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PERICYCLIC REACTIONS & AROMATICITY

(A HANDBOOK FOR M.Sc. STUDENTS)

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CONTENTS

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PREFACE

Ever since the classic The Conservation of Orbital Symmetry by Woodward and Hoffmann, there has been a need in the publication of many books and excellent review articles dealing with this topic. Now, focus had shifted to uncover the mechanisms of the so-called "no-mechanism reactions." The uncovering of the fact that orbital symmetry is conserved in concerted reactions was a turning point in our understanding of organic reactions. It is possible to predict the stereochemistry of such reactions by following the simple rule that stereochemical consequences of reactions of reactions initiated thermally will be opposite to those performed under photochemical conditions. Study of pericyclic reactions, is an integral part of our understanding of organic reaction mechanisms.

The book opens with an introduction (chapter 1), which, besides providing background information needed for appreciating different types of pericyclic reactions, outlines simple ways to analyse these reactions using orbital symmetry correlation diagram, frontier molecular orbital (FMO), and perturbation molecular orbital (PMO) methods.

Electrocyclic, sigmatropic, and cycloaddition reactions are subsequently in chapter 3. Chelotropic and 1,3-dipolar cycloaddition reactions as examples of concerted reactions are also discussed in chapter 3. Aromaticity of benznoid and benzanoid compounds, Frost Muslin diagrams are discussed in chapter 4.

Assuming that a student has taken courses in organic chemistry that include reaction mechanisms and stereochemistry, The book is meant to be taught as a one-semester course to graduate and senior undergraduate students majoring in chemistry. One has to remember that a book designed for a one-semester course cannot include all the reactions reported in the literature.

We hope that our book will be well received by students and teachers. We encourage all those who read and use this book to contact us with any comments, suggestions, or corrections for future editions.

Our email addresses are: roopamgu@gmail.com and mandalajyothi@yahoo.co.in

We thank our reviewers for carefully reading the manuscript and offering valuable suggestions. Finally, we thank the editorial staff of for bringing the book to fruition.

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We wish to express my immense sense of gratitude to Late Prof. K.C. Rajanna, O.U. , Prof. Ashok, O.U., Hyderabad and Prof.M. Sarangapani, K.U. Warangal for their encouragement, support and blessings.

We wish to thank our colleagues and friends for their encouragement, cooperation and support.

It is not appropriate if we do not mention the whole hearted cooperation rendered our family members to complete this book.

We express our sincere thanks to our publisher for bringing out this book promptly. I would be indebted to the readers of this book for sending their suggestions, comments and criticism towards further improvement. We highly appreciate their efforts.

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Dr. Mandala Jyothi joined Mahatma Gandhi University in 2012 as an Assistant Professor in the Department of Chemistry. She has been teaching chemistry to post-graduate students and has been undertaking research independently in organic chemistry and medicinal chemistry. An alumnus of the Department of Chemistry, kakatiya University , Warangal (India) for an M. Sc. (chemistry) degree. She has done her Ph.D at Kakatiya University in 2011. She has 20 publications in various national and international journals.

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PERICYCLIC REACTIONS

Pericyclic reactions are concerted reactions, taking place through a cyclic transition state i.e., cyclic rearrangement of electrons.
These reactions are reversible, induced by heat or light and highly stereo specific reactions.

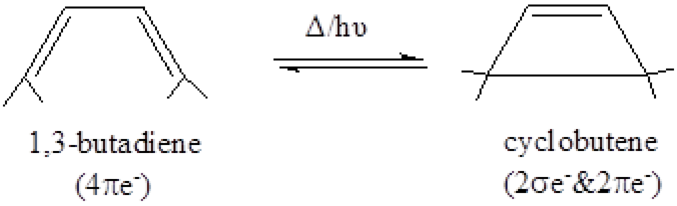
The products from thermal and photochemical conditions are stereo specifically different. These reactions do not involve a reactive intermediate like a carbocation, carboanion or a free radicals. Pericyclic reactions are largely unaffected by catalysts or solvent polarity.

Classification of pericyclic reactions

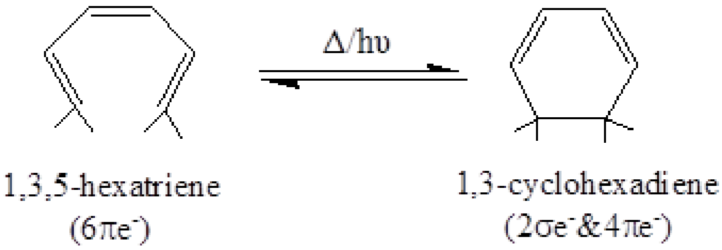
Pericyclic reactions are classified into three main groups via electro cyclic reactions, cycloaddition reactions and sigma tropic reactions.

Electro cyclic reactions:

An electro cyclic reaction may be defined as formation of a σ-bond between the termini of a conjugated π system or the reverse process.



Forward reaction is called electro cyclic ring closure of 4ne-(n=1).
Reverse reaction is called electro cyclic ring opening. These two reactions depend as the thermodynamic stability of the corresponding products.



Electro cyclic reactions of a 6e- or (4n+2)e- system.

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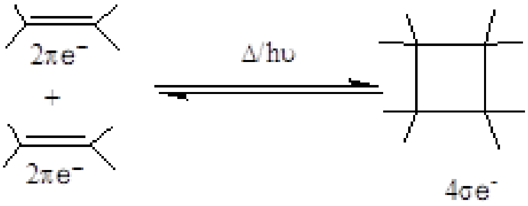
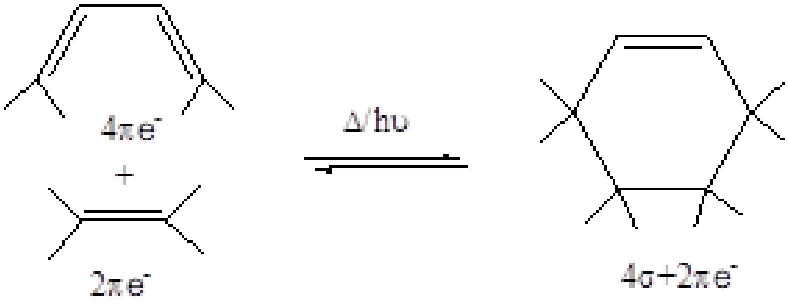
Cycloaddition reactions:

A cycloaddition reaction may be defined as an addition reaction between two or more π system to form a cyclic adduct or the reverse process.



In the forward reaction, two σ-bonds are formed at the expense of two π bonds. This reaction is known as cycloaddition. In the reverse reaction in which two π bonds develop at the expense of two σ-bonds is called cyclo reversion reaction. The cycloaddition reactions are generally classified as [m+n] cycloaddition reactions. In a [m+n] cycloaddition two components with m and n πe- reacts to give a cyclic adduct. In the above example, two components each with 2πe- undergo addition. The reaction is called [2+2] cycloaddition.



In the forward reaction, two σ-bonds and one π-bond are formed at the expense of three π bonds. This reaction is known as cycloaddition. In the reverse reaction in which three π-bonds develop at the expense of two σ-bonds and one π-bond is called cyclo reversion reaction. The cycloaddition reactions are generally classified as [m+n] cycloaddition reactions. In a [m+n] cycloaddition two components with m and n πe- react to give a cyclic adduct. In the above example, two components with 6πe- of 1,3-butadiene and ethylene undergo addition. The reaction is called [4+2] cycloaddition.

Sigmatropic reactions:

These are also called sigmatropic rearrangements. In these reactions an atom (H or D) or a group migrates with its σ- bond, from the a-position of double bond to a new position in the π-system. The sigmatropic reactions are classified as [i,j] shifts or shifts of order [i,j]. Following is an example of [1,5] sigmatropic shift of a H.

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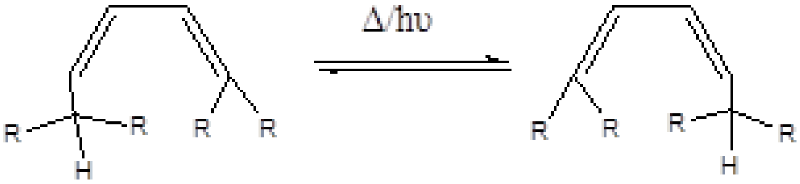
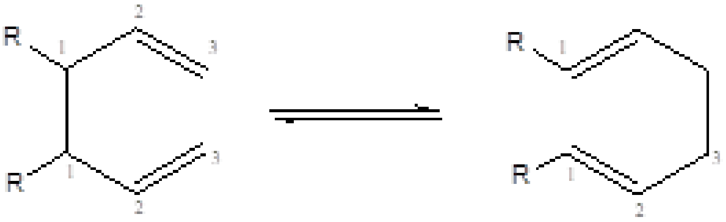
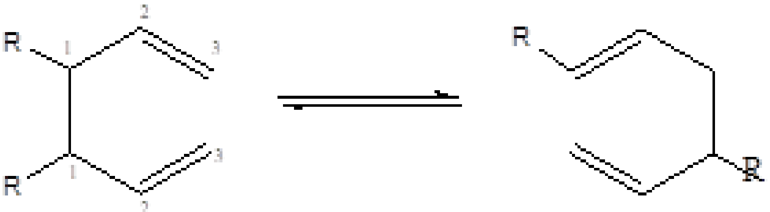


While determining the order of a sigmatropic shifts the system is numbered by taking the migrating σ-bond as the reference. The atoms in the system are numbered on either side of the σ-bond. If the product, the new sigma bond appears between i and j atoms, the reaction is called [i,j] shift. In other words, in an [i, j] sigmatropic shift, the σ-bond migrates from position i to position j.

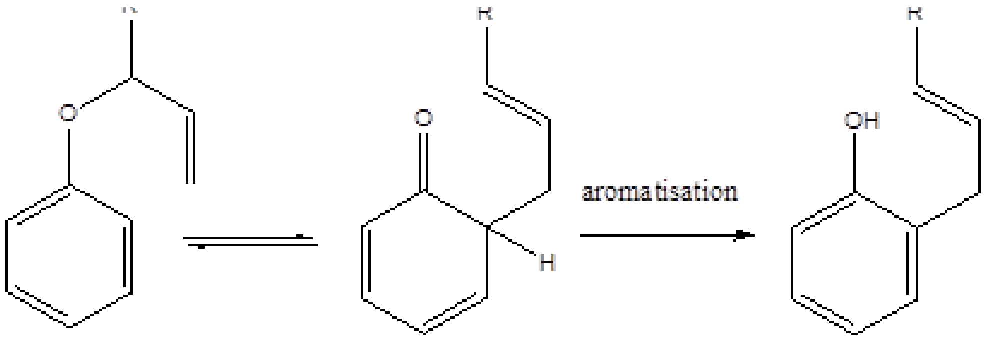


(3,3 -sigmatropic shift)

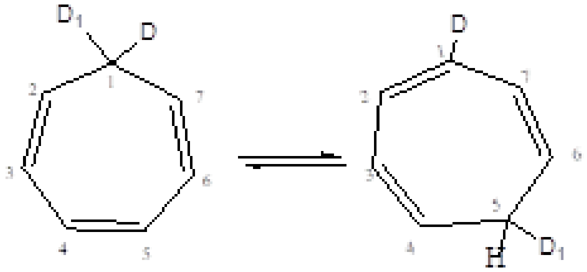


(1,3 -sigmatropic shift)

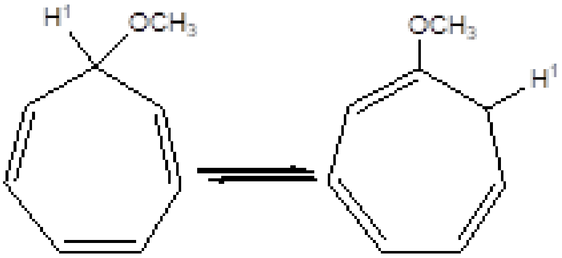
In the following example, an allylphenylether is converted to o-allylphenol through allylcyclohexdienone. The first in this sequence is a [3,3] sigmatropic shift.



Allylphenylether **allyl cyclohexadienone** **O-allyl phenol**



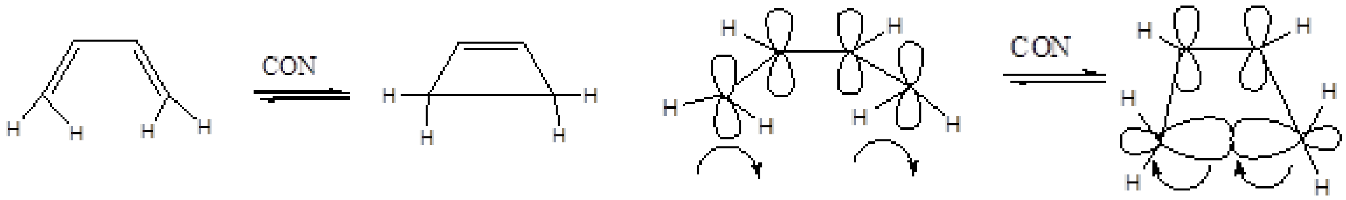
[1,5] sigmatropic shift of D_1



[1,7] sigmatropic shift of H^1

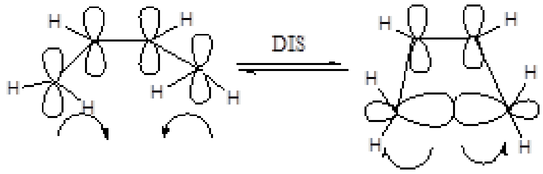
Stereochemistry of percyclic reactions:

a)Electrocyclic reactions: The two different types that are conrotatory and disrotatory electrocyclic reactions have been designated by Woodward and Hoffmann (CON and DIS).



A σ bond is formed between the two termini of diene system by the linear overlap of p orbital on the terminal olefinic carbon atoms. If the rotation of the two p-orbitals is in the same direction (both clockwise or both anti clockwise), the cyclisation is called conrotatory or con electrocyclicsation.

Other hand the ratotion of the two p orbitals in opposite direction (one is clockwise and other is anti clockwise) is called disrotatory or diselectrocyclisation.



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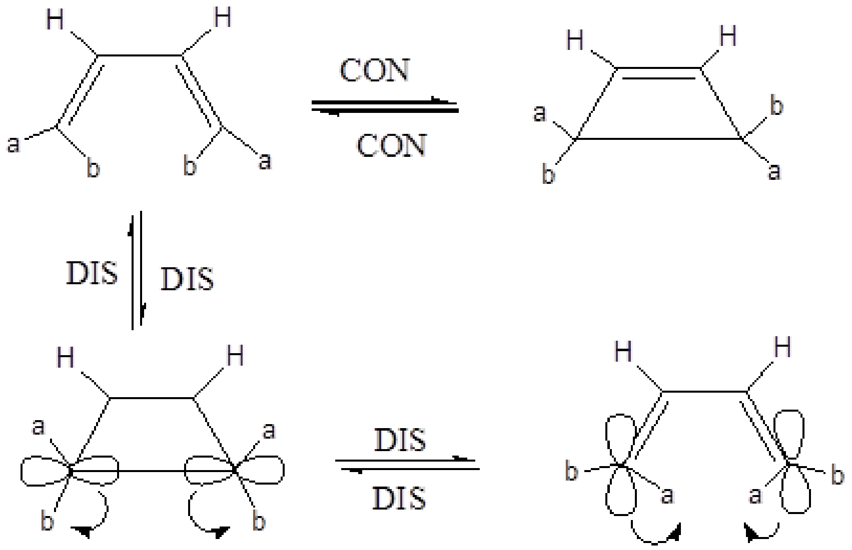
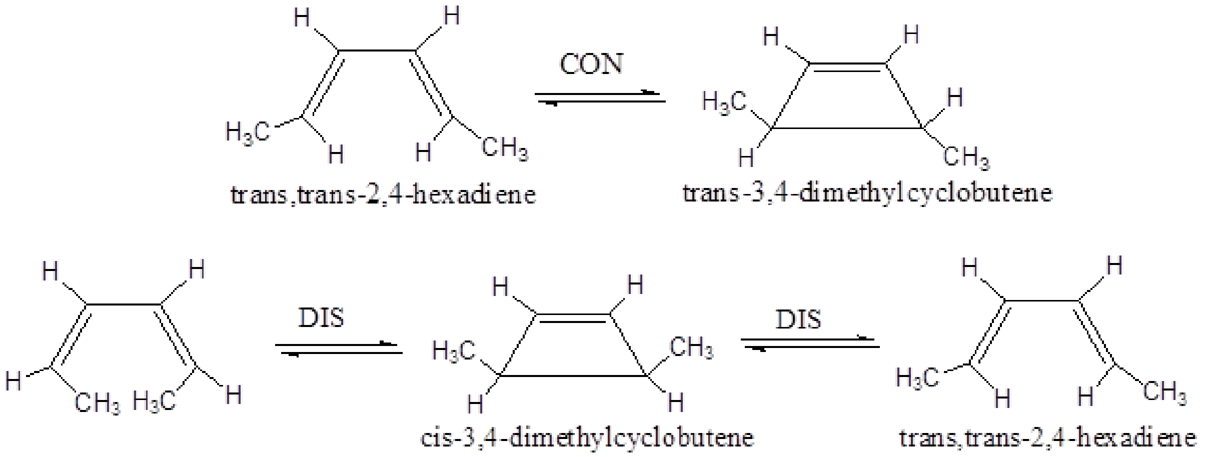
Similarly in the electrocyclic ring of cyclobutane, the orbital constituting the σ-bond should be pulled apart to generate p-orbitals at the terminal olefinic carbons in the product. This process could, again, be conrotatory or disrotatory ring opening. The stereochemical significance of these two modes of ring closure (or ring opening) becomes clear when substituted reactants are considered.



Con ring closure- Two outer groups or two inner groups will be trans in the products
Dis ring closure- Two outer groups or two inner groups will be cis in the products
Con ring opening- Out of two cis groups, one will become inner group and the other will become outer group in the product.

Dis ring opening- Two cis groups, will become either inner groups or outer groups.



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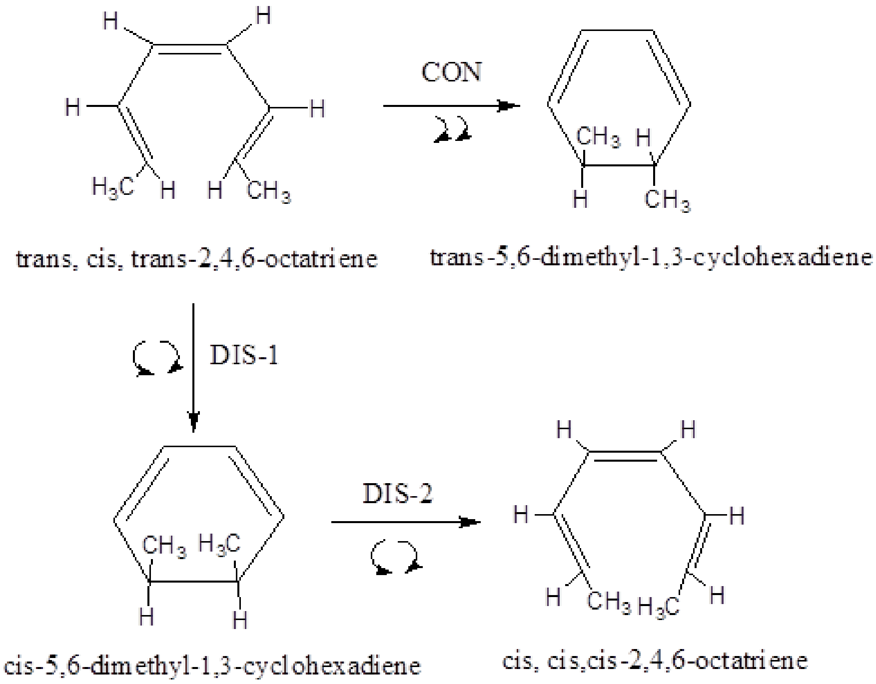

Cycloaddition reactions: Suprafacial and Antarafacial additions

Addition to a π system can take place in two methods. Addition may be on the same face (side) of the π system or on the opposite faces. These are known as suprafacial and antarafacial additions respectively

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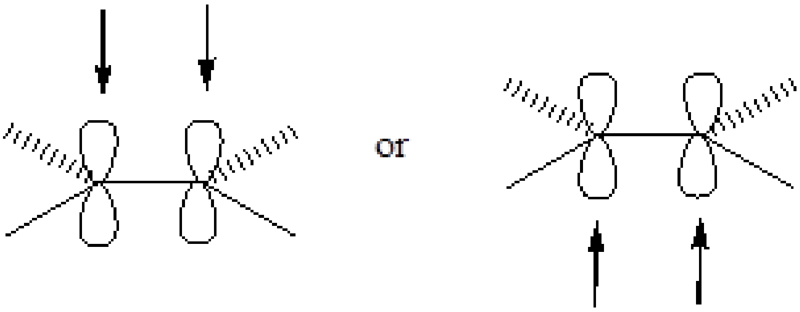

supra facical (or) supra addition

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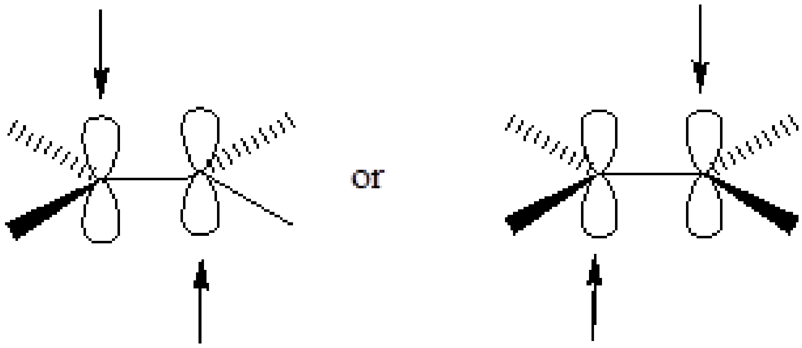


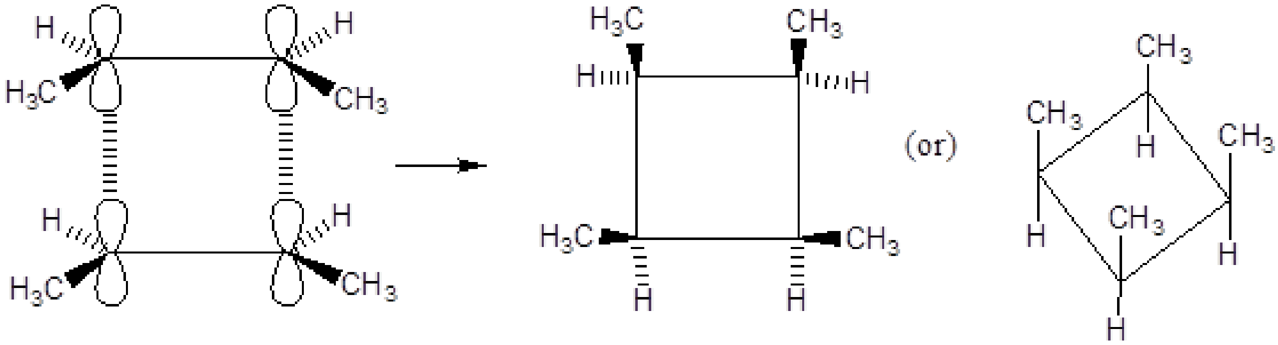
antarafacial (or) antara addition

In cycloadditions, two or more components patyicipates, therefore stereochemical mode of cycloaddition has to be specified with respect to each component. Thus in the [π2+π2] cycloadditions involving two molecule of cis-2-butene, four stereochemically different cycloadditions viz.

1. supra-supra
2. supra-antara
3. antara- supra
4. antara-antara cycloadditions are possible.

