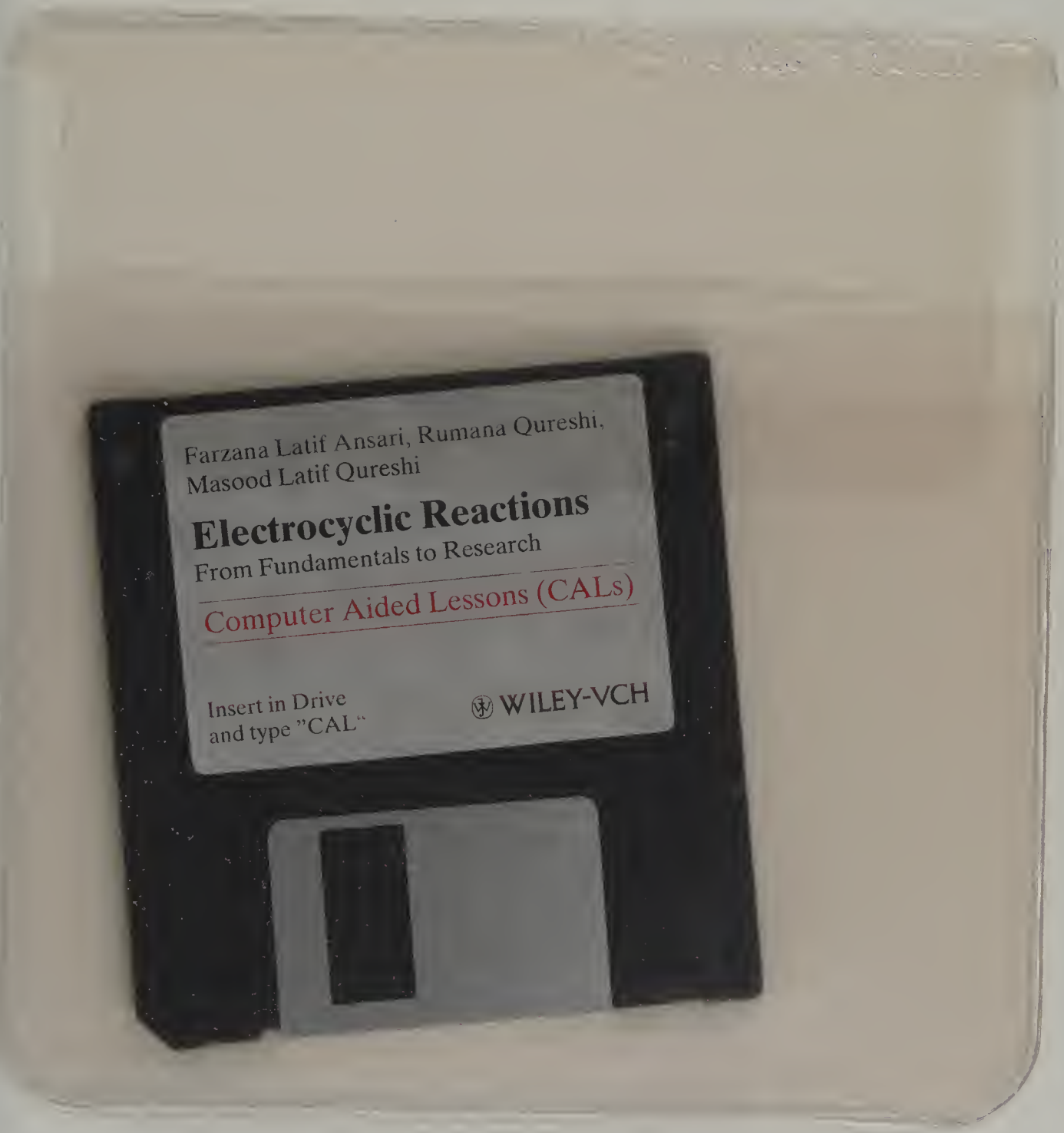

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