Cycloaddition Reactions with 4ne- System:

1. Supra-supra cycloaddition: [π2s+ π2s] cycloadditions



Transition state for $[\pi^2_s + \pi^2_s]$ cyclo addition

All cis 1,2,3,4-tetramethyl cyclobutane

2. Supra-antara cycloaddition: [π2s+ π2a] cycloadditions

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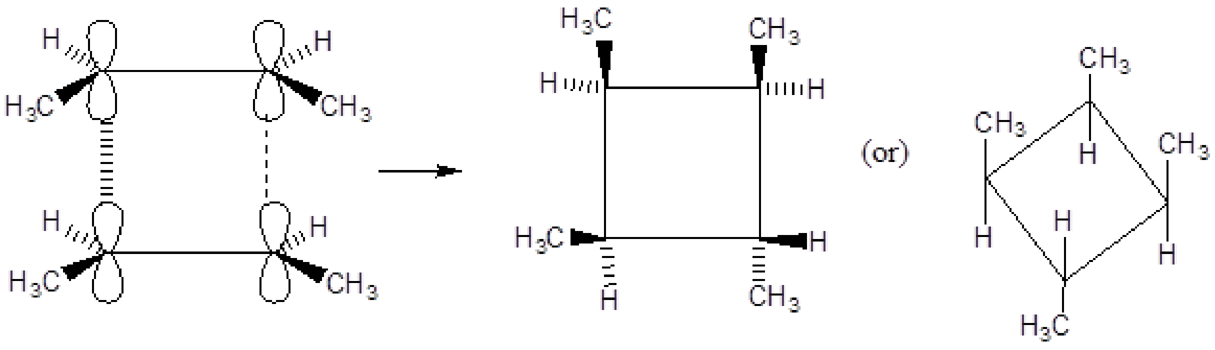
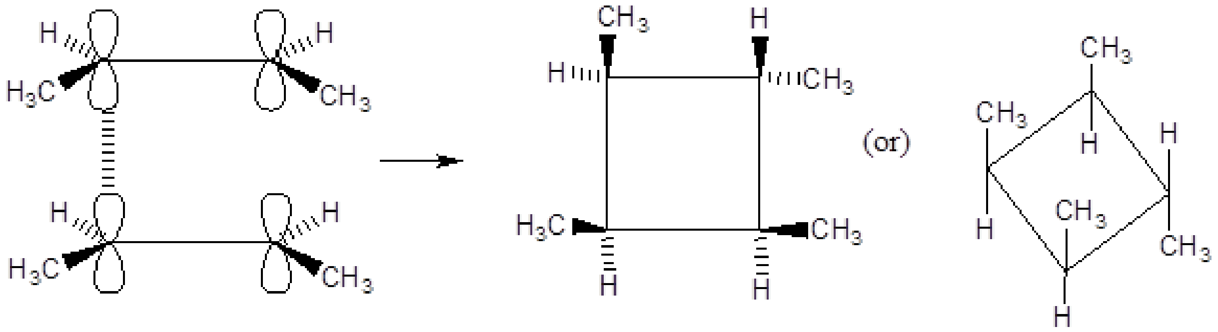


Transition state for
[$\pi^2_s + \pi^2_a$] cyclo addition

cis,cis,trans,trans 1,2,3,4-tetramethyl cyclobutane

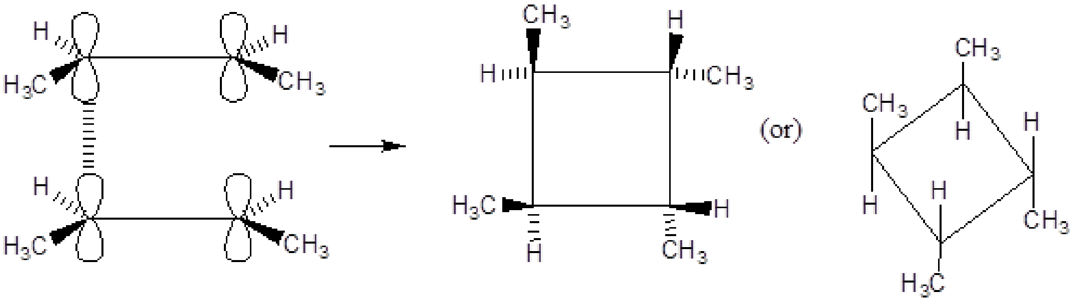
3. Antara-supra cycloaddition: [π2a+ π2s] cycloadditions



Transition state for
[$\pi^2_a + \pi^2_s$] cyclo addition

cis,cis,trans,trans 1,2,3,4-tetramethyl cyclobutane

4. Antara-antara cycloadditions: [π2a+ π2a] cycloadditions



Transition state for
[$\pi^2_a + \pi^2_a$] cyclo addition

cis,trans,cis,trans 1,2,3,4-tetramethyl cyclobutane

It can be seen from the above examples that

a) In a supra-supra cycloaddition: The stereochemistry of both the components is retained in the product.

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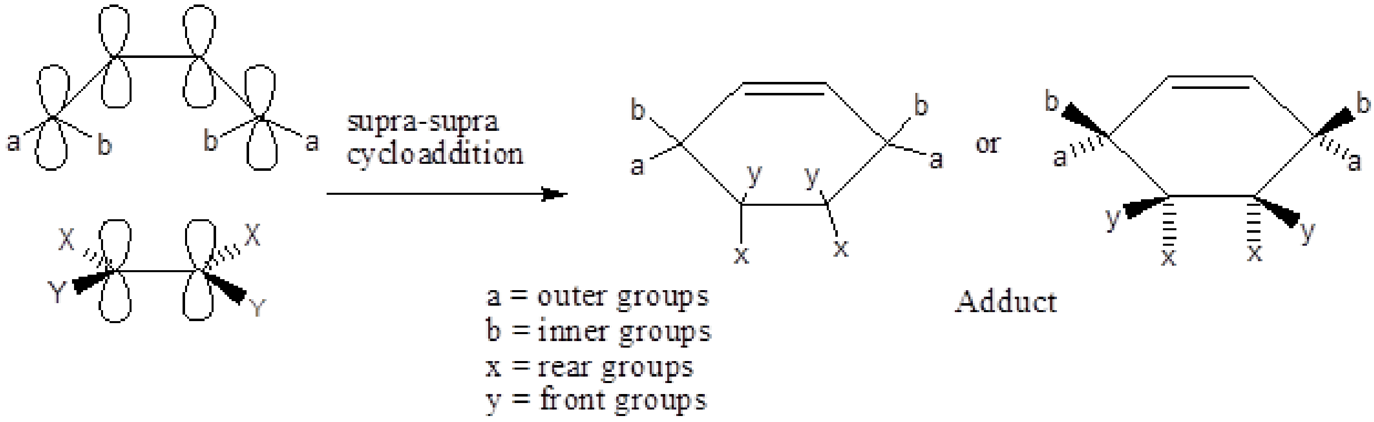
b)In a supra-antara or antara-supra cycloadditions, the stereochemistry of supra component is retained in the adduct, while that of the antara component changes at one centre in the adduct, and

c)In an antara -antara cycloaddition, the stereochemistry of each component changes at one centre in the adduct.

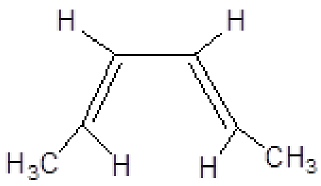
Cycloaddition Reactions with 6ne- System:

1. supra-supra cycloaddition: [π4s+ π2s] cycloadditions [Diels-Alder reaction]
The diene (4πe) and dienophile (2πe-) approach one on each other, during supra-supra cycloaddition.

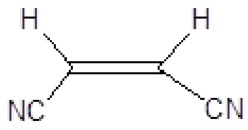


In the supra-supra cycloaddition product
(a)Two outer groups will be cis
(b) Two inner groups will be cis
(c) Two year groups will be cis
(d) Two front groups will be cis
(e) An inner group and a front group will be cis and
(f) An outer group and a rear group will be cis

Example for the cycloaddition reactions with 6ne- System is the addition of maleonitrile (dienophile) with trans,trans-2,4-hexadiene (diene) gives the adduct. Structures of diene and dienophile are as follows:

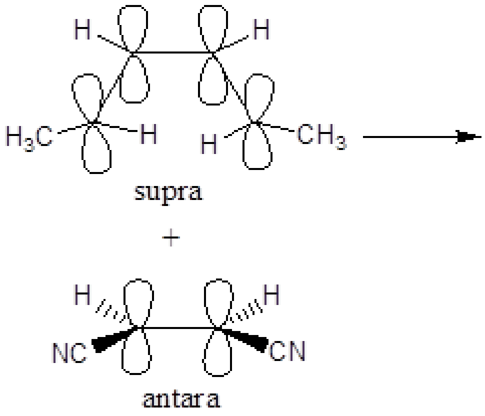


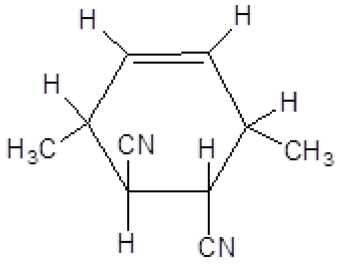
trans, trans-2,4-hexadiene



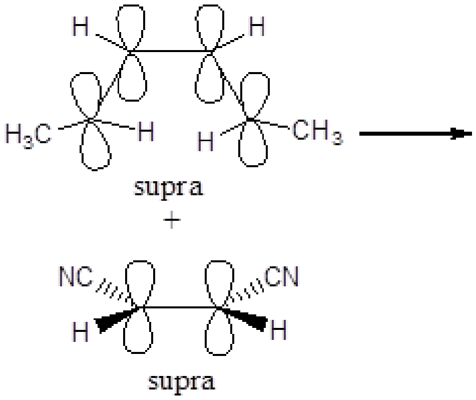
maleonitrile (dienophile)

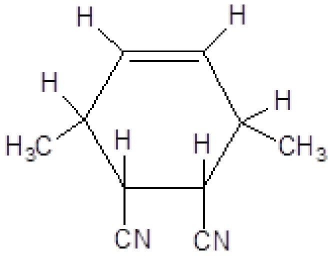
1. Supra-supra cycloaddition: [π4s+ π2s] cycloadditions





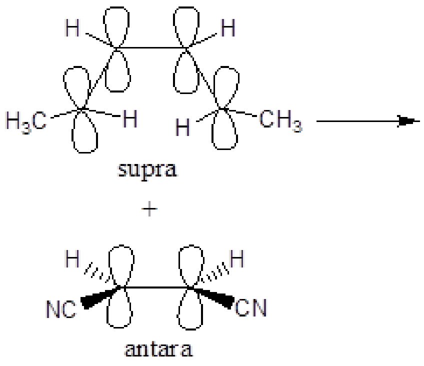
trans,trans,cis product

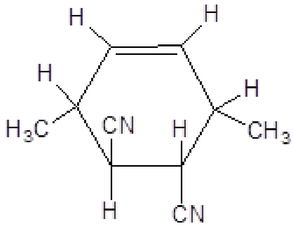




all cis product

2. Supra-antara cycloaddition: [π4s+ π2a] cycloadditions





trans,trans,cis product

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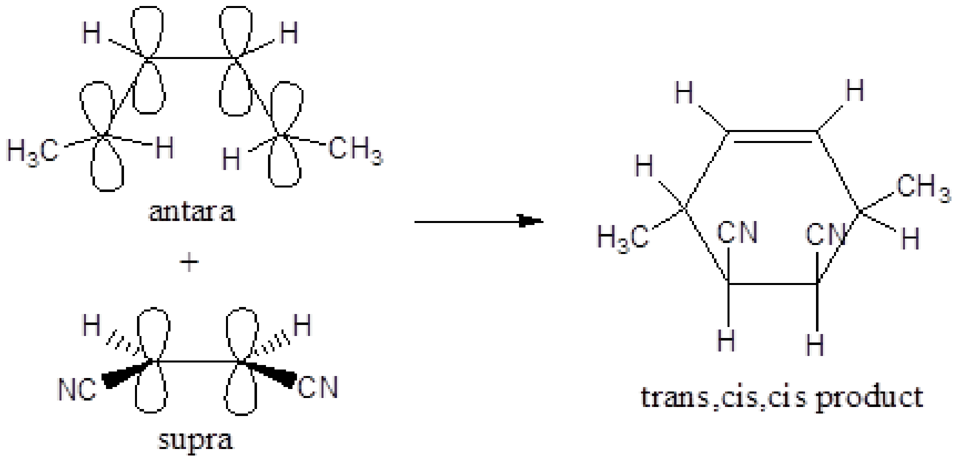
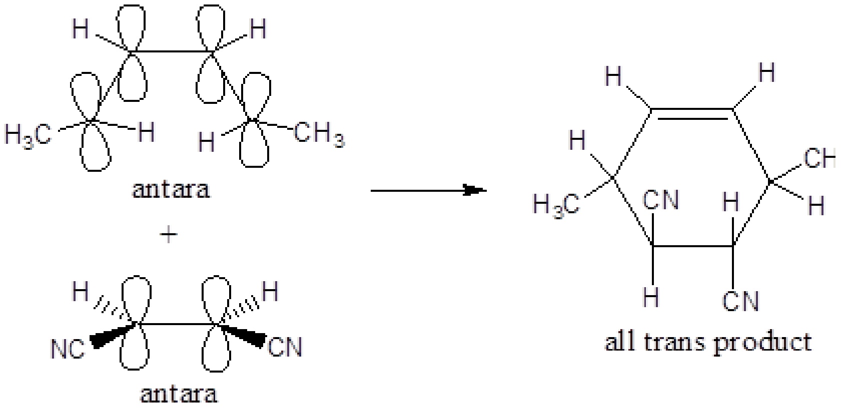
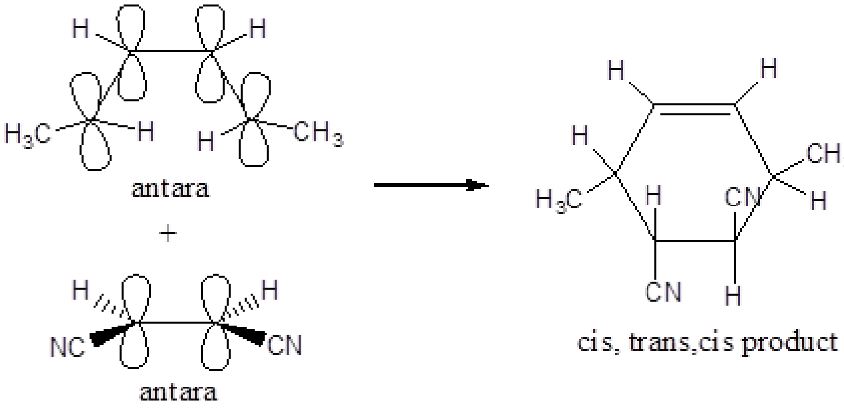
3. Antara-supra cycloaddition: [π4a+ π2s] cycloadditions



4. Antara-antara cycloadditions: [π4a+ π2a] cycloadditions





Sigmatropic reactions:

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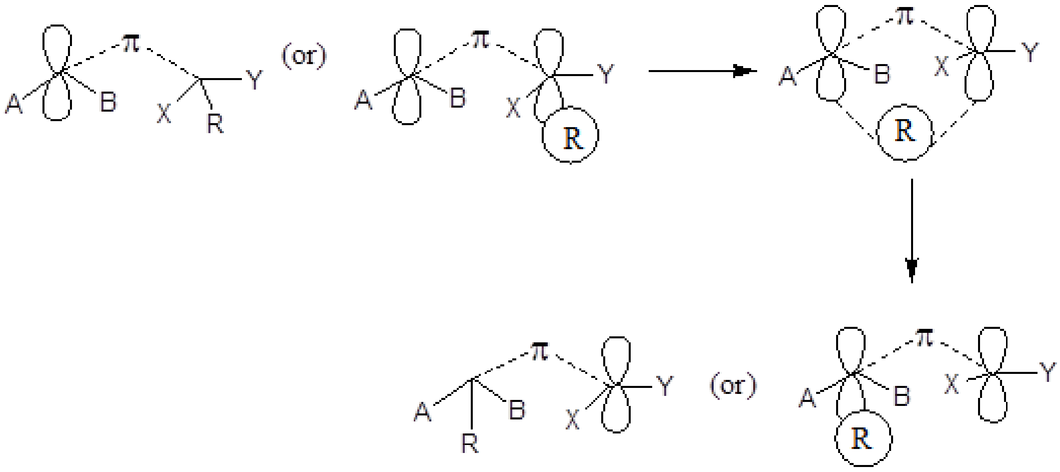
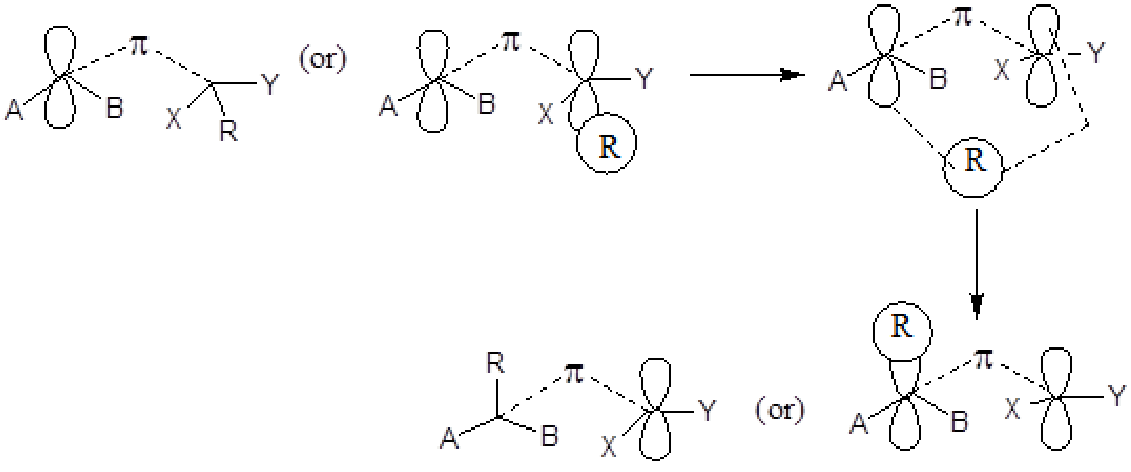
In a sigmatropic reaction, an atom or group migrates with its σ-bond across the π electron system. This may take place by two different stereochemical pathways. When the migrations of σ-bond moves across the same face or side of the π –system, it is called a suprafacial shift. On the other hand, in the antarafacial shifts the migrating σ-bond moves of the opposite are of its π-system. In general, suprafacial and antarafacial shifts can be described as follows:



(suprafacial shift of R, R= an atom or group)



(antarafacial shift of R, R= an atom or group)

In a suprafacial shift, the migrating group remain on the same side of the Õ molecule frame work through the course of reaction. In an autarafacial shift, the group is transferred from the top fare of the migration. Sourse to the bottom fare of the migration termine and vice versa. Following are the example of [1,5] suprafacial and [1,5]-autarafacial shifts of a H.

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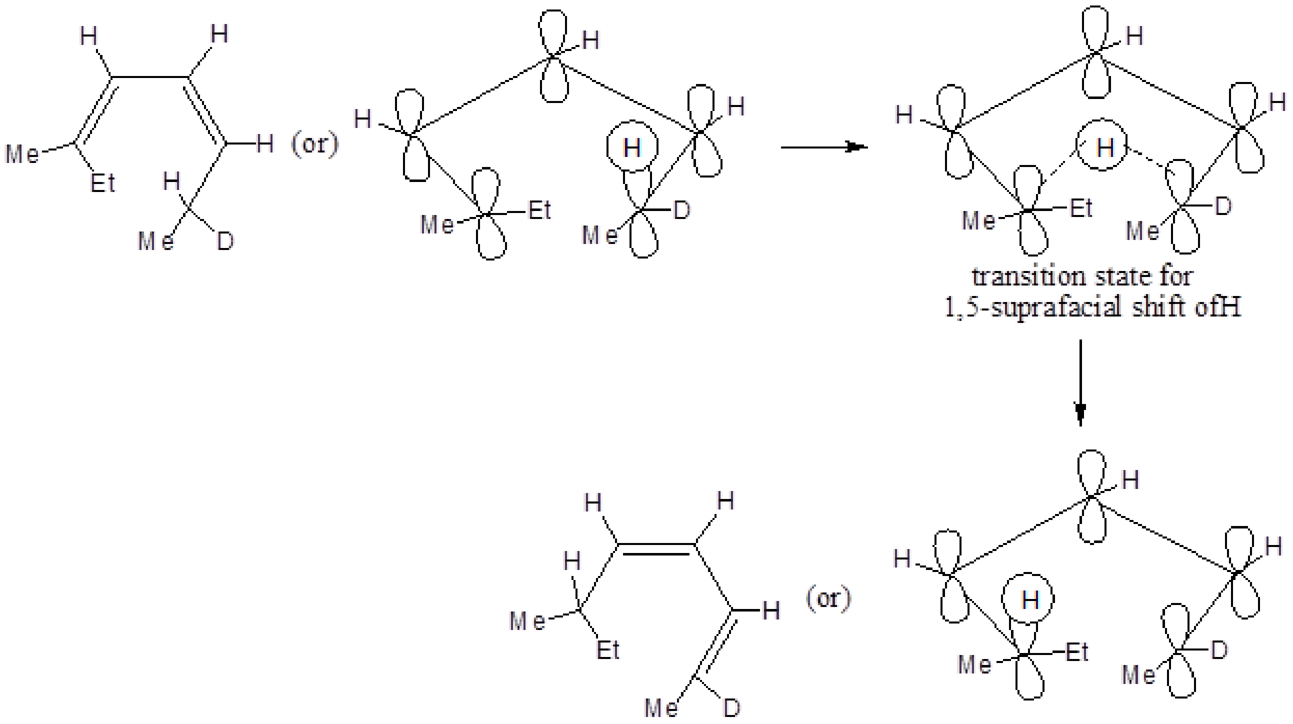
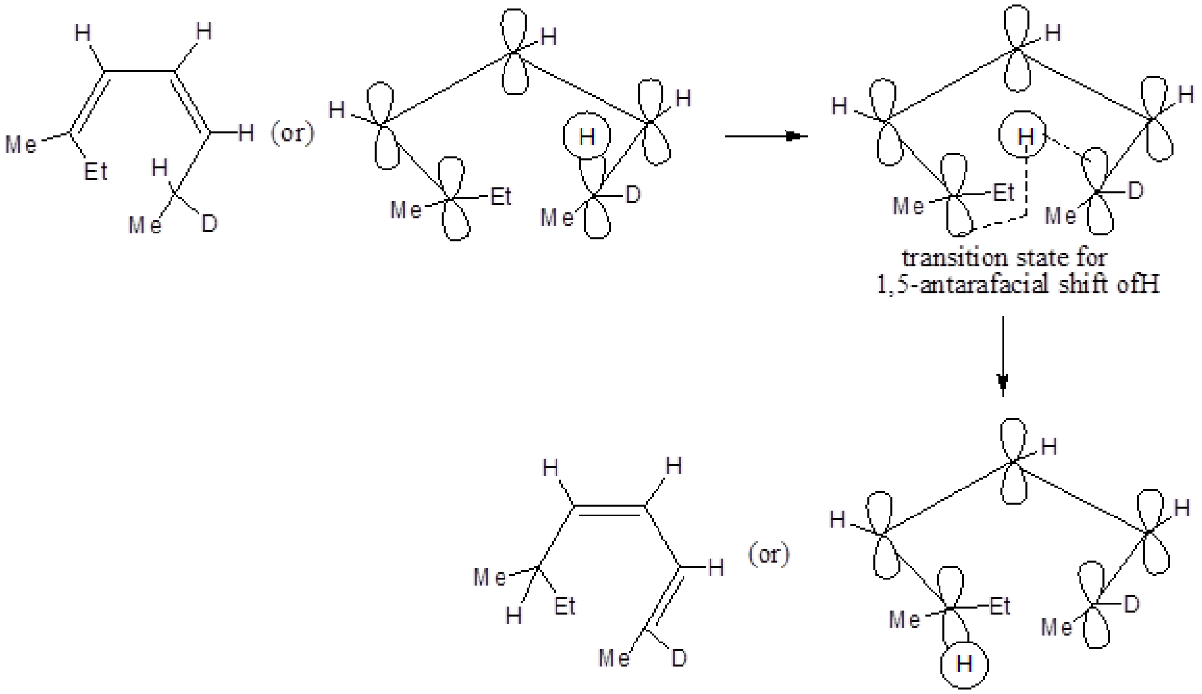
[1,5]- antarafacial shift of H:



[1,5]- antarafacial shift of H:



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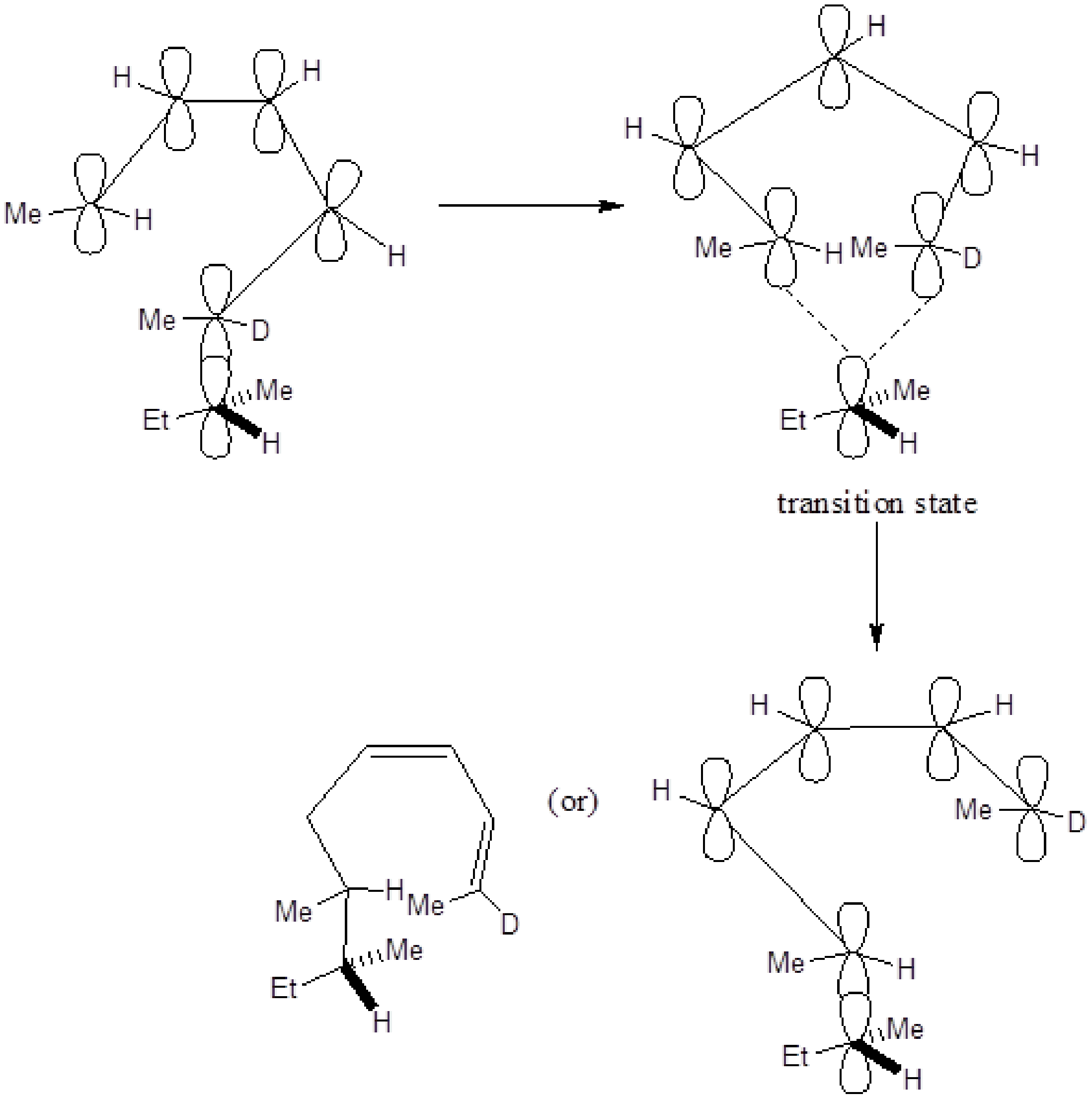
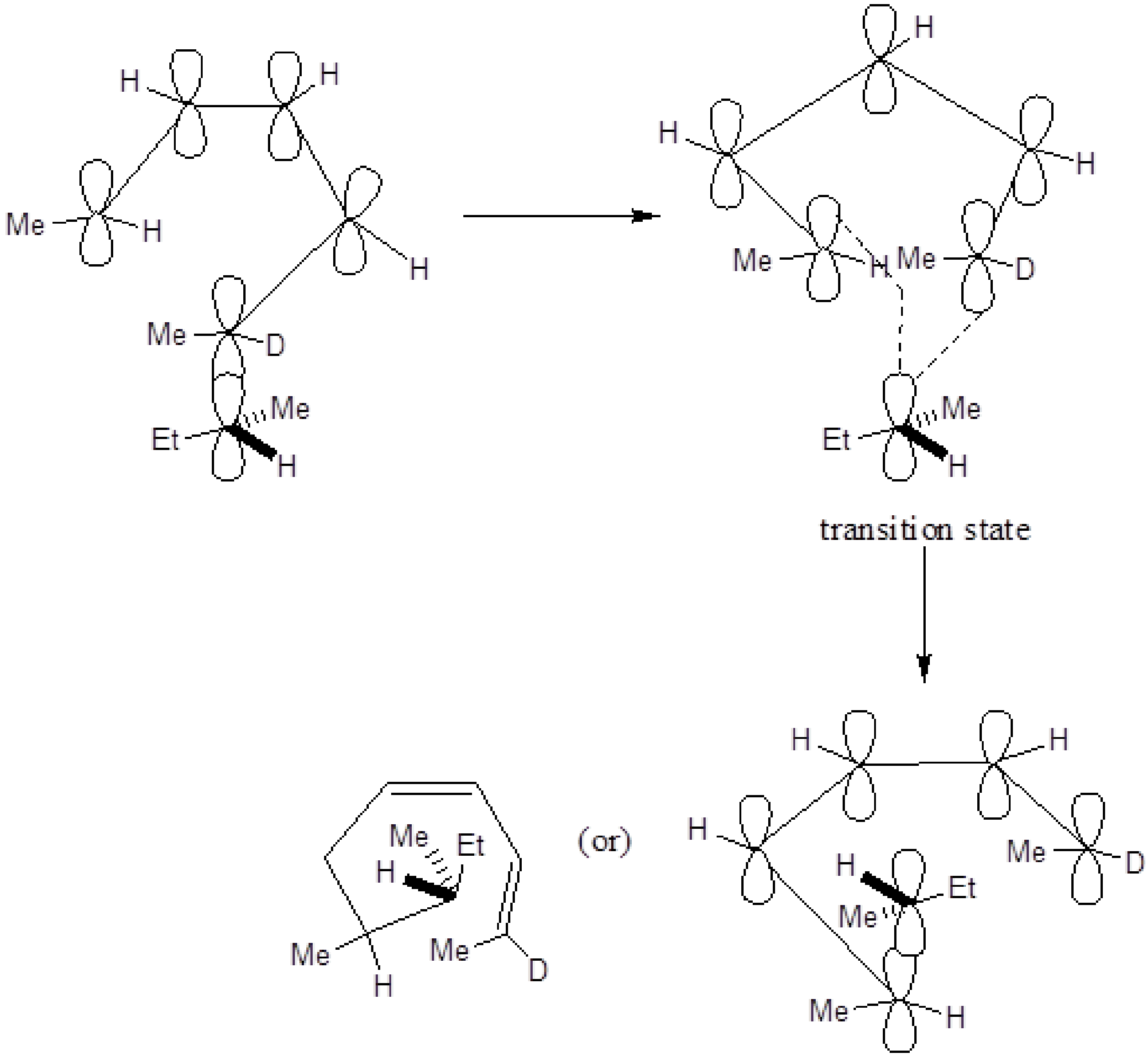
Due to steric reasons, antarafacial migrations are less common. In a lengths conjugated π-system, however, antarafacial shifts are possible. [1,7] antarafacial shift of a H can take place. When the migrating group R, is chiral,four stereochemical modes of sigmatropic shifts are possible. They are

a)Suprafacial shift of the group with retention of configuration
b)Antarafacial shift of the group with retention of configuration
c)Suprafacial shift of the group with inversion of configuration
d)Autarafacial shift of the group with inversion of configuration

a) [1,5]-suprafacial shift of the group with retention of configuration:



b) [1,5]-antarafacial shift of the group with retention of configuration:



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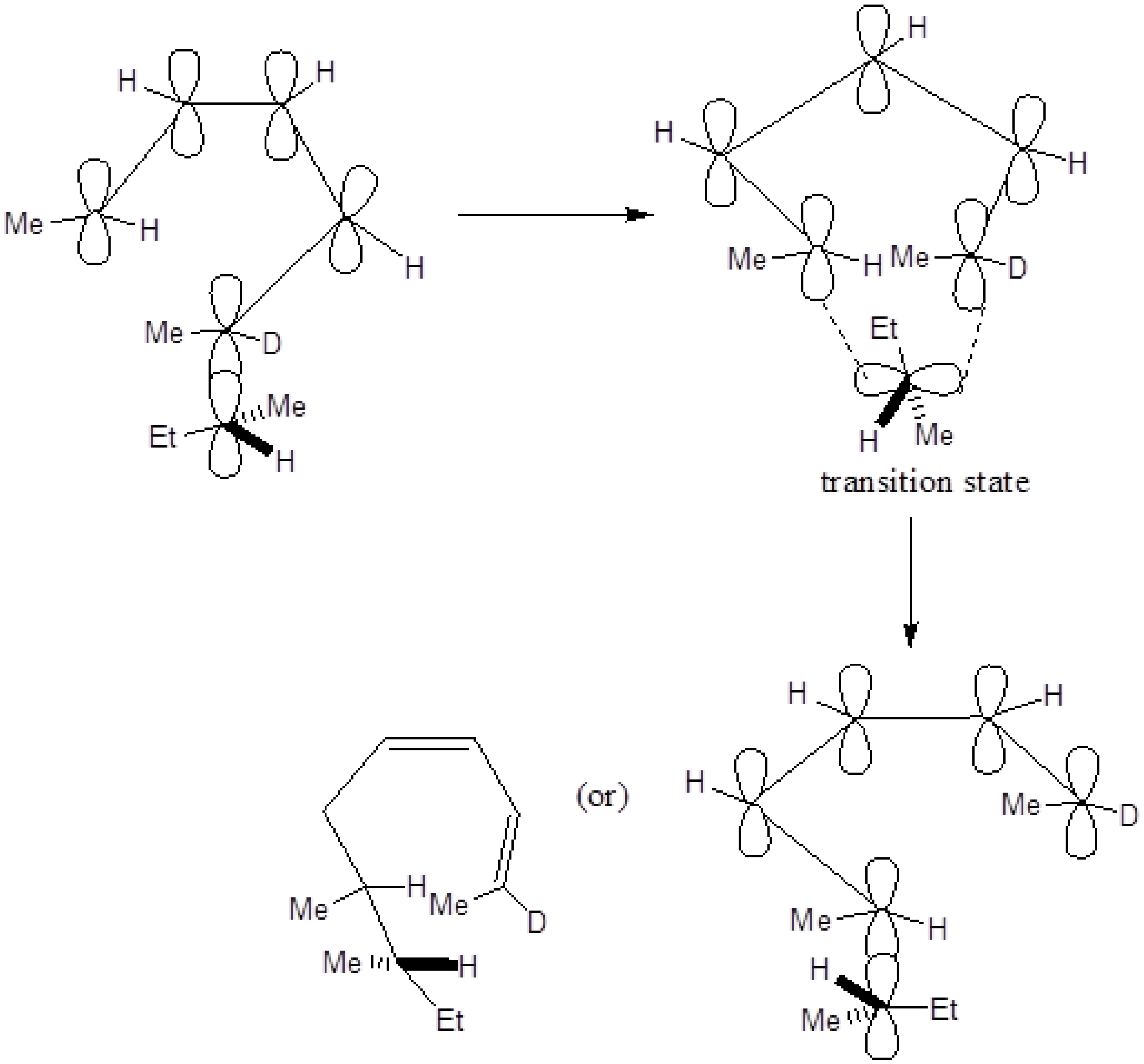
c) [1,5]- suprafacial shift of the group with inversion of configuration:



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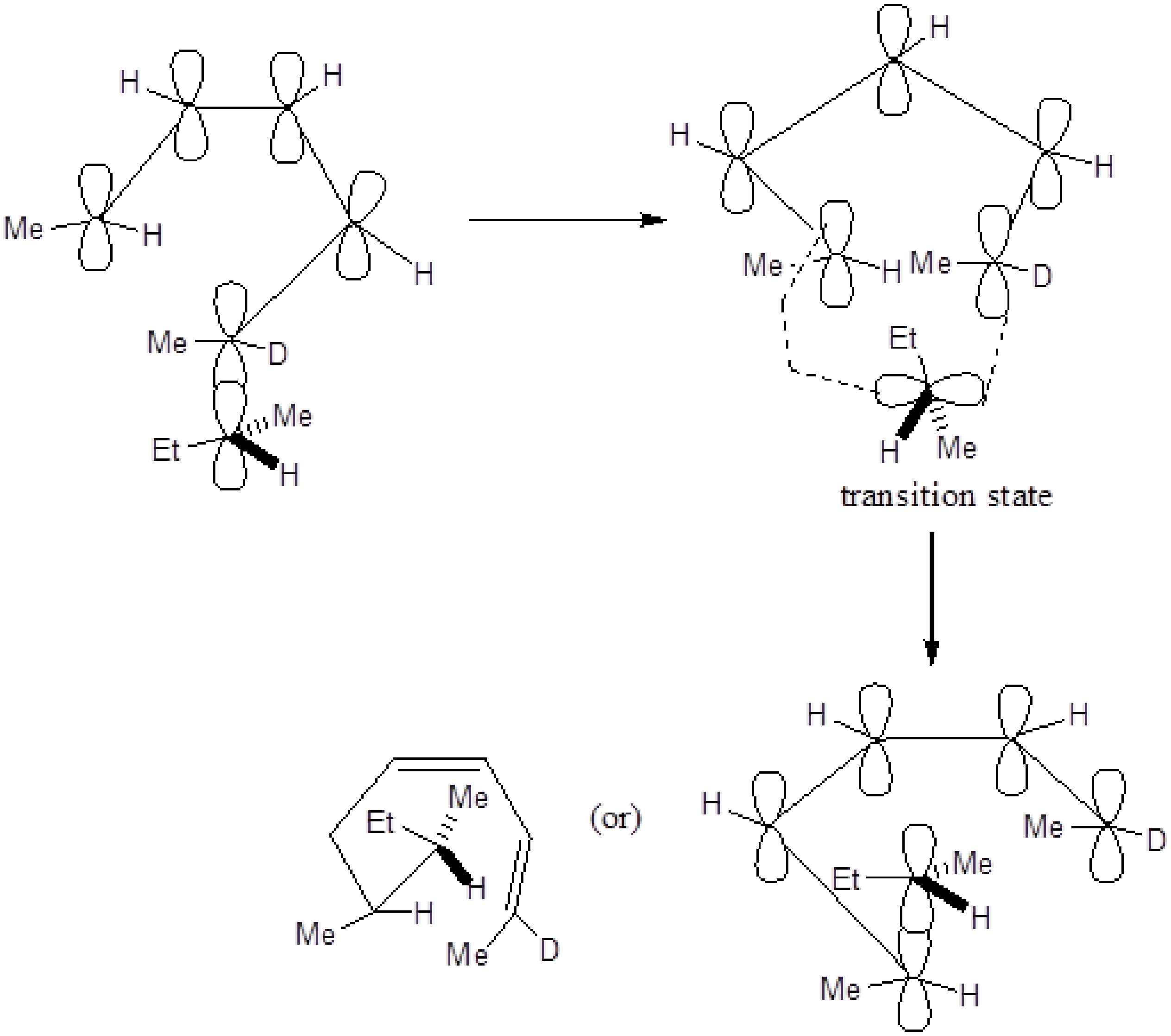
d) [1,5]-antarafacial shift of the group with inversion of configuration:



Molecular orbitals and their symmetry

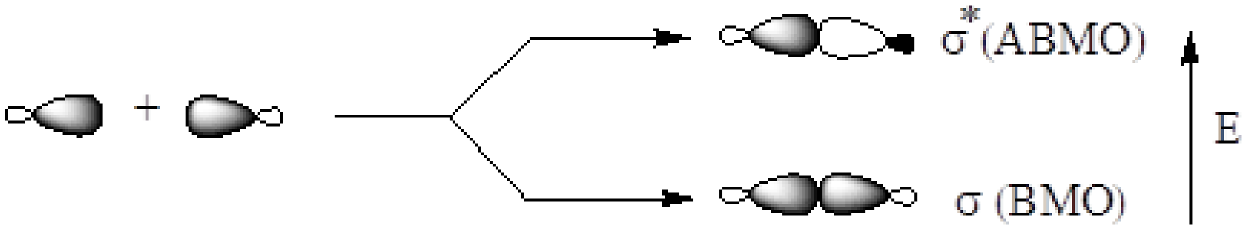
The stereochemistry of pericyclic reactions can be analysed by three methods viz

- **Perturbation molecular orbital**
- **Frontier molecular orbital method and**
- **Orbital symmetry correlation diagram method**

For understanding the above methods, we require knowledge of the molecular orbitals of an σ bond, π bond and conjugated π systems and their symmetry properties.

Molecular orbitals of carbon-carbon single bond or σ bond:

Overlap of two atomic orbitals or linear combination of atomic orbitals (LCAO) produces two molecular orbitals. One of these is bonding molecular orbitals (BMO) and the other is anti bonding molecular orbitals (ABMO).



Bonding molecular orbitals BMO is more stable because of its low energy and anti bonding molecular orbitals ABMO is less stable because of its high energy compared to the atomic orbitals. The energy of a molecular orbitals increases with increasing number of nodes. In anti bonding molecular orbital (σ*) there is a one node. On the other hand there is no node in bonding molecular orbital (σ). Thus bonding molecular orbital is more stable than anti bonding molecular orbitals.

The electrons are accommodated in bonding molecular orbital whereas anti bonding molecular orbital is vacant. Thus the ground state configuration of C-C σ bond is σ2 σ*. The absorption of light of suitable wave length (about 154mm) promotes an electron from σ molecular orbital to σ* molecular orbital.

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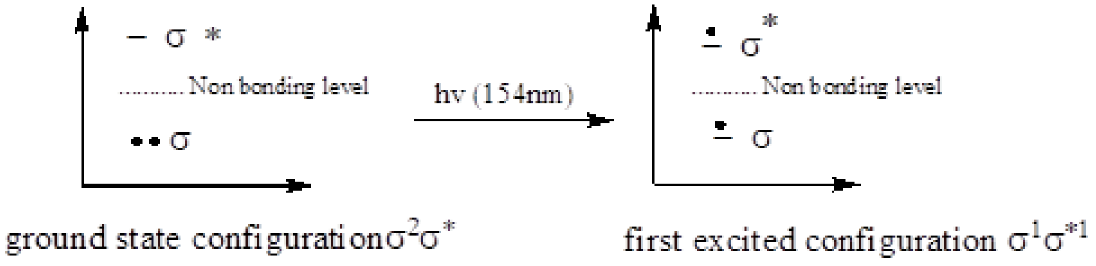
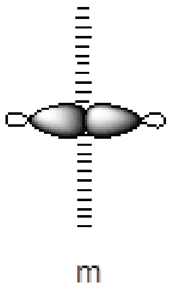
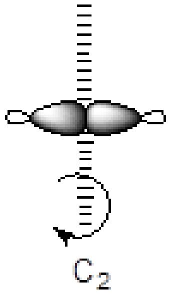
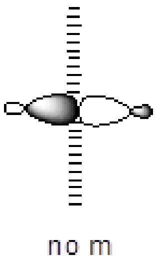


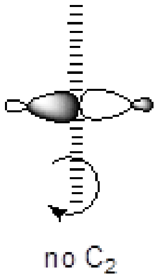
The bonding molecular orbital (σ) has mirror plane symmetry (m) and it is also symmetric (S) with respect to principle axis of symmetry (C2).





The anti bonding molecular orbitals (σ*)is antisymmetric (A) with respect to both mirror plane symmetry (m) and principle axis of symmetry (C2).



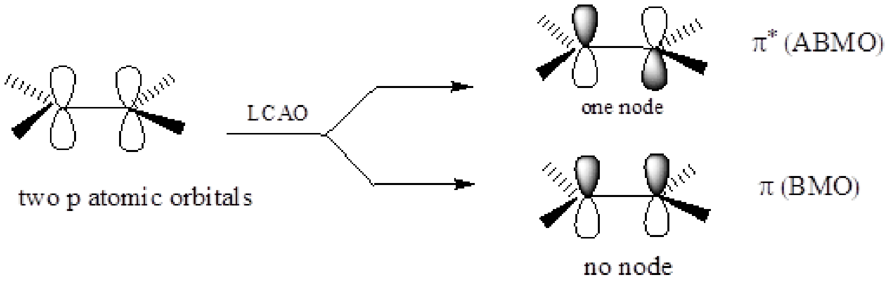


The symmetry properties of the bonding molecular orbitals and anti bonding molecular orbitals can be summarized as follows:

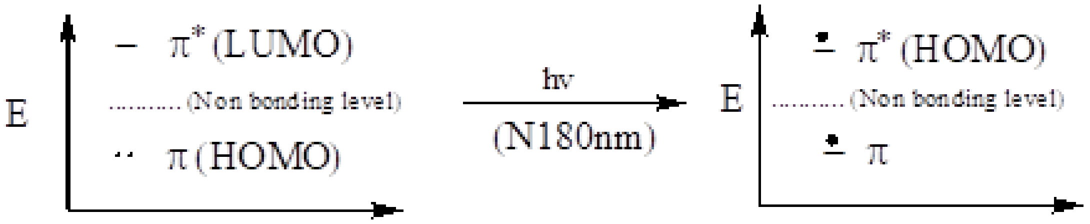
Molecular orbitals	m-symmetry	C2-symmetry
*	**A**	**A**
	S	**S**

Molecular orbitals of carbon – carbon double bond or π bond:

Molecular orbitals of a π -bond (multiple bond) are also known as π molecular orbitals. Linear combination of atomic orbitals (LCAO) of two p-atomic orbitals in ethylene produces the bonding atomic orbitals (π) and anti bonding molecular orbitals (π*) molecular orbitals. Bonding molecular orbitals (π) with zero or no nodes and is anti-bonding molecular orbital (π*) with one nodes.



The two p electrons are accommodated in bonding molecular orbital (π) whereas the anti bonding molecular orbital (π*) is vacant. Thus the ground state configuration of a carbon carbon double-bond is π2π*0. Upon absorption of light (N180nm) an electron from bonding molecular orbital (π) is promoted to anti bonding molecular orbital (π*) that is π-π* transition takes place, producing first excited state of carbon-carbon double bonds. Thus the first excited state configuration of a carbon carbon double-bond is π1π*1.

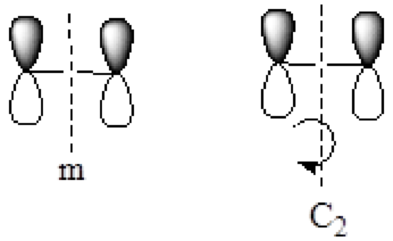


ground state πe^- configuration of $C = C$ is $\pi^2\pi^{*0}$

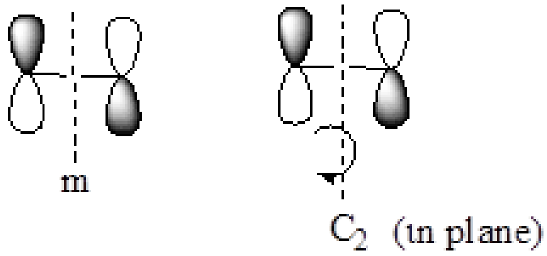
first excited state πe^- configuration of $C = C\pi^1\pi^{*1}$

In the ground state, the highest occupied molecular orbital (HOMO) π, and the lowest unoccupied molecular orbital (LUMO) is π* .On the other hand in the first excited state HOMO is π* is no LUMO in the first excited state.

The bonding molecular orbital is symmetric (s) with respect to mirror plane symmetry (m) and anti symmetric (A) with respect to principal axis of symmetry (C2).



On the other hand, the anti bonding molecular orbital (π*) is antisymmetric (A) with respect to the mirror plane symmetry (m), and symmetric (s) with respect to the Principal axis of symmetry (C2).



Molecular orbitals	m-symmetry	C2-symmetry
π*	A	S
π	S	A

π - Molecular orbitals of conjugated π-systems:

The number, symmetry, stability and electron distribution in the molecular orbitals of an acyclic conjugated π-system are summarized below:

1. Linear combination of atomic orbitals (LCAO) of n-p atomic orbitals produced nπ molecular orbitals.

2. When n=even number, n/2 are bonding molecular orbitals (BMO) and n/2 are anti bonding molecular orbital (ABMO).

3. When n=odd number, (n-1)/2 will be bonding molecular orbitals (BMO), (n-1)/2 are anti bonding molecular orbital (ABMO), and one is non bonding molecular orbital (NBMO). NBMO is of same energy as that of p atomic orbitals.

4. Molecular orbitals are designated as ψ1, ψ2, ψ3.... ψn in order of increasing energy.

5. In ψn molecular orbital, there will be (n-1) nodes.

6. ψn with n = odd number, will be symmetric with respect to mirror plane symmetry (m) and anti symmetric with respect to principal axis of symmetry (C2).

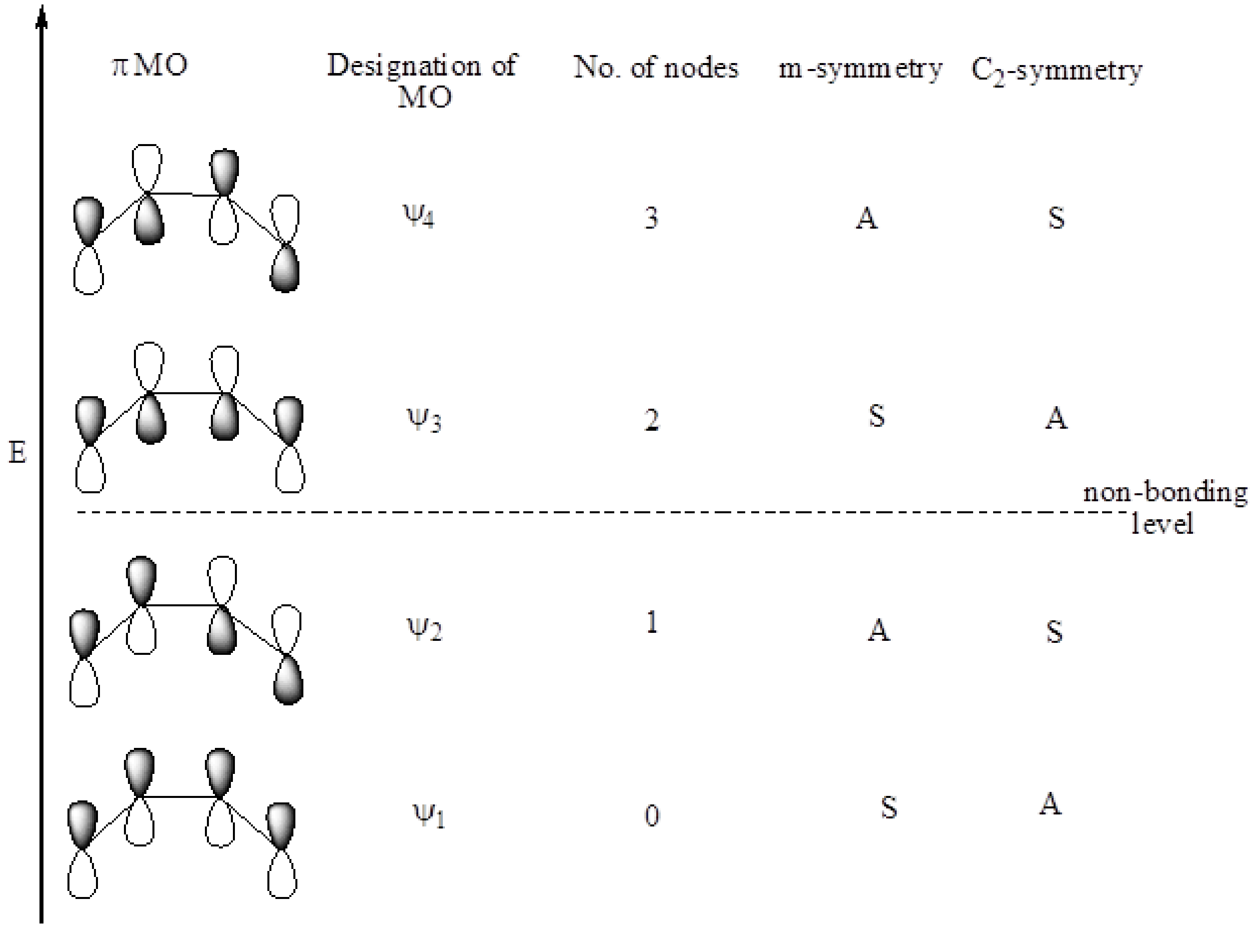
7. When n = even number, ψn will be anti symmetric with respect to mirror plane symmetry (m) and symmetric with respect to principal axis of symmetry (C2).

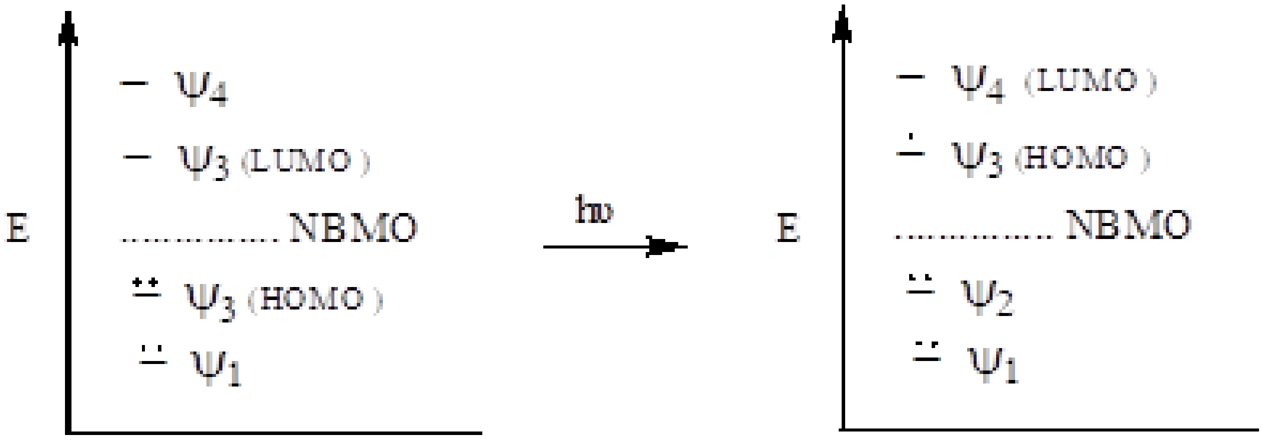
8. **The ground state (GS) is converted to first excited state (FES) by promotion of an electron from bonding molecular orbital of highest energy to anti bonding molecular orbital of least energy.**

9. **Occupied molecular orbital of highest energy is called highest occupied molecular orbital (HOMO) and unoccupied (vacant) molecular orbital of lowest energy is called lowest unoccupied molecular orbital (LUMO).**

1.π- Molecular orbitals of 1,3-butadiene:

This conjugated diene system consists of four p orbitals and four p electrons. Linear combination of four p atomic orbitals gives four πmolecular orbitals ψ1, ψ2, ψ3and ψ4 in order of increasing energy.





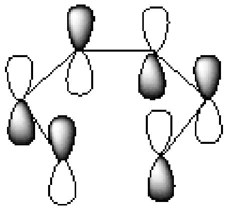
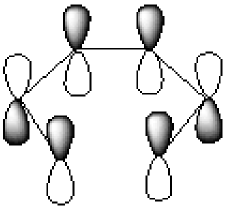
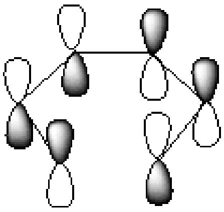
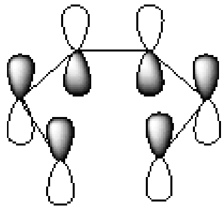
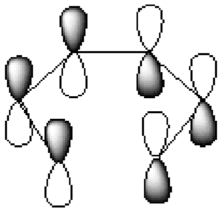
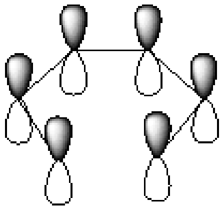
ψ1 and ψ2 are bonding molecular orbitals and ψ3and ψ4 are anti bonding molecular orbitals. In the ground state, the four πe- are accommodated in ψ1 and ψ2 whereas ψ3and ψ4 are empty. The πe- configuration in the ground state is ψ12ψ22ψ30ψ40.

Therefore HOMO and LUMO in the ground state of butadiene are ψ2 and ψ3 respectively. First excited state obtained from the ground state by promotion of the electron from ψ2 to ψ3. The πe- configuration in the first excited state (FES) is ψ12ψ21ψ31ψ40. The HOMO and LUMO in the FES of butadiene are ψ3 and ψ4 respectively.

2. **π - Molecular orbitals of 1,3,5-hexatriene:**

There are three conjugated double bonds in the molecule that is six p atomic orbitals and six πe-. The six p atomic orbitals on linear combination gives six π molecular orbitals ψ1, ψ2, ψ3, ψ4, ψ5 and ψ6.

E

π MO	Designation of MO	No. of nodes	m-symmetry	C_2-symmetry
	ψ_6	5	A	S
	ψ_5	4	S	A
	ψ_4	3	A	S
	ψ_3	2	S	A
	ψ_2	1	A	S
	ψ_1	0	S	A

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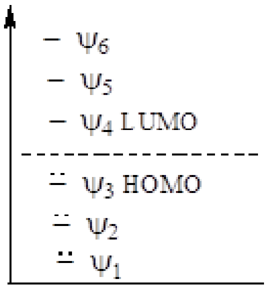
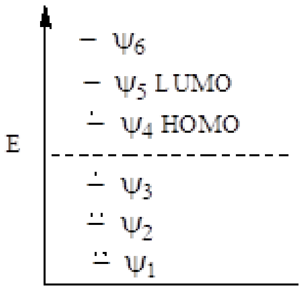


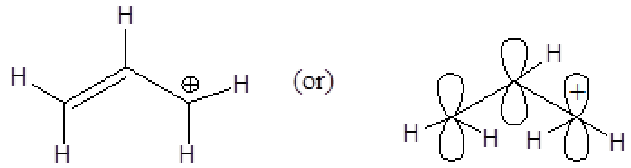
πe⁻ configuration of 1,3,5 - butadiene in GS is $\psi_1^2\psi_2^2\psi_3^2\psi_4^0\psi_5^0\psi_6^0$



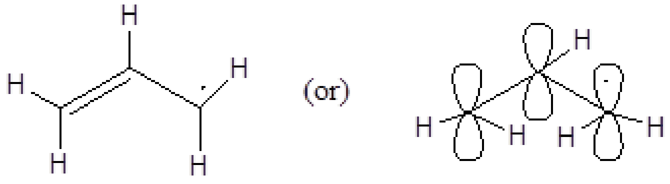
πe⁻ configuration of 1,3,5 - butadiene in FES $\psi_1^2\psi_2^2\psi_3^1\psi_4^1\psi_5^0\psi_6^0$

3. π-Molecular orbital of conjugated system with odd number of p atomic orbitals:
In this category, we have to study about the carbocations, free radicals and carbanions belong to this group of π-systems.

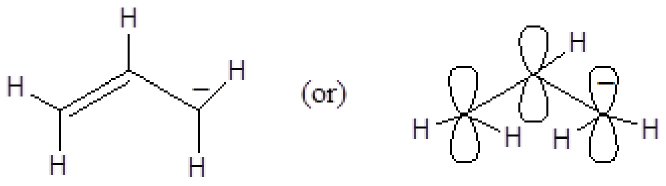
a) Allylic system (CH2-CH-CH2-)



allyl carbocation (3 atomic orbitals, 2 pe⁻)



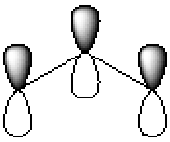
allyl free radical (3 atomic orbitals, 3 pe⁻)



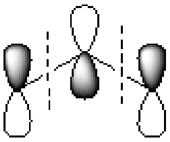
allyl carbanion (3 atomic orbitals, 4 pe⁻)

Linear combination of three p atomic orbitals of an allyl system gives the three molecular orbitals ψ1, ψ2 and ψ3. ψ1 is bonding molecular orbital (BMO), in which no nodes are present. ψ1

is nonbonding molecular orbital (NBMO), in which one node is present. ψ3 is anti bonding molecular orbital (ABMO), in which two nodes are present.

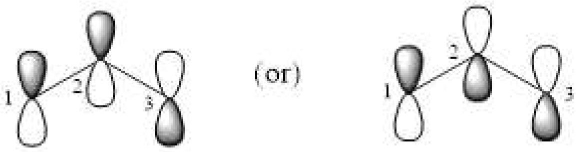


ψ_1 (BMO)

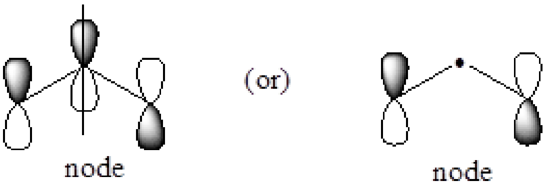


ψ_3 (ABMO) 2 nodes

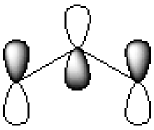
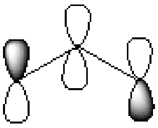
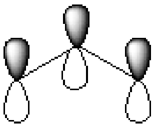
The node of ψ2 nonbonding molecular orbital (NBMO) can be shown between C2 and C3 or C1 and C2 that is either side of the C2. In other words the sign of wave function changes on either side of C2.



Therefore ψ2 is depicted with a node located at C2



The stabilities and symmetry properties of the π molecular orbitals of an allyl system are as following:

πMO	Designation of MO	No. of nodes	m-symmetry	C_2-symmetry
	ψ_3	2	S	A
	ψ_2	1	A	S
	ψ_1	0	S	A

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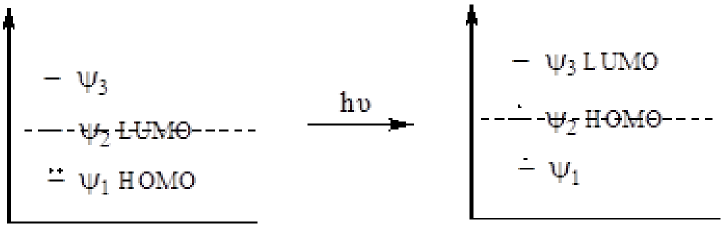
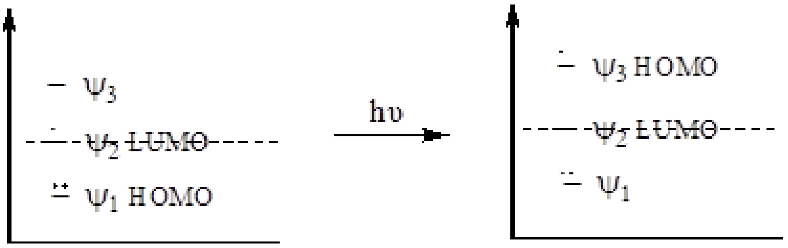
Allyl carbocation (CH=CH-CH2+-):



πe⁻ configuration in GS
$\psi_1^2\psi_2^0\psi_3^0$

πe⁻ configuration in FES
$\psi_1^1\psi_2^1\psi_3^0$

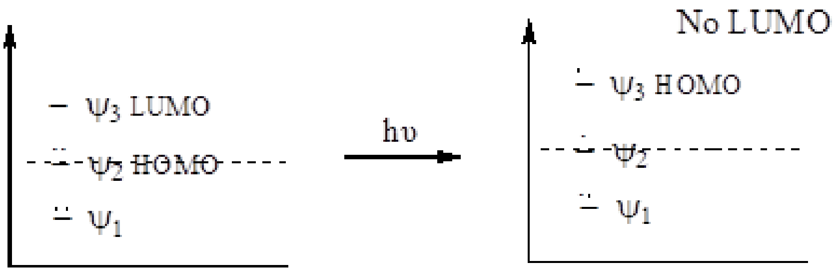
Allyl free radical (CH=CH-CH2-):



πe⁻ configuration in GS
$\psi_1^2\psi_2^1\psi_3^0$

πe⁻ configuration in FES
$\psi_1^2\psi_2^0\psi_3^1$

Allyl carbanion (CH=CH-CH2--):



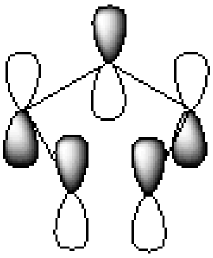
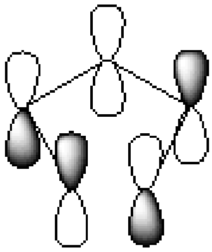
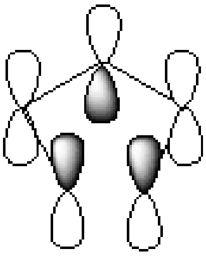
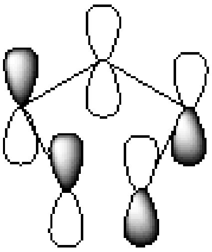
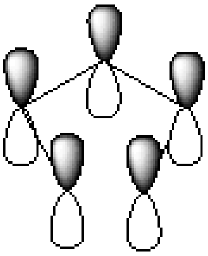
πe⁻ configuration in GS
$\psi_1^2\psi_2^1\psi_3^0$

πe⁻ configuration in FES
$\psi_1^2\psi_2^0\psi_3^1$

a)π-Molecular orbitals of 2, 4-pentadienyl system:

In 2, 4-pentadienyl system, there are five p atomic orbitals. Linear combination of atomic orbitals (LCAO) generates five π molecular orbitals namely,ψ1, ψ2, ψ3, ψ4, andψ5. Out of these ψ3

is nonbonding molecular orbital (NBMO), ψ1and ψ2 are bonding molecular orbital (BMO), ψ4 and ψ5 are antibonding molecular orbital (ABMO).

πMO	Designation of MO	No. of nodes	m-symmetry	C_2-symmetry
	ψ_5	4	S	A
	ψ_4	3	A	S
	ψ_3	2	S	A
	ψ_2	1	A	S
	ψ_1	0	S	A

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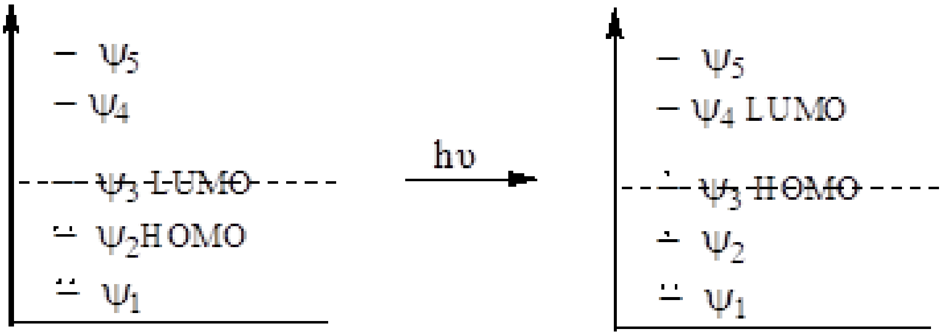
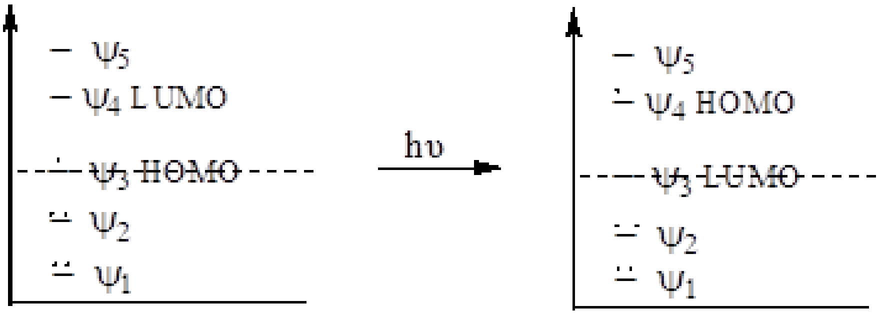
i) 2,4 – pentadienyl carbocation:



πe^- configuration in GS is $\psi_1^2\psi_2^2\psi_3^0\psi_4^0\psi_5^0$

πe^- configuration in FES is $\psi_1^2\psi_2^1\psi_3^1\psi_4^0\psi_5^0$

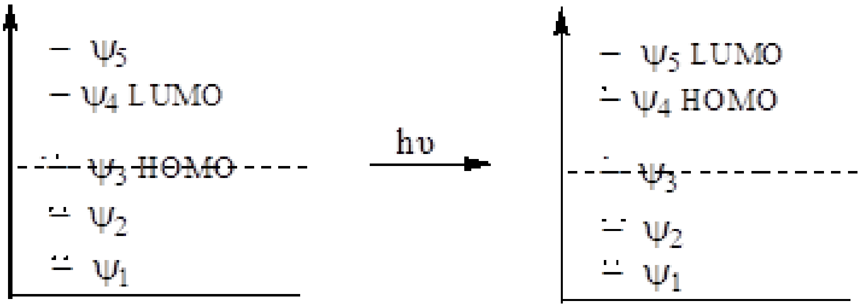
ii) 2,4-pentadienyl free radical:



πe^- configuration in GS is $\psi_1^2\psi_2^2\psi_3^1\psi_4^0\psi_5^0$

πe^- configuration in FES is $\psi_1^2\psi_2^2\psi_3^0\psi_4^1\psi_5^0$

c) 2,4-pentadienyl carbanion:



πe^- configuration in GS is $\psi_1^2\psi_2^2\psi_3^2\psi_4^0\psi_5^0$

πe^- configuration in FES is $\psi_1^2\psi_2^2\psi_3^1\psi_4^1\psi_5^0$

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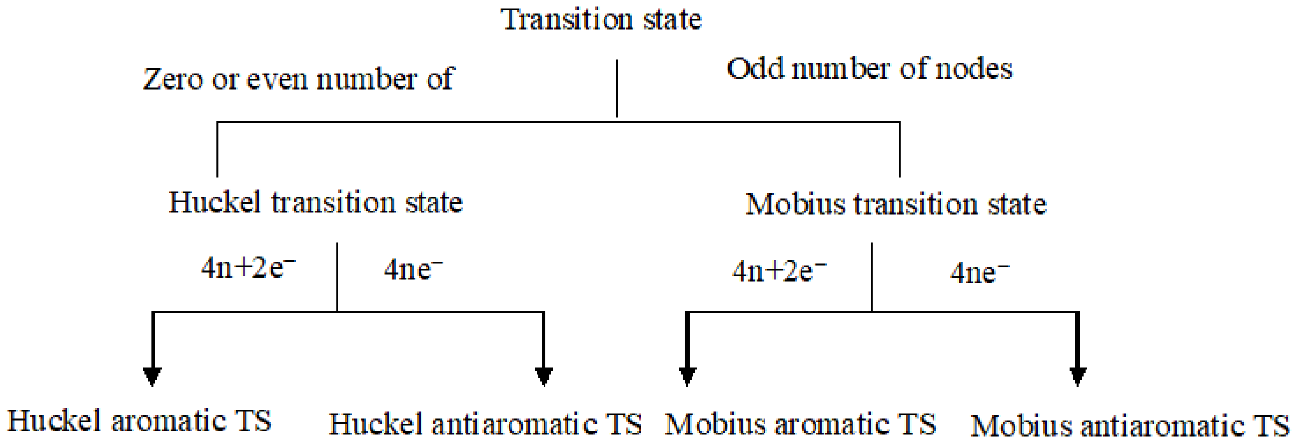
Mechanism of Pericyclic Reactions

The approaches for the interpretation of the stereochemistry of the pericyclic reactions of 4ne- and (4n+2)e- systems under thermal and photochemical conditions by
a)Perturbational Molecular Orbital (PMO) method or Aromatic Transition (ATS) method
b)Frontier Molecular Orbital (FMO) Method and
c)Orbital Symmetry Correlation Diagram Method

A. Perturbational Molecular Orbital (PMO) method:

This is also known as aromatic and antiaromatic transition state method (ATS). This concept was developed by M.G Evans and MJS. Dewar. In this simple method, the transition state of a pericyclic reaction is classified as aromatic and antiaromatic on the basis of number of nodes and the electrons participating in the transition state. A transition state with zero or even number of nodes is called Huckel transition state (HTS) with (4n+2)e-; n, is an integer is called Huckel aromatic transition state. On the other hand, Huckel transition state with 4ne- is called Huckel antiaromatic transition state. A transition state with odd number of nodes is known as Mobius or anti-Huckel transition state. Mobius transition state with 4ne- is called Mobius aromatic transition state. Mobius transition state with (4n+2)e- is called Mobius anti aromatic transition state.



According to Evans and Dewar's rules, the pericyclic reaction taking place through an aromatic transition state (Huckel or Mobius) have lower activation energy and are allowed under thermal conditions whereas forbidden photochemically. On the other hand, photochemical pericyclic

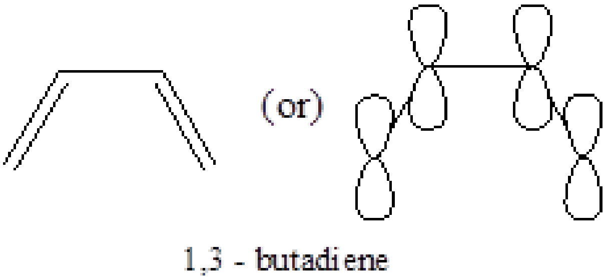
reactions are associated with higher energy of activation and involve excited form of an antiaromatic transition state. These reactions are photochemically allowed reactions and are forbidden under thermal conditions.

To predict the allowed reaction conditions for an electrocyclic reactions by PMO method
i. Show the transition state as a cyclic array of atomic orbital undergoing change through CON or Dis electrocyclisation.
ii. Assign the signs to the wave function in the best manner for overlap.
iii. Count the number of nodes in the transition state.
iv. Count the number of electrons participating in the transition state.
v. Classify the transition state as aromatic or anti aromatic and
vi. Predict the reaction conditions for that stereochemical mode of electrocyclisation.

I. Electrocyclic reactions of 4nπe- system:

The reaction may involve conrotatory or Disrotatory electrocyclic ring closure or ring opening.

a) CON electrocyclic ring closure of a 1,3-butadiene



Four πe- participate in the ring closure. The ring closure of 1,3-butadiene can take place by two conrotatory processes.

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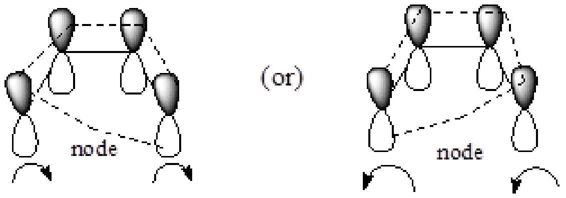
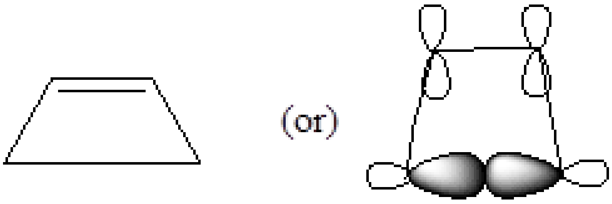


transition state for CON electrocyclic ring closure
one node
$4\pi e^-$ or $4n\pi e^-$ (n=1)
Mobius aromatic transition state

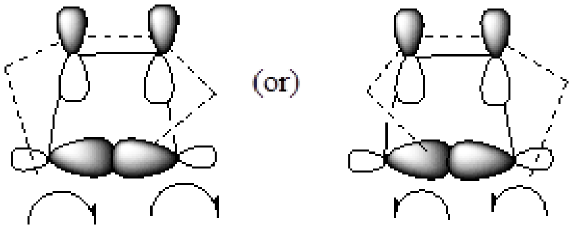
CON electrocyclic ring closure of a 1,3-butadiene is thermally allowed and photochemically forbidden.

b**)** **CON electrocyclic ring opening of cyclobutene**



cyclobutene

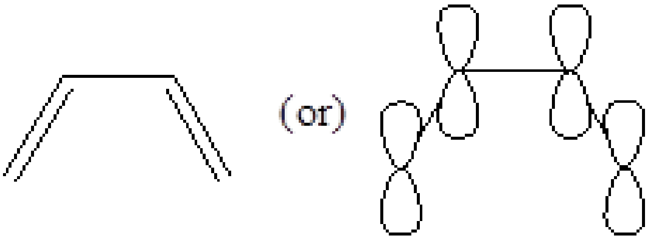
Four electrons (2πe- and 2σe-) participate in the ring opening. The ring opening of cyclobutene may involve two conrotatory processes.



transition state for CON electrocyclic ring opening
one node
$4e^-$ or $4ne^-$(n=1)
Mobius aromatic transition state

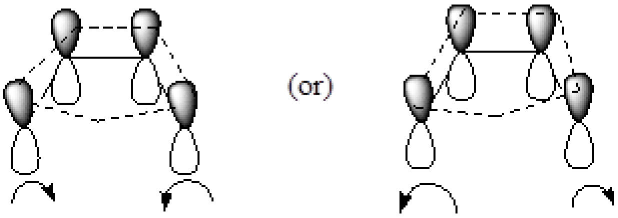
CON electrocyclic ring opening of a cyclobutene is thermally allowed and photochemically forbidden.

c) DIS electrocyclic ring closure of a 1,3-butadiene:



1,3 - butadiene

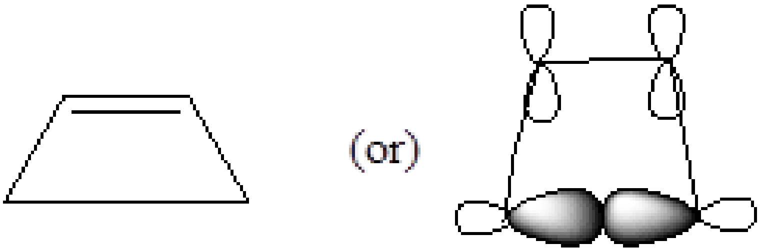
Four πe- participate in the ring closure. The ring closure of 1,3-butadiene can take place by two disrotatory processes.



transition state for DIS electrocyclic ring closure
zero nodes
$4\pi e^-$ or $4n\pi e^-$ (n=1)
Huckel anti aromatic transition state

Dis electrocyclic ring closure of a 1,3-butadiene is photochemically allowed and thermally forbidden.

d**) DIS electrocyclic ring opening of a cyclobutene.**



cyclobutene

Four electrons (2πe- and 2σe-) participate in the ring opening. The ring opening of cyclobutene may involve two disrotatory processes.

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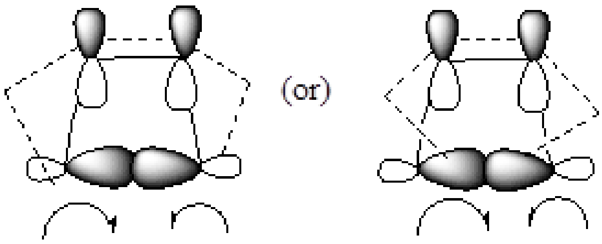
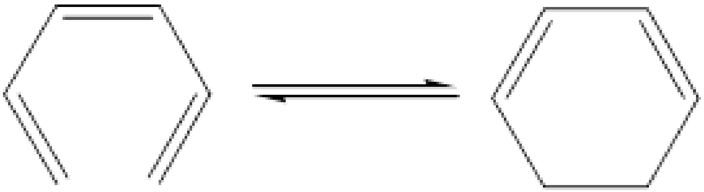


transition state for DIS electrocyclic ring opening
two or zero nodes
$4e^-(2\pi e^-$ and $2\sigma e^-)$or $4ne^-(n=1)$
Huckel anti aromatic transition state

Dis electrocyclic ring opening of a cyclobutene is photochemically allowed and thermally forbidden.

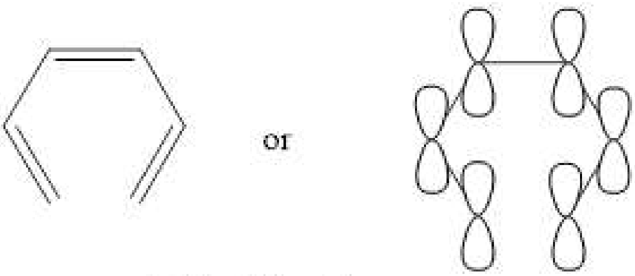
II. Electrocyclic reactions of 4n+2e- systems:

Ex



The reaction may involve conrotatory or Disrotatory electrocyclic ring closure or ring opening.

a) CON electrocyclic ring closure of 1,3,5-hexatriene



1.3.5 - Hexatriene

Six πe- participates in the ring closure. The ring closure of 1,3,5-hexatriene can take place by two conrotatory processes.

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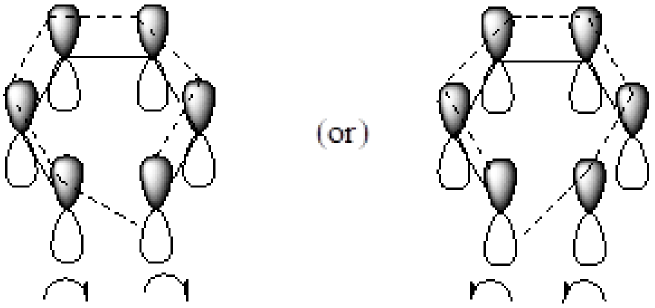
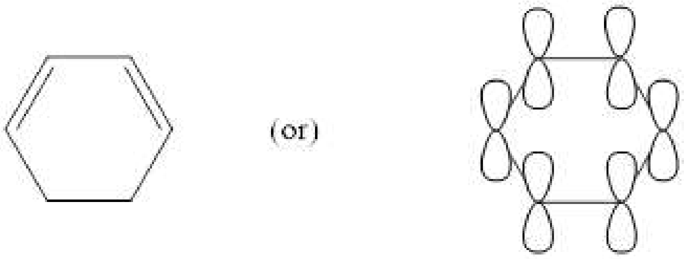


transition state for CON ring closure of a 1,3,5-hexatriene
one node
$6\pi e^-$ or $4n+2\pi e^-(n=1)$
Mobius anti aromatic transition state

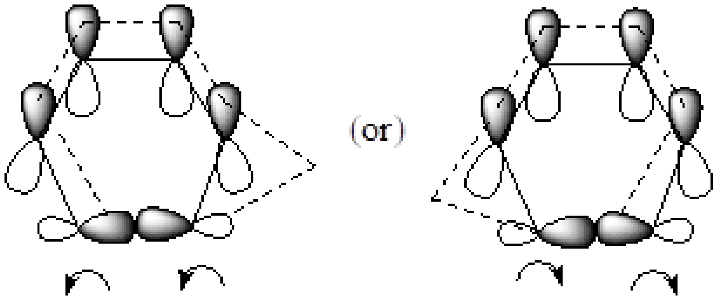
CON electrocyclic ring closure of a 1,3,5-hexatriene is photochemically allowed and thermally forbidden.

b) CON electrocyclic ring opening of 1,3-cyclohexatriene



1,3,5 - cyclohexadiene

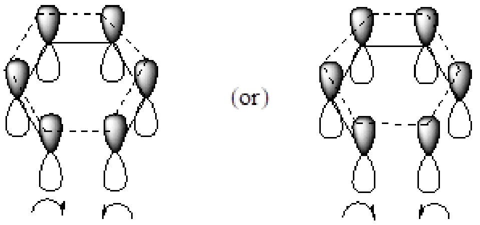
Six electrons ($4\pi e^-$ and $2\sigma e^-$) participate in the ring opening reaction. The ring opening of cyclohexadiene can take place by two conrotatory processes.



transition state for CON ring opening of a 1,3,5-hexatriene
one node
$6e^-$ or $4n+2\pi e^-(n=1)$
Mobius anti aromatic transition state

CON electrocyclic ring opening of a 1,3-hexadiene is photochemically allowed and thermally forbidden.

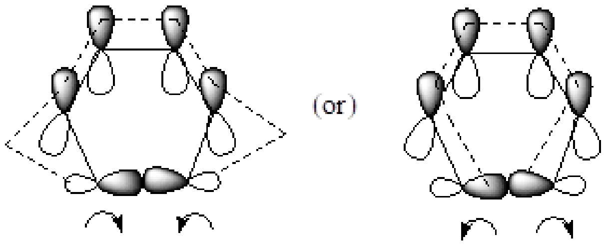
c) DIS electrocyclic ring closure of a 1,3,5- hexatriene



transition state for DIS ring closure of a 1,3,5-hexatriene
zero nodes
$6\pi e^-$ or $4n+2\pi e^-(n=1)$
Huckel aromatic transition state

DIS electrocyclic ring closure of a 1,3,5- hexatriene is thermal allowed and photochemically forbidden.

d) DIS electrocyclic ring opening of a 1,3- cyclohexadiene:



transition state for DIS ring opening of a 1,3,5-hexatriene
two or zero nodes
$6e^-$ or $4n+2\pi e^-(n=1)$
Huckel aromatic transition state

DIS electrocyclic ring opening of a 1,3- cyclohexadiene is thermally allowed and photochemically forbidden.

Selection rules for electrocyclic reactions

From the above considerations it become clear that conrotatory electrocyclic reaction of a 1,3-butadiene to a cyclobutene or the reverse process is allowed under thermal conditions, while the dis rotatory interconversion is allowed photochemically. These generalization are two for all

systems involving 4ne- (when n is an integer, including zero) in the transition state. However in the electrocyclisation of a 1,3,5-hexatriene to a 1,3 cyclohexadiene, conrotatory process is photochemically allowed while disrotatory process is thermally allowed. These predictions are actually observed in the case of all systems containg 4n+2 electrons in the transition state. These selection rules for electrocyclic reactions by Perturbational molecular method may be summed up in the following table.

Selection rules for electrocyclisation reactions by PMO method:

No. of e- in the TS	Stereochemical mode of the reaction	No. of nodes in the TS	Aromaticity of the TS	Reaction conditions	
				Allowed	Forbidden
4 n	Conrotatory	odd	aromatic	▯	hυ
4 n	Disrotatory	even or zero	antiaromatic	hυ	▯
4 n+2	Conrotatory	odd	aromatic	hυ	▯
4 n+2	Disrotatory	zero or even	antiaromatic	▯	hυ

In general all electrocyclic reactions follows the selection rules. However, under drastic conditions, symmetry-forbidden reactions may also take place, but then they follow a non-concerted path and their energy of activation is 10-15 k.cal/mole higher than those for symmetry allowed electrocyclic reactions.

A. Frontier Molecular orbital (FMO) method:

This is also known as highest occupied molecular orbitals (HOMO) lowest unoccupied molecular orbitals (LUMO) method. HOMO and LUMO of the reactants are called Frontier Molecular orbitals. The importance of HOMO and LUMO in determining the steric course of pericyclic reactions has been pointed out by K. Fukut, R.B woodward and R. Hoffmann.

In the FMO approach to electrocyclic reactions, attention is paid to the symmetry of HOMO of the open chain partner in the reaction. If HOMO has principal axis of symmetry (C2), the reaction follows a conrotatory path and if it has mirror plane symmetry (m), a disrotatory mode is observed.

I. Electrocyclic reactions of 4ne- system:

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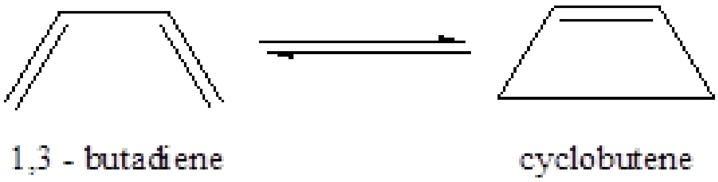
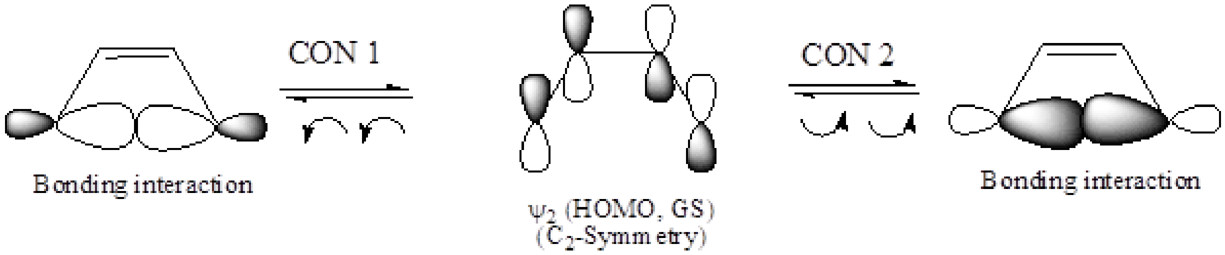


a) **Under thermal conditions:**

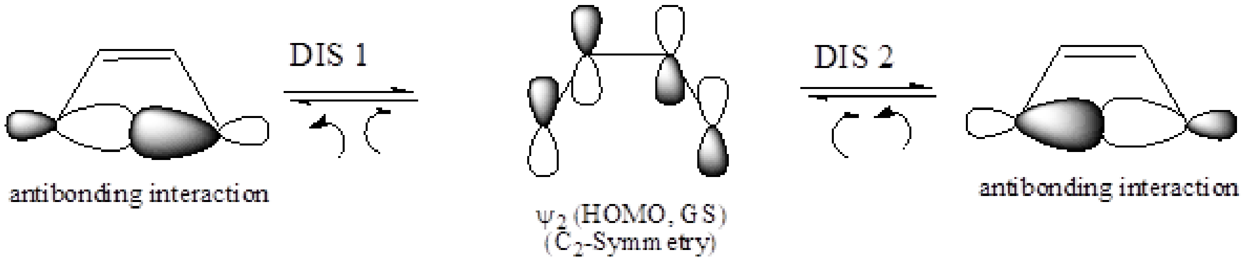
The open chain partner in the reaction is 1,3-butadiene. Under thermal conditions, the butadiene is present in the ground state. The πe- configuration of the 1,3-butadiene in the ground state is ψ12ψ22ψ30ψ40. Under thermal conditions, the symmetry of ψ2 (HOMO) is considered.

i. CON electrocyclisation



It can be seen that both conrotatory processes lead to the overlapping of the wave functions of the same phase or bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus CON electrocyclisation of a 1,3-butadiene is thermally allowed.

ii. DIS electrocyclisation:

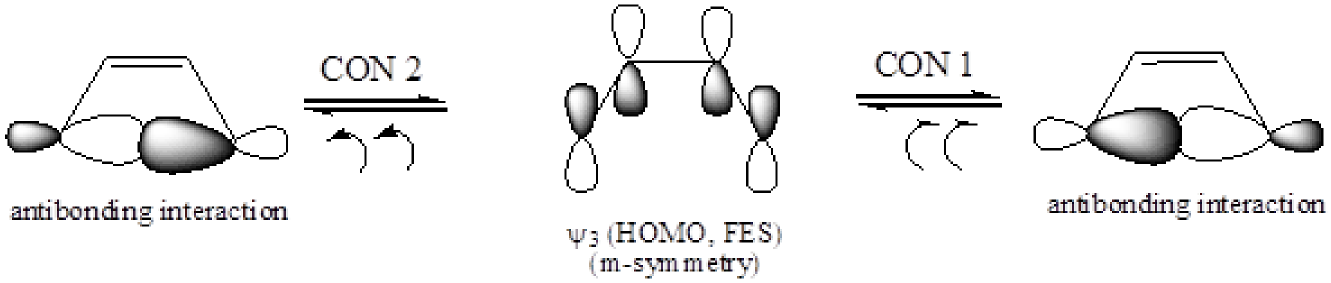


It can be seen that both disrotatory processes lead to the non overlapping of the wave functions of the same phase or anti bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus DIS electrocyclisation of a 1,3-butadiene is thermally forbidden.

b) **Under photochemical conditions:**

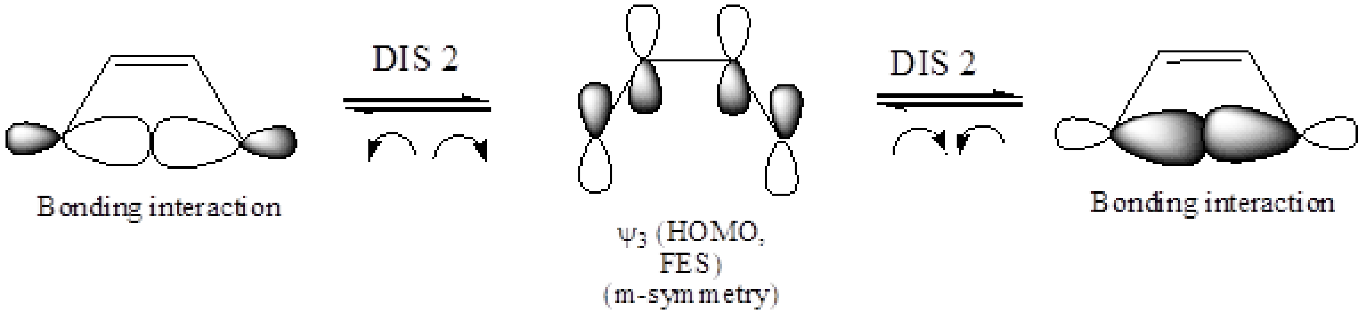
Under photochemical conditions, the butadiene is in the first excited state. The πe-configuration of the butadiene in the first excited state is ψ12ψ21ψ31ψ40. (In the FES both ψ2 and ψ3 are singly occupied molecular orbitals. Some times ψ2 and ψ33 in the first excited state are designated as SOMO and SOMO1 respectively). Under photochemical conditions, the symmetry of ψ3 (HOMO or SOMO1) is considered.

i. CON electrocyclisation:



It can be seen that both conrotatory processes lead to the non overlapping of the wave functions of the same phase or anti bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus CON electrocyclisation of a 1,3-butadiene is photochemically forbidden.

ii. DIS electrocyclisation



It can be seen that both disrotatory processes lead to the overlapping of the wave functions of the same phase or bonding interactions, which is essential for the formation of an σ

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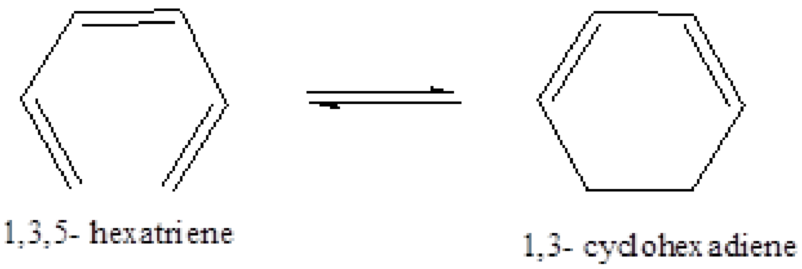
bond between the two termini of the conjugated system. Thus DIS electrocyclisation of a 1,3-butadiene is photochemically allowed.

The fore mentioned analysis points out that CON electrocyclisation of a conjugated diene is thermally allowed and photochemically forbidden, whereas DIS electrocyclisation of a conjugated diene is photochemically allowed but thermally forbidden. The same conclusions are reached in the electrocyclisations of any conjugated polyene containing 4nπe-.

II. Electrocyclic reactions of 4n+2e systems:

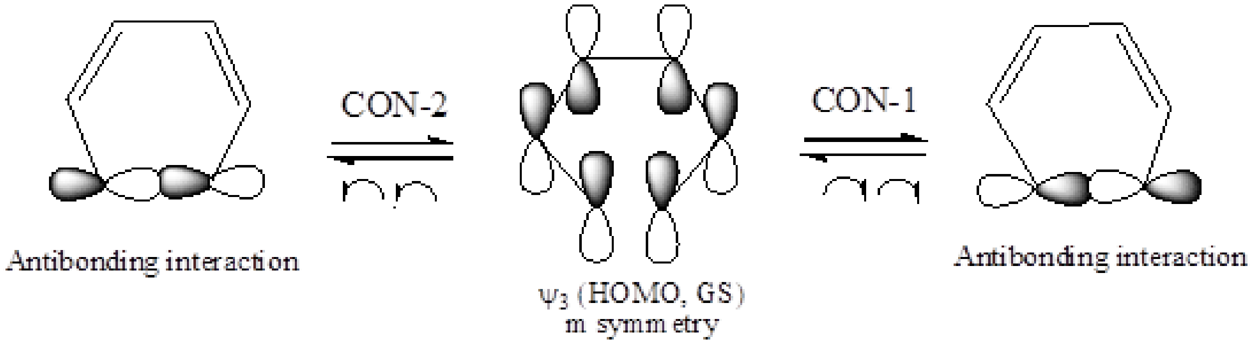


The open chain partner in the reaction is 1,3,5-hexatriene

a. Under thermal conditions:

The πe- configuration of the 1,3,5-hexatriene in the ground state is ψ12ψ22ψ32ψ40ψ50ψ60. For thermal cyclisation, the symmetry of HOMO in the ground state (ψ3) is considered.

i. CON electrocyclisation:



It can be seen that both conrotatory processes lead to the non overlapping of the wave functions of the same phase or anti bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus CON electrocyclisation of a 1,3,5-hexatriene is thermally forbidden.

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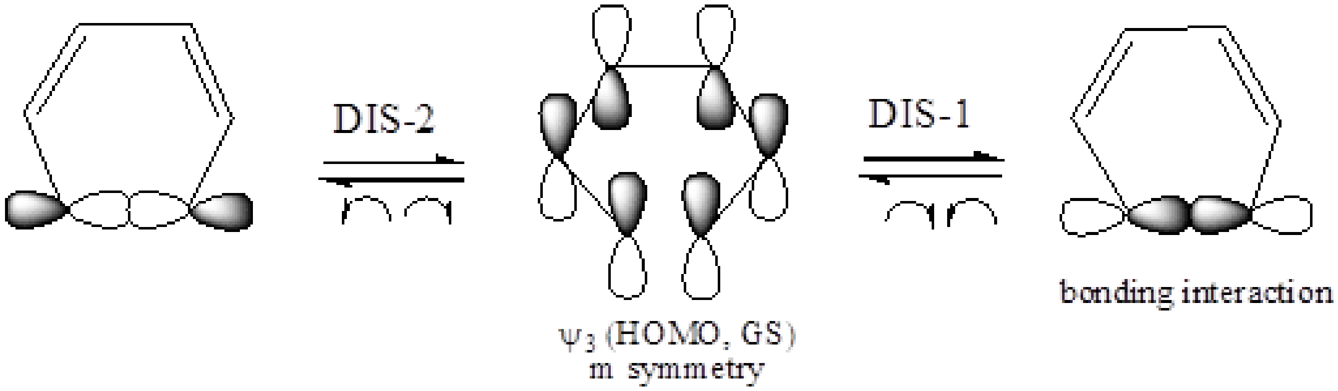
iii. DIS electrocyclisation:

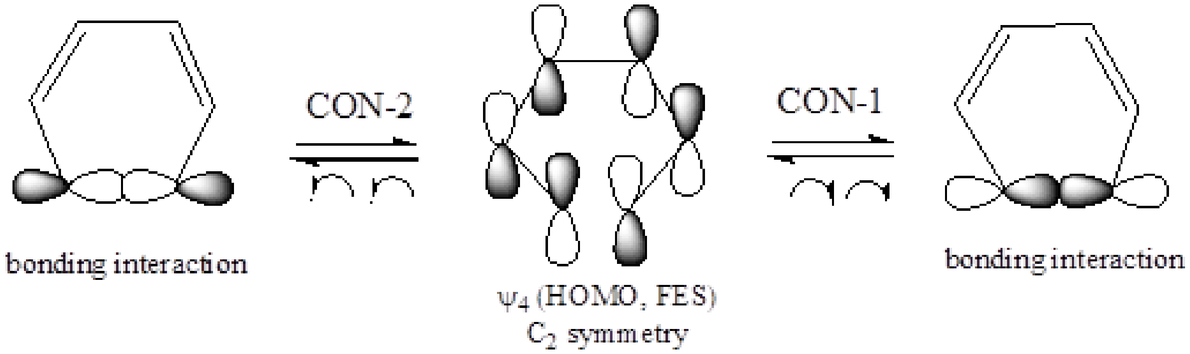


It can be seen that both disrotatory processes lead to the overlapping of the wave functions of the same phase or bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus CON electrocyclisation of a 1,3,5-hexatriene is thermally allowed.

b) Under photochemical conditions:

The πe- configuration of the 1,3,5-hexatriene in the first excited state is ψ12ψ22ψ31ψ41ψ50ψ60. Under photochemical conditions the symmetry of highest occupied molecular orbital (HOMO) in the FES (ψ4) is considered.

i. Con electrocyclisation:



It can be seen that both conrotatory processes lead to the overlapping of the wave functions of the same phase or bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus CON electrocyclisation of a 1,3,5-hexatriene is photochemically allowed.

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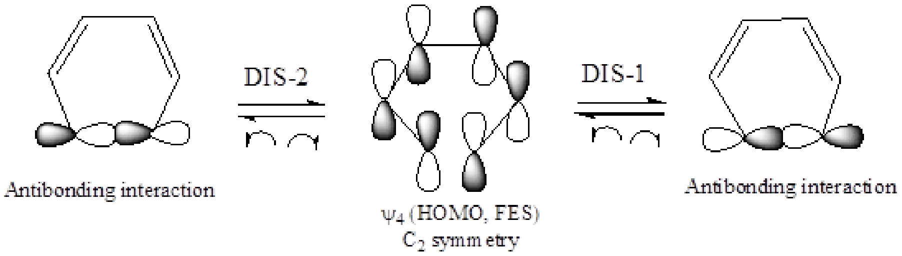
ii. DIS electrocyclisation:



It can be seen that both disrotatory processes lead to the non overlapping of the wave functions of the same phase or anti bonding interactions, which is essential for the formation of an σ bond between the two termini of the conjugated system. Thus DIS electrocyclisation of a 1,3,5-hexatriene is photochemically forbidden.

Therefore it may be considered concluded that DIS electrocyclisation of a 1,3,5-hexatriene is thermally allowed and photochemically forbidden. On the other hand, CON electrocyclisation of 1,3,5-hexatriene is photochemically allowed and thermally forbidden. These conclusions hold good in the electrocyclisation of any conjugated polyene containing 4n+2πe-.
Selection rules for electrocyclisation reactions by FMO method:

No. of e- in the TS	Stereochemical mode of the reaction	Reaction conditions	
		Allowed	Forbidden
4 n	Conrotatory	▯	hυ
4 n	Disrotatory	hυ	▯
4 n+2	Conrotatory	hυ	▯
4 n+2	Disrotatory	▯	hυ

C). Orbital symmetry correlation Diagrams:

This concept was developed by R.B woodward and R. Hoffmann. It is applicable to the all concerted reactions in which the reactant(s), product(s) and transition state all possess same symmetry characteristic. According to the principle of conversation of orbital symmetry, in a concerted reaction the molecular orbitals of reactant(s) are transformed into that of the product(s) of same symmetric characteristic. [In other words, a symmetric (S) molecular orbital in the

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product and an antisymmetric (A) molecular in the reactant must transform into an antisymmetric (A) molecular orbital of the product]

Guide lines for construction of orbital symmetry correlation diagrams:

Þ The molecular orbital of the reactant(s) and product(s) of a concerted reaction are arranged in order of increasing energy.

Þ The molecular orbital are classified as symmetric (s) and antisymmetric (A) with respect to a suitable symmetry element.

Þ Each molecular orbital of reactant(s) is correlated (joined by a straight line) with a molecular orbital at like symmetry in the product(s) (the transformation of an orbital of reactant into orbital of products of same symmetry is called correlation).

Useful information is available from the resulting orbital symmetry correlation diagrams:
In a symmetry allowed thermal reaction the molecular orbital of the reactant in the ground state correlate with molecular orbital of the product in ground state (BMO of the reactant correlate with the BMO of the product), on the other hand in a symmetry allowed photochemical reaction, molecular orbital of the reactant in first excited state correlate with those of the product in the first excited state (BMO of the reactant do not correlate with the BMO of the product).

Orbital correlation diagrams for electrocyclic reaction:

Electrocyclic reactions may be conrotatory or disrotatory. In the conrotatory electrocyclisations the reactant, product and the transition state all possess two fold (C2) symmetry axis. In other words, throughout a conrotatory elctrocyclic reaction C2 symmetry is maintained. Therefore, while drawing orbital symmetry correlation diagram for a conrotatory process the molecular orbital of reactant and product are classified with respect to C2 symmetry.

Principal axis symmetry (C2) in CON electrocyclic reaction of 1,3-butadiene:

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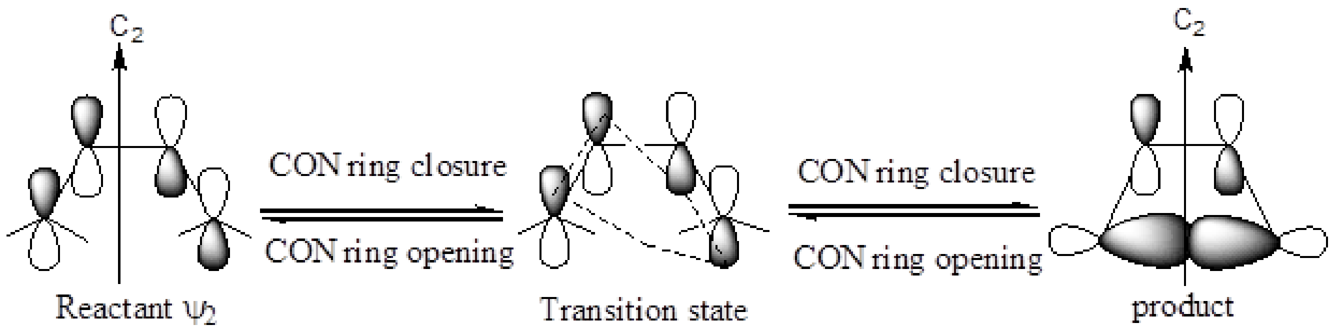
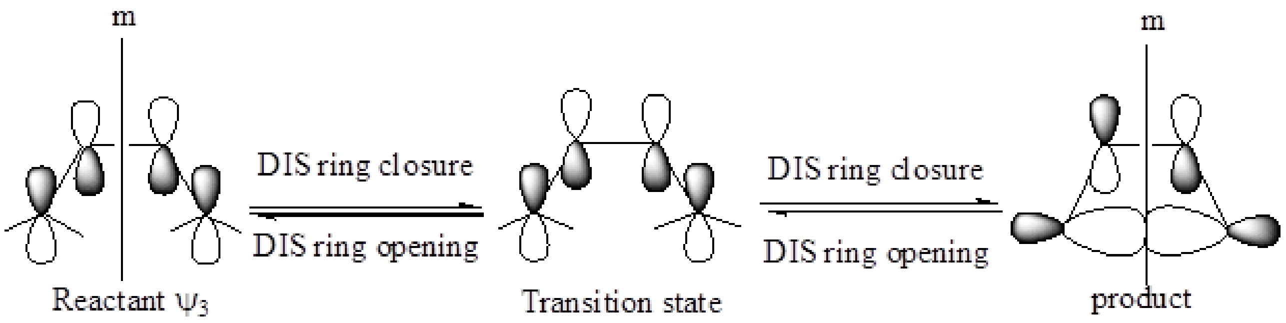
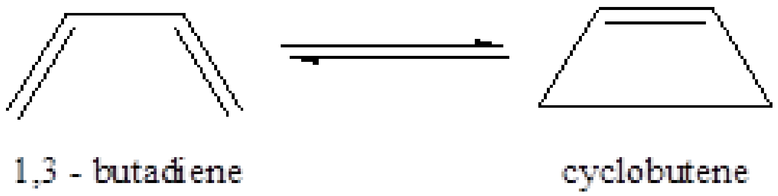


Mirror plane symmetry (m) in DIS electrocyclic reaction of a 1,3-butadiene:



On the other hand in DIS electrocyclic reactions throughout the course of reaction mirror plane (m) symmetry is maintained. Therefore while drawing orbital symmetry correlation diagrams for a disrotatory process. The molecular orbital of reactant and product are classified with respect to mirror plane symmetry.

Orbital symmetry correlation diagram for electrocyclic reactions of 4ne-systems:



a). CON electrocyclisation reactions: Principal axis (C2) symmetry is maintained throughout the CON electrocyclisation.

Orbital symmetry correlation diagram for electrocyclic reaction of cyclobutadiene to cyclobutene:

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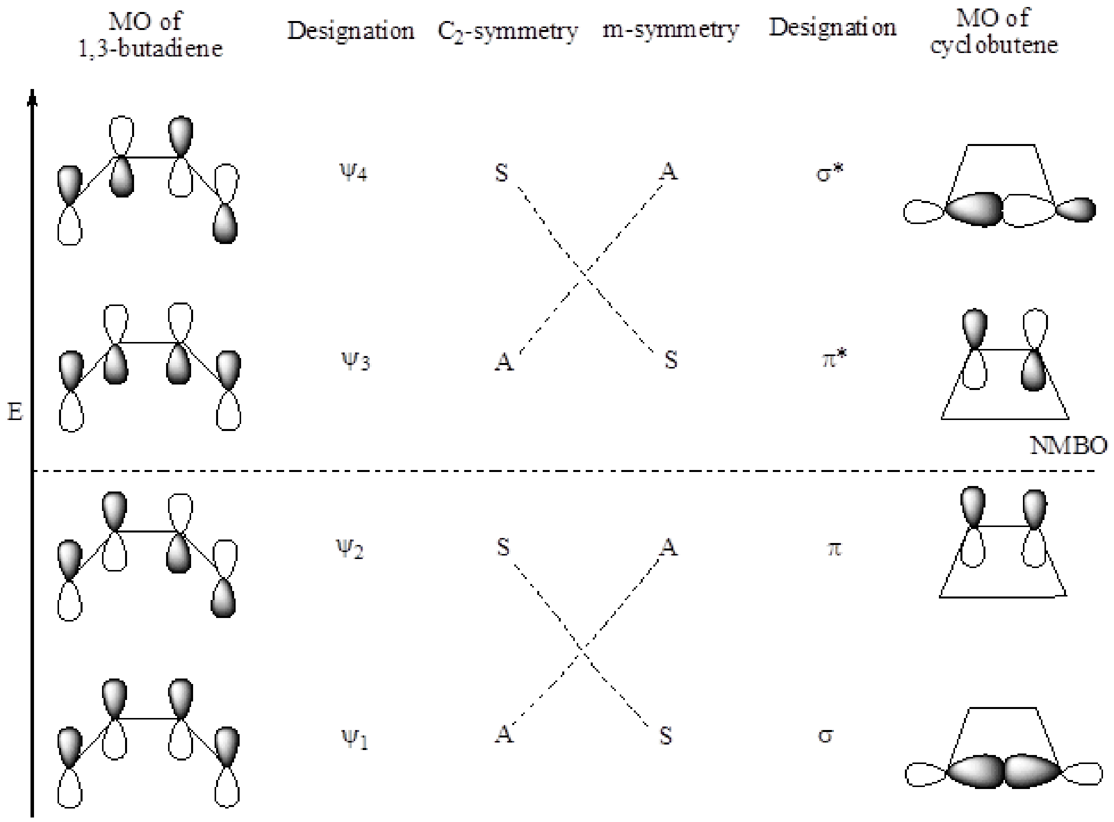

The following conclusions can be drawn from the orbital symmetry correlation diagram:

i. Since ψ2, correlates with π2 ψ22 correlates with σ2, we can refer that ground state of 1,3-butadiene correlates with the ground state of cyclobutadiene.

$$\psi_1^2\psi_2^2 \longleftrightarrow \pi^2\sigma^2 \text{ or } \sigma^2\pi^2$$

GS of 1,3-butadiene GS of cyclobutene

A thermal CON rotatory process in either direction is symmetry allowed.

ii. It is observed that the first excited state of 1,3-butadiene correlates with the upper excited state (UES) of cyclobutene that is, it does not correlates with first excited state.

$$\psi_1^2\psi_2^1\psi_3^1\psi_4 \longrightarrow \pi^2\sigma^1\sigma^{*1} \text{ or } \sigma^1\sigma^{*1}\pi^2$$

FES of 1,3-butadiene UES of cyclobutene

Similarly first excited state of cyclobutene correlates with upper excited state of 1,3-butadiene.

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$$\sigma^2\pi^1\pi^{*1} \longrightarrow \psi_2^2\psi_1^1\psi_4^1 \quad \text{or} \quad \psi_1^1\psi_2^2\psi_4^1$$

FES of cyclobutene UES of 1,3-butadiene

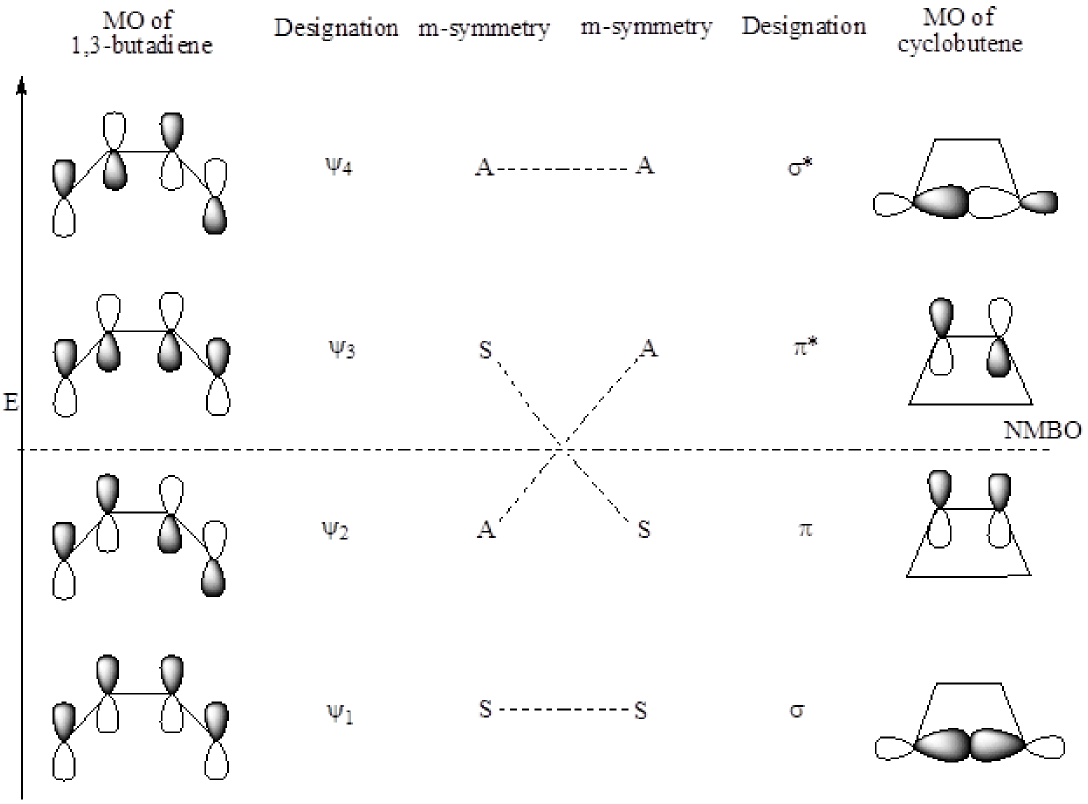
In a other words, the first excited state of 1,3-butadiene does not correlates with the first excited state of cyclobututene.

$$\psi_1^2\psi_2^1\psi_3^1 \not\longleftrightarrow \sigma^2\pi^1\pi^{*1}$$

A photochemically conrotatory process in either direction is symmetry forbidden.

b) DIS electrocyclisation Reactions:

We can construct another orbital symmetry correlation diagram for disrotatatory interconversion of 1,3-butadiene-cyclobutene system, in which mirror plane symmetry is maintained throughout the reaction.



The following conclusions can be drawn from the orbital symmetry correlation diagram:

i). Since ψ2, does not correlates with σ2 π2, we can refer that ground state of 1,3-butadiene correlates with the first excited state of cyclobutadiene.

$$\psi_1^2\psi_2^2 \longleftrightarrow \sigma^2\pi^{*2}$$

GS of 1,3 - butadiene FES of cyclobutene

$$\sigma^2\pi^2 \longleftrightarrow \psi_1^2\psi_3^2$$

GS of cyclobutene FES of 1,3 - butadiene

In other words

$$\psi_1^2\psi_2^2 \not\longleftrightarrow \sigma^2\pi^2$$

The ground state of 1,3, butadiene does not correlate with gound state of cyclobutene. Thus thermal transformation of 1,3-butadiene to cyclobutene and vice versa process by disrotatory is symmetry forbidden.

ii). ψ12ψ21 and ψ31 molecular orbital of 1,3-butadiene correlates with σ2π1 and π*1 respectively of cyclobutene.

$$\psi_1^2\psi_2^1\psi_3^1 \longleftrightarrow \sigma^2\pi^{*1}\pi^1 \text{ or } \sigma^2\pi^1\pi^{*1}$$

FES of 1,3 - butadiene FES of cyclobutene

$$\sigma^2\pi^1\pi^{*1} \longleftrightarrow \psi_1^2\psi_2^1\psi_3^1$$

FES of cyclobutene FES of 1,3 - butadiene

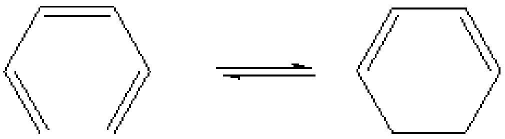
In other words

$$\psi_1^2\psi_2^1\psi_3^1 \longleftrightarrow \sigma^2\pi^{*1}\pi^1$$

FES of 1,3 - butadiene FES of cyclobutene

The first excited state of 1,3-butadiene correlates with the first excited state of cyclobutene. Therefore disrotatory interconversion of 1,3-butadiene-cyclobutene is a photochemically symmetry allowed process.

Orbital symmetry correlation diagram for electrocyclic reactions of 4n+2e-systems:



1,3,5 - hexatiene 1,3 - cyclohexadiene

a) CON electrocyclisation Reactions: The molecular orbitals of the reactants and products are classified with respect to principal axis symmetry (C2).

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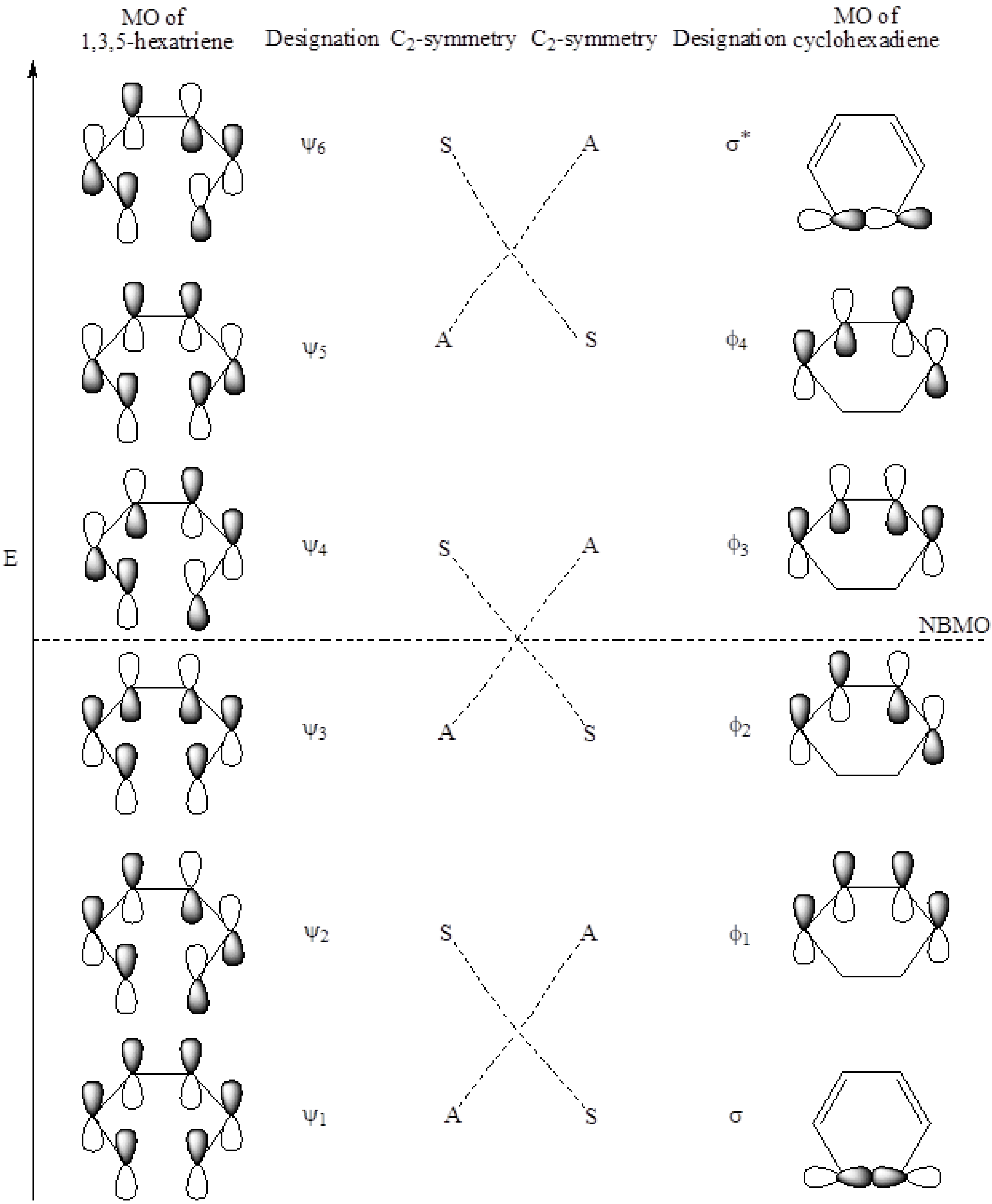

The following conclusions can be drawn from the orbital symmetry correlation diagram:

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i. Bonding molecular orbital of hexatriene do not correlate with the bonding molecular orbital of cyclohexadiene.

$$\psi_1^2\psi_2^2\psi_3^2 \longleftrightarrow \phi_1^2\sigma^2\phi_3^2 \text{ or } \sigma^2\phi_1^2\phi_3^2$$

GS of1,3,5- hexatriene UES of cyclohexadiene

$$\phi_1^2\sigma^2\phi_2^2 \longleftrightarrow \psi_2^2\psi_1^2\psi_4^2 \text{ or } \psi_1^2\psi_2^2\psi_4^2$$

GS of cyclohexadiene UES of 1,3,5-hexatriene

In other words, the ground state of 1,3,5-hexatriene does not correlates with the ground state of cyclohexadiene.

$$\Psi_1^2\Psi_2^2\Psi_3^2 \longleftrightarrow \sigma^2\phi_1^2\phi_3^2$$

Thermal conrotatory mode transformation of 1,3,5-hexatriene to 1,3-cyclohexadiene and vice versa process is symmetry forbidden.

ii. First excited state of 1,3,5-hexatriene correlates with the first excited state of cyclohexadiene

$$\psi_1^2\psi_2^2\psi_3^1\psi_4^1 \longleftrightarrow \phi_1^2\sigma^2\phi_3^1\phi_2^1 \text{ or } \sigma^2\phi_1^2\phi_2^1\phi_3^1$$

FES of 1,3,5-hexatriene FES of cyclohexadiene

$$\sigma^2\phi_1^2\phi_2^1\phi_3^1 \longleftrightarrow \psi_2^2\psi_1^2\psi_4^1\psi_3^1 \text{ or } \psi_1^2\psi_2^2\psi_3^1\psi_4^1$$

FES of cyclohexadiene FES of 1.3.5-hexatriene

Therefore photochemical conrotatory mode transformation of 1,3,5-hexatriene to 1,3-cyclohexadiene and vice versa process is symmetry allowed.

b). DIS electrocyclisation Reactions: Orbital symmetry correlation diagram for disrotatory interconversion of 1,3,5-hexatriene to 1,3-cyclohexadiene can be constructed as follows. The molecular orbitals of the reactants and products are classified with respect to mirror plane symmetry (m).

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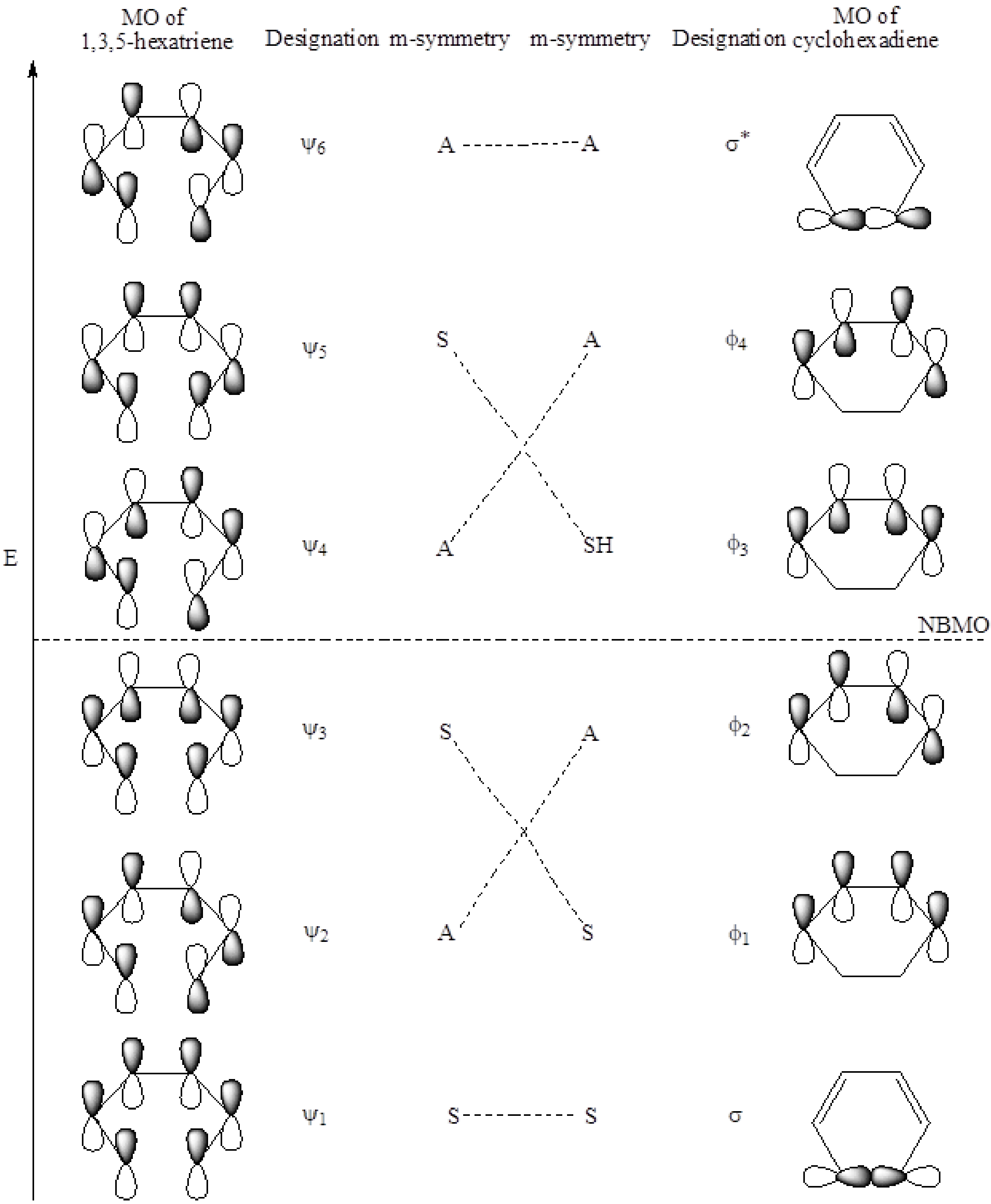

The following conclusions can be drawn from the orbital symmetry correlation diagram

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i. Bonding molecular orbital of 1,3,5-hexatriene correlate with the bonding molecular orbital of 1,3-cyclohexadiene and ground state of 1,3,5-hexatriene correlates with ground state of 1,3-cyclohexadiene

$$\underset{\text{GS of 1,3,5-hexatriene}}{\psi_1^2\psi_2^2\psi_3^2} \longleftrightarrow \underset{\text{GS of cyclohexadiene}}{\sigma^2\phi_1^2\phi_2^2}$$

A thermal disrotatory process in either direction is symmetry allowed.

ii. The first excited state of 1,3,5- hexatriene does not correlates with the first excited state of cyclohexatriene.

$$\underset{\text{FES of 1,3,5-hexatriene}}{\psi_1^2\psi_2^2\psi_3^1\psi_4^1} \longleftrightarrow \underset{\text{UES of cyclohexadiene}}{\sigma^2\phi_2^2\phi_1^1\phi_4^1}$$

$$\underset{\text{FES of cyclohexadiene}}{\sigma^2\phi_1^2\phi_2^1\phi_3^1} \longleftrightarrow \underset{\text{UES of 1,3,5-hexatriene}}{\psi_1^2\psi_3^2\psi_2^1\psi_5^1}$$

Therefore photochemical conrotatory mode transformation of 1,3,5-hexatriene to 1,3-cyclohexadiene and vice versa process is symmetry forbidden.

Orbital symmetry correlation diagrams can be drawn for electrocyclisation of other 4n, 4n+2e- systems. The conclusion reaches by orbital symmetry correlation diagram method are same as those arrived by PMO and FMO methods and as follows:

Selection rules for electrocyclisation reactions by PMO method:

No. of e- in the TS	Stereochemical mode of the reaction	Reaction conditions Allowed	 Forbidden
4 n	Conrotatory	□	hυ
4 n	Disrotatory	hυ	□
4 n+2	Conrotatory	hυ	□
4 n+2	Disrotatory	□	hυ

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Cycloaddition Reactions:

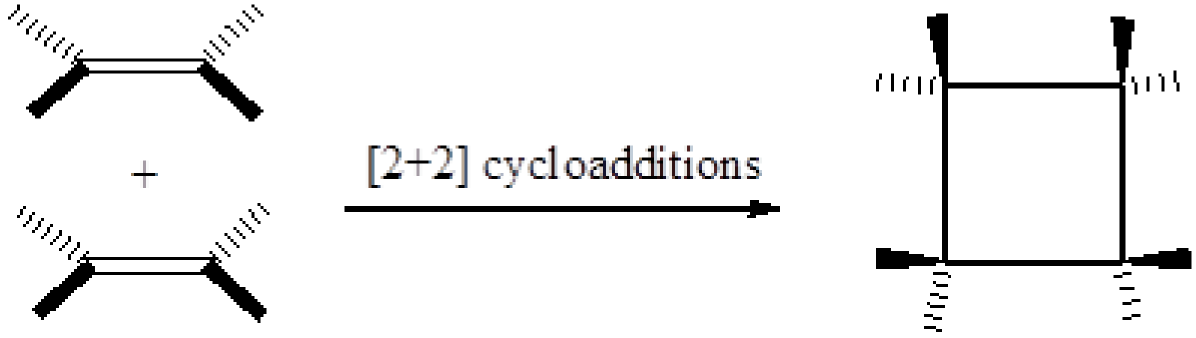
The stereochemical mode of cycloadditions can be analysed by three methods viz Perturbational Molecular Orbital method, Frontier Molecular Orbital method and orbital symmetry correlation diagram method. The first two methods are applicable to all stereochemical modes of cycloadditions. However, the last method is applicable only supra-supra cycloaddition reactions.

Perturbational Molecular Orbital method:

To predict the stereochemistry of a [m+n] cycloaddition,
i. Show the transition state of a stereochemical mode of the cycloaddition as a cyclic array of atomic orbitals
ii. Assign signs to the wave functions in the best manner to overlap.
iii. Count the number of nodes in the transition state.
iv. Count the number of electrons participating in the transition state.
v. Classify the transition state as aromatic or antiaromatic.

A cycloaddition reaction taking place through an aromatic transition is thermally allowed and photochemically forbidden, whereas that involving an antiaromatic transition state is photochemically allowed and thermally forbidden.

[m+n] cycloaddition reactions involving 4ne- :
Example is[2+2] cycloaddition reactions



Stereochemically four different [2+2] cycloaddition reactions viz: [π2s+π2s], [π2s+π2a], [π2a+π2s] and [π2a+π2a] cycloadditions are possible.

a) [π2s+π2s] cycloaddition:

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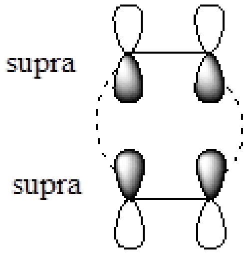
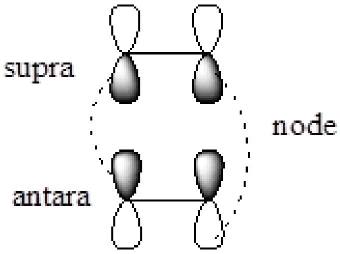


transition state
zero node
4e$^-$ or 4ne$^-$ (n=1)
Huckel anti aromatic transition state

[π2s+π2s] cycloaddition is photochemically allowed and thermally forbidden.

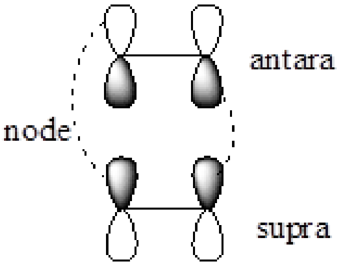
b)**[π2s+π2a] cycloaddition:**



transition state
one node
4e$^-$ or 4ne$^-$ (n=1)
Mobius aromatic transition state

[π2s+π2a] cycloaddition is thermally allowed and photochemically forbidden.

c) **[π2a+π2s] cycloaddition:**



transition state
one node
4e$^-$ or 4ne$^-$ (n=1)
Mobius aromatic transition state

[π2a+π2s] cycloaddition is thermally allowed and photochemically forbidden.

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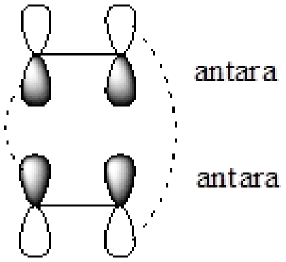
d) [π2a+π2a] cycloaddition:



transition state

zero node

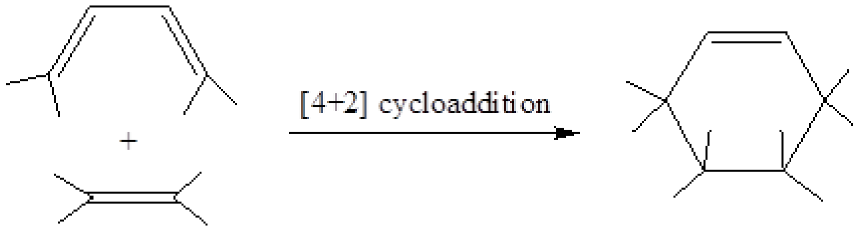
$4e^-$ or $4ne^-$ (n=1)

Huckel anti aromatic transition state

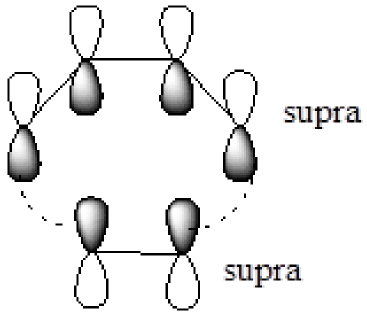
[π2a+π2a] cycloaddition is photochemically allowed and thermally forbidden.

[m+n] cycloaddition reactions involving [4n+2e-]:

Example is [4+2] cyclo addition reactions



a) [π4s+π2s] cycloaddition:



transition state

zero node

$6e^-$ or $4n+2e^-$ (n=1)

Huckel aromatic transition state

[π4s+π2s] cycloaddition is thermally allowed and photochemically forbidden.

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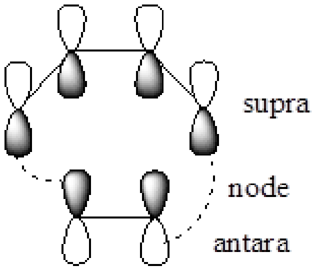
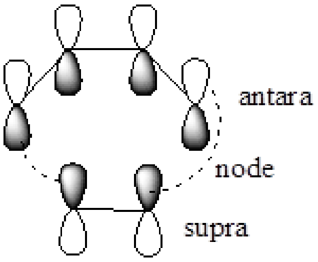
b) [π4s+π2a] cycloaddition:



transition state
one node
6e- or 4n+2e- (n=1)
Mobius antiaromatic transition state

[π4s+π2a] cycloaddition is photochemically allowed and thermally forbidden.

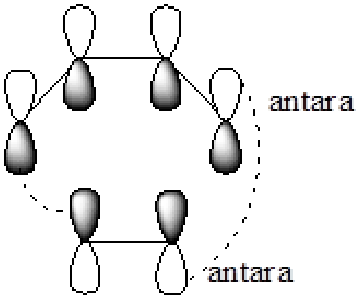
c)**[π4a+π2s] cycloaddition:**



transition state
one node
$6e^-$ or $4n+2e^-$ (n=1)
Mobius anti aromatic transition state

[π4a+π2s] cycloaddition is photochemically allowed and thermally forbidden.

d) [π4a+π2a] cycloaddition:



transition state
zero node
$6e^-$ or $4n+2e^-$ (n=1)
Huckel aromatic transition state

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[π4a+π2a] cycloaddition is thermally allowed and photochemically forbidden.

Selection rules for cycloaddition reactions:

Thus, in the [2+2] cycloadditions supra-supra and antara-antara cycloadditions are photochemically allowed where as supra-antara and antara-supra cycloadditions are thermally allowed. These rules are observed in all [m + n] cycloadditions, where the sum of m and nelectrons corresponds to the 4n electrons (n = an integer, including zero)

On the other hand, supra-supra and antara-antara [4+2] cycloadditions are thermally allowed and the supra-antara and antara-supra [4+2] cycloadditions are photchemically allowed. This is true in case of all [m + n] cycloaddition where the sum of m and n corresponds to 4n+2 electrons (n = an integer, including zero).

The selection rules for cycloadditions and cycloreversions are summerised by PMO method:

No. of e- in m+n cycloaddition	Streochemical mode of reaction	No. of nodes in the T.S	Aromaticity of the TS	Reaction Conditions	
				Allowed	Forbidden
4n	**supra-supra** **antara-antara**	zero or even	antiaromatic	hυ	D
4n	supra-antara supra -antara	odd	aromatic	D	hυ
4n+2	supra-supra antara-antara	zero or even	aromatic	D	hυ
4n+2	supra-antara antara- supra	odd	antiaromatic	hυ	D

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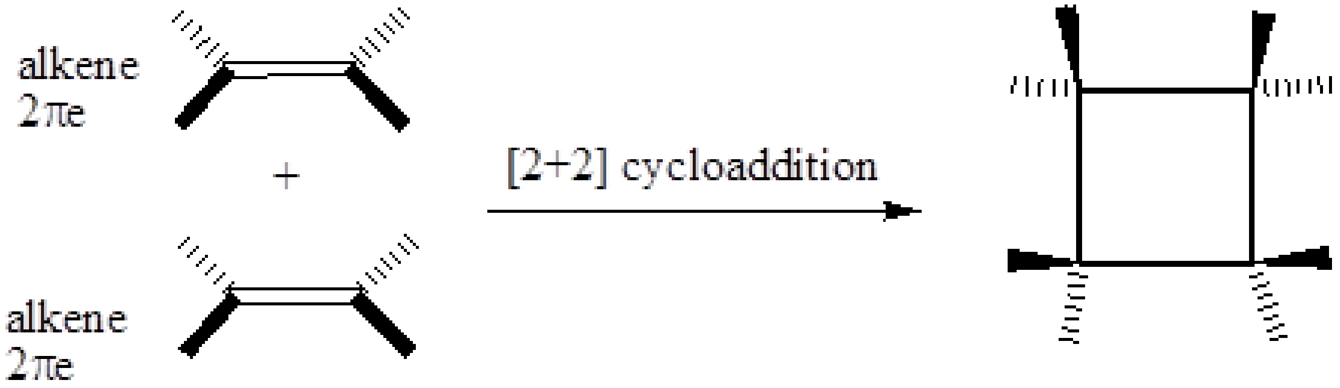
Same set of rules are applicable to cycloaddition reaction involving ionic species.

Frontier Molecular Orbital (FMO) method:

In this approach, attention is paid to electrons in the molecular orbitals which participate in the bond formation and bond orbitals which participate in the bond formation and bond breaking processes i.e. HOMO and LUMO.

In cycloaddition at least two components are involved. Electron transfer between HOMO of one reactant and LUMO of the other reactant and vice versa is assumed. In thermal reactions overlap between HOMO of one reactant and LUMO of the other reactant (both in ground state) or vice versa is considered. In photochemical reactions, overlap between HOMO of one reactant in the first exicited state and LUMO of the other reactant in ground state or vice versa (LUMO of first component in the first excited state and HOMO of the second component in the ground state) is considered. If interaction between the frontier molecular orbitals (HOMO and LUMO) in a particular stereochemical mode of cycloaddition under given reactions leads to bonding (inphase overlap that reaction is symmetry allowed or otherwise it is symmetry forbidden).

[m+n] Cycloaddition reactions involving 4ne-:



Thermal conditions involving 4ne-:

In thermal reactions, interaction between the HOMO of an alkene in the ground state (π) and the LUMO of the other in the ground state (π*) are considered.

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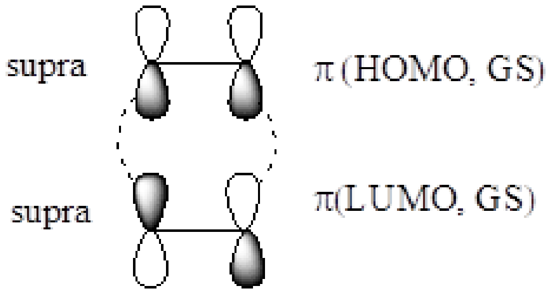
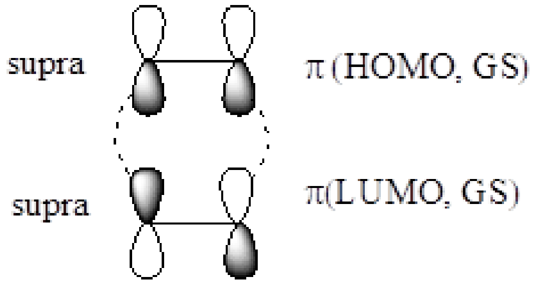
a) [π2s+π2s] cycloaddition:



transition state for $[\pi^2_s+\pi^2_s]$ cycloaddition
antibonding interaction

Therefore, [π2s+π2s] cycloaddition is symmetry forbidden under thermal conditions.

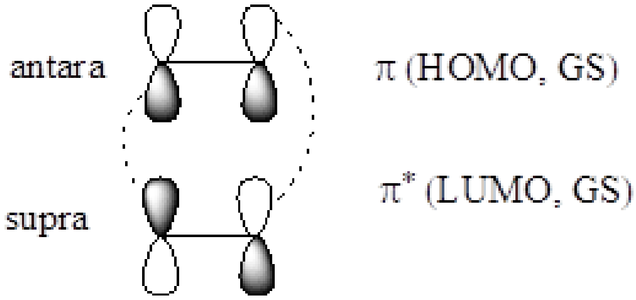
b**)** **[π2s+π2a] cycloaddition:**



transition state for $[\pi^2_s+\pi^2_s]$ cycloaddition
antibonding interaction

Therefore, [π2s+π2a] cycloaddition is symmetry allowed under thermal conditions.

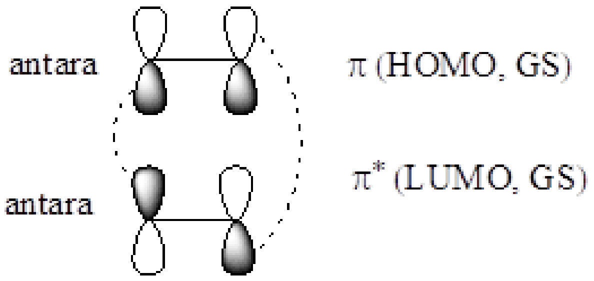
c**)** **[π2a+π2s] cycloaddition:**



transition state for $[\pi^2_a+\pi^2_s]$ cycloaddition
bonding interaction

Therefore, [π2a+π2s] cycloaddition is symmetry allowed under thermal conditions.

d) **[π2a+π2a] cycloaddition**



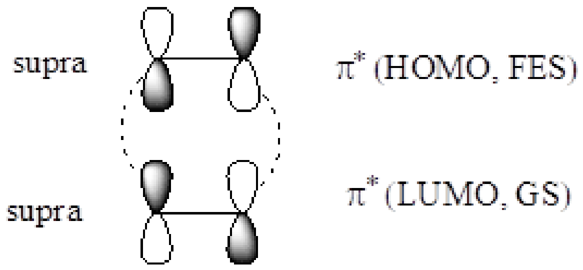
transition state for $[\pi^2_a+\pi^2_a]$ cycloaddition
anti bonding interaction

Therefore, [π2a+π2a] cycloaddition is symmetry forbidden under thermal conditions.

Photochemical conditions involving 4ne-:

In photochemical reactions, interaction between the HOMO of an alkene in the first excited state (π) and LUMO of the other alkene in the ground state (π) is considered.

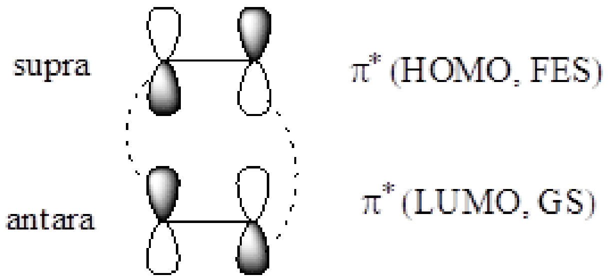
a) [π2s+π2s]cycloaddition:



transition state for $[\pi^2_s+\pi^2_s]$ cycloaddition
bonding interaction

Therefore, [π2s+π2s] cycloaddition is symmetry allowed under photochemical conditions.

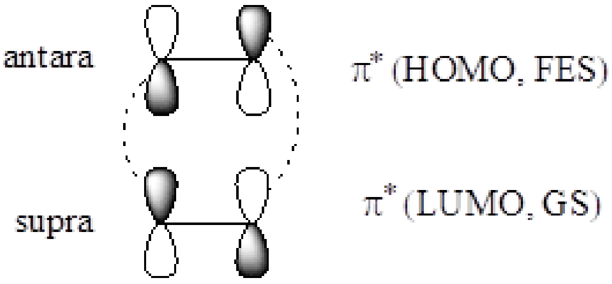
b) [π2s+π2a]cycloaddition:



transition state for $[\pi^2_s+\pi^2_a]$ cycloaddition
anti bonding interaction

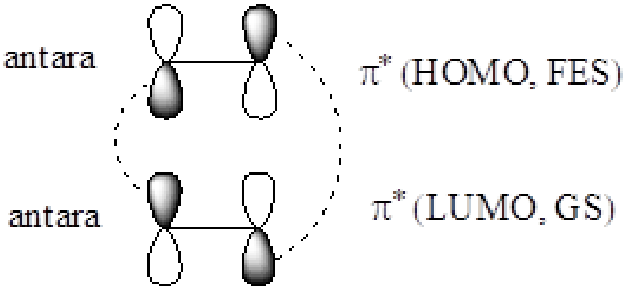
Therefore, [π2s+π2a] cycloaddition is symmetry forbidden under photochemical conditions.

c). [π2a+π2s] cycloaddition:



transition state for $[\pi^2_a+\pi^2_s]$ cycloaddition
anti bonding interaction

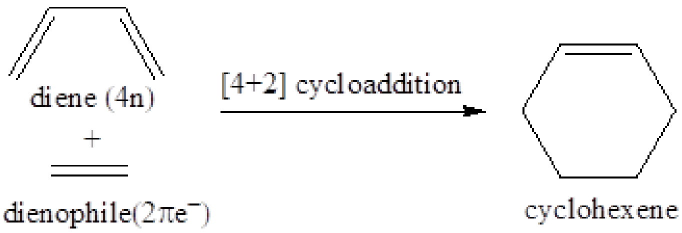
Therefore, [π2a+π2s] cycloaddition is symmetry forbidden under photochemical conditions.
d). [π2a+π2a]cycloaddition:



transition state for $[\pi^2_a+\pi^2_a]$ cycloaddition
bonding interaction

Therefore, [π2a+π2a] cycloaddition is symmetry allowed under photochemical conditions. It can be seen in the [2+2] cycloadditions supra-supra, or antara-antara reactions are allowed photochemically and forbidden under thermal conditions. It contrast supra-antara or antara-supra cycloadditions are thermally allowed and photochemically forbidden. These generalized rules may be extended to all [m+n] cycloadditions where the sum of m and nelectrons corresponds to 4ne- (n=integer).

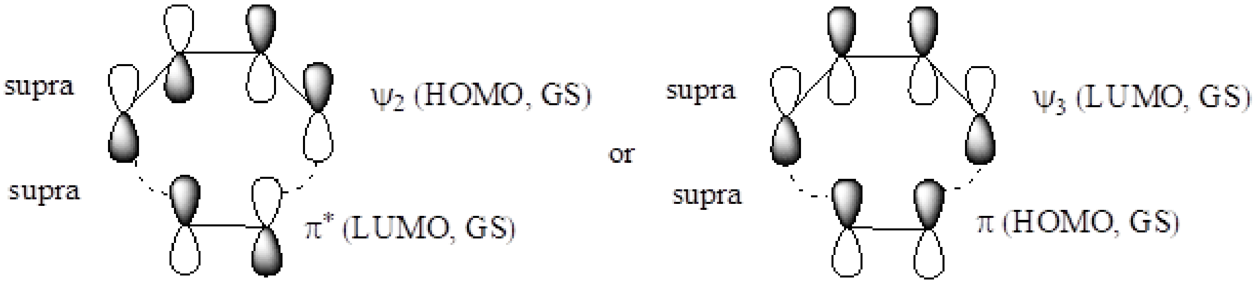
[m+n] cycloaddition reactions involving 4n+2e-:



Thermal conditions involving 4n + 2e-:

In thermal [4+2] cycloadditions the symmetries HOMO of the diene in the ground state (ψ2) and LUMO of the dienophile in the ground state (π*) or less appropriately the symmetries of LUMO of the diene in the ground state (ψ3) and HOMO of the dienophile in the ground state (π) are considered.

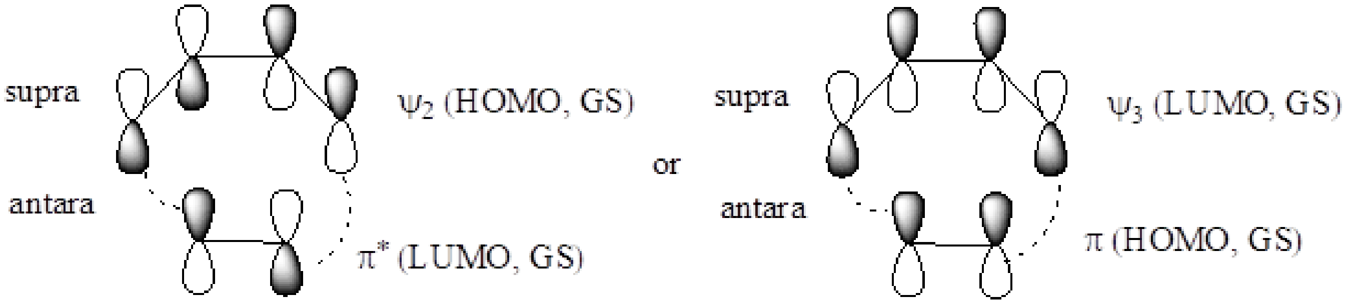
a). [π4s+π2s] cycloaddition:



transition state for $[\pi^4_s+\pi^2_s]$ cycloaddition
bonding interaction

Therefore, [π4s+π2s] cycloaddition is symmetry allowed under thermal conditions.

b). (π4s+π2a) cycloaddition:



transition state for $[\pi^4_s+\pi^2_a]$ cycloaddition
anti bonding interaction

Therefore, [π4s+π2a] cycloaddition is symmetry forbidden under thermal conditions.

c). [π4a+π2s] cycloaddition:

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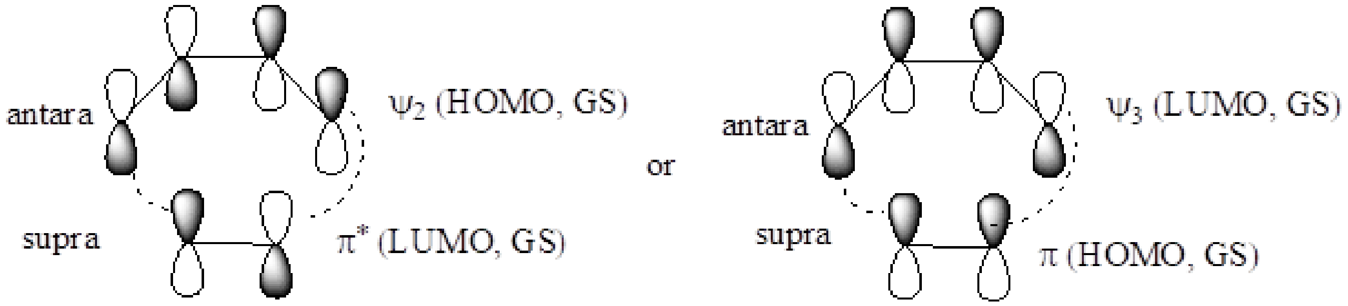
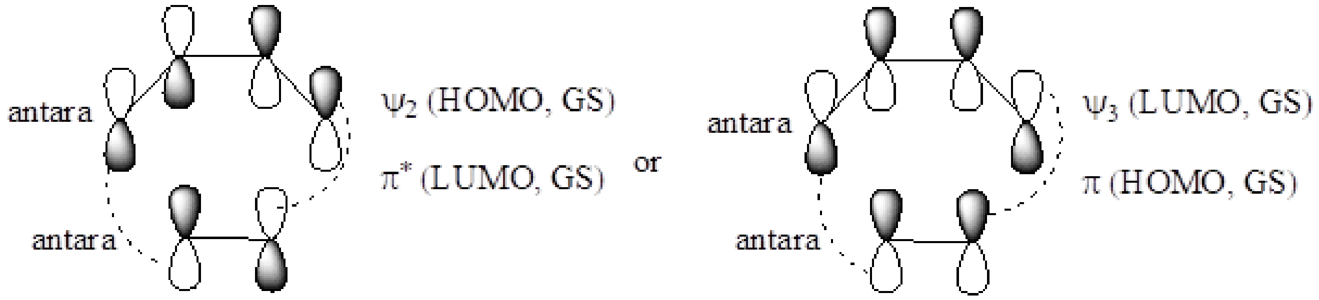


transition state for [$\pi^4_a+\pi^2_s$] cycloaddition
anti bonding interaction

Therefore, [π4a+π2s] cycloaddition is symmetry forbidden under thermal conditions.

d). [π4a+π2a] cycloaddition:



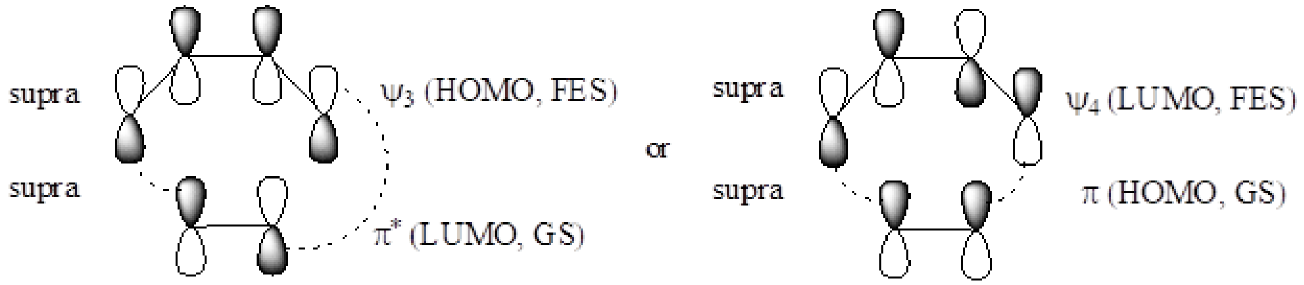
transition state for [$\pi^4_a+\pi^2_a$] cycloaddition
bonding interaction

Therefore, [π4a+π2a] cycloaddition is symmetry allowed under thermal conditions.

Photochemical conditions involving 4n+2e-:

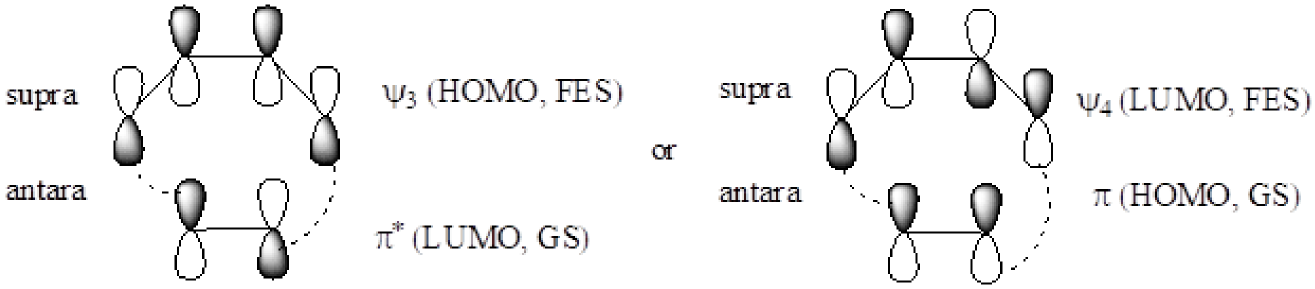
In photochemical [4+2] cycloadditions the symmetries HOMO of the diene in the first excited state (ψ3) and LUMO of the dienophile in the ground state (π*) or less appropriately the symmetries of LUMO of the diene in the first excited state (ψ4) and HOMO of the dienophile in the ground state (π) are considered.

a). [π4s+π2s] cycloaddition:



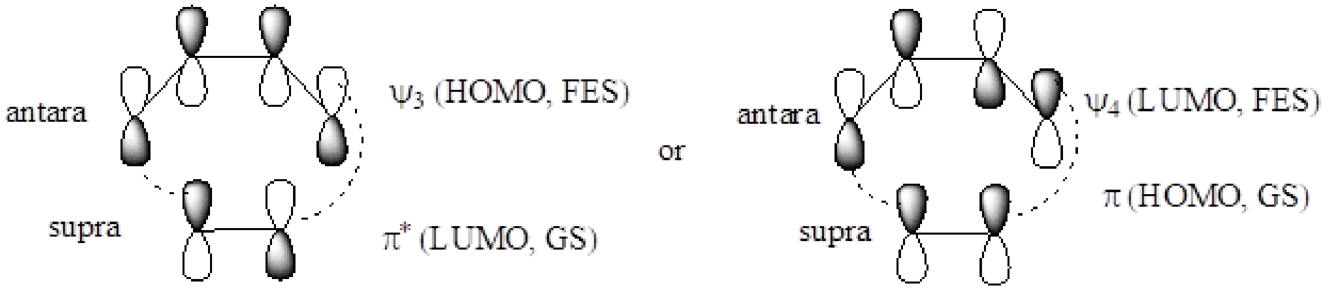
transition state for $[\pi^4_s+\pi^2_s]$ cycloaddition

Therefore, [π4s+π2s] cycloaddition is symmetry forbidden under photochemical conditions.
b). [π4s+π2a] cycloaddition:



transition state for $[\pi^4_s+\pi^2_a]$ cycloaddition
bonding interaction

Therefore, [π4s+π2a] cycloaddition is symmetry allowed under photochemical conditions.
c). [π4a+π2s] cycloaddition:



transition state for $[\pi^4_a+\pi^2_s]$ cycloaddition
bonding interaction

Therefore, [π4a+π2s] cycloaddition is symmetry allowed under photochemical conditions.
d). [π4a+π2a] cycloaddition:

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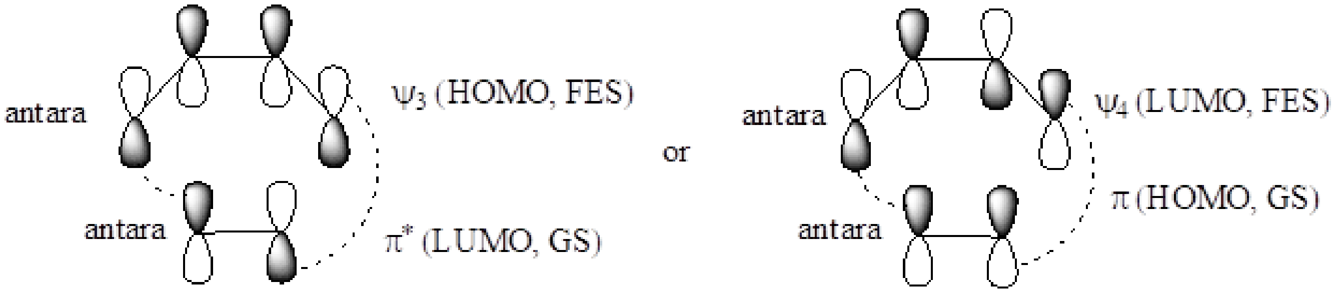


transition state for $[\pi^4_a+\pi^2_a]$ cycloaddition
anti bonding interaction

Therefore, [π4a+π2a] cycloaddition is symmetry forbidden under photochemical conditions.

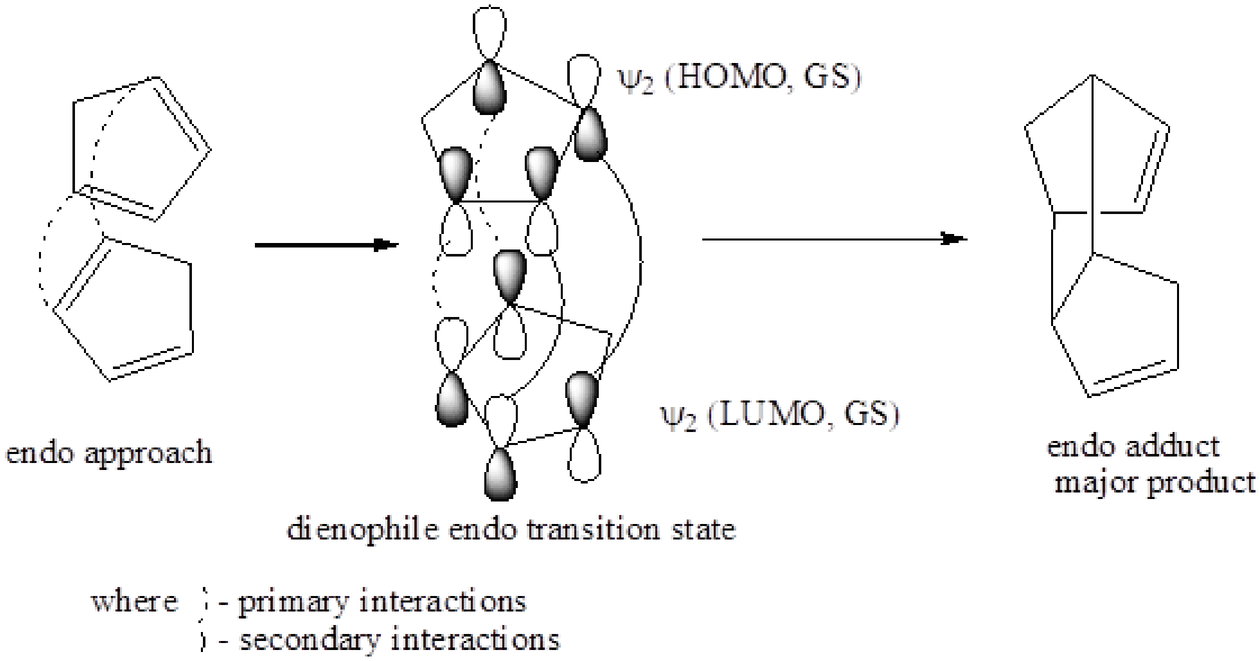
It can be seen in the [4+2] cycloadditions supra-supra, or antara-antara reactions are allowed thermally and forbidden under photochemical conditions. It contrast supra-antara or antara-supra cycloadditions are photochemically allowed and thermally forbidden. These generalized rules may be extended to all [m+n] cycloadditions where the sum of m and n electrons corresponds to 4n+2e- (n=integer).

Secondary orbital Interactions:

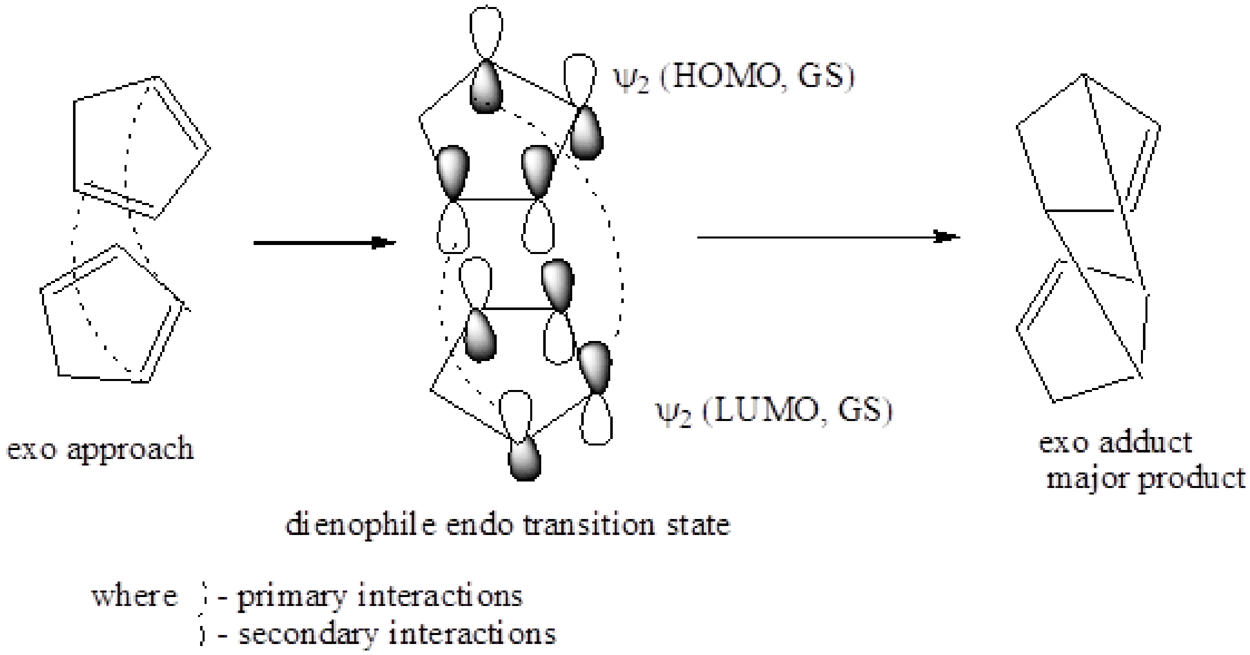
Alder's endorule

The well known Diels-Alder reaction is thermally allowed [π2s+π2s] cycloaddition. In the Diels-Alder reaction, involving a dienophile and a cyclic diene, two products viz endo and exo adducts are possible. It was observed by Alder that under, Kinetically controlled conditions, invariably the endo adduct is formed rather than the exo adduct. This can be explained due to the favourable secondary interactions between Frontier orbitals of diene and dienophile in the endo transition state. This lowers the energy of the endo transition state leading to the endo product. Dimerization of cyclopentadiene serves as an example.

[π4s+π2s] cycloaddition:



[π4s+π2s] cycloaddition:



In the exo transition state secondary interactions are absent therefore energy will be higher (less-stable) than that of endo transition state. Frontier Molecular Orbital method predicts that in thermally allowed [π4s+π2s] cycloadditions, due to the unfavourable secondary interactions between frontier orbitals, the endo transition state is destabilized leading to the formation of exo product.

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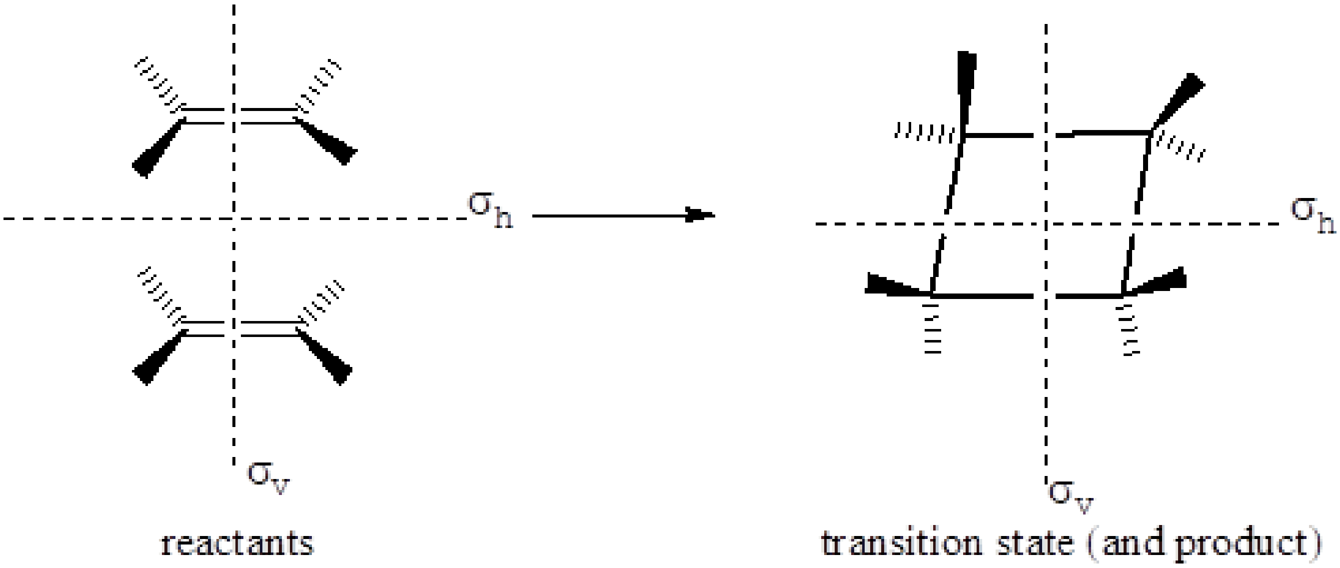
Orbital symmetry correlation diagrams:

Orbital symmetry correlation diagrams can be constructed for supra-supra cycloconditions. The conclusions drawn from the diagram are same as of those derived by Perturbational Molecular Orbital and Frontier Molecular orbital method. However, orbital symmetry correlation diagrams cannot be drawn for supra-antara, antara-supra antara-antara cycloadditions.

Orbital symmetry correlation diagram for [π2s+π2s] cycloadditions:
Example for [π2s+π2s] cycloaddition:



In this reaction two alkene molecules approach one over the other in parallel planes. The reactants, transition state and the product all posses both vertical plane of symmetry (σv) and horizontal plane of symmetry (σh). Therefore, while drawing orbital symmetry correlation diagram for [π2s+π2s] cycloaddition, the symmetry of molecular orbitals of the reactants and product is considered will respect to both vertical plane of symmetry (σv) and horizontal plane of symmetry (σh).

The four pi orbitals of two interacting alkene molecules (ϕ1 to ϕ4) are derived by the bonding and antibonding combinations of π and π* orbitals of two alkenes. Similarly the four sigma orbitals of cyclobutane (ψ1 to ψ4) are obtained by the bonding and antibonding combinations of σ and σ* orbitals of two new sigma bonds, in the product.

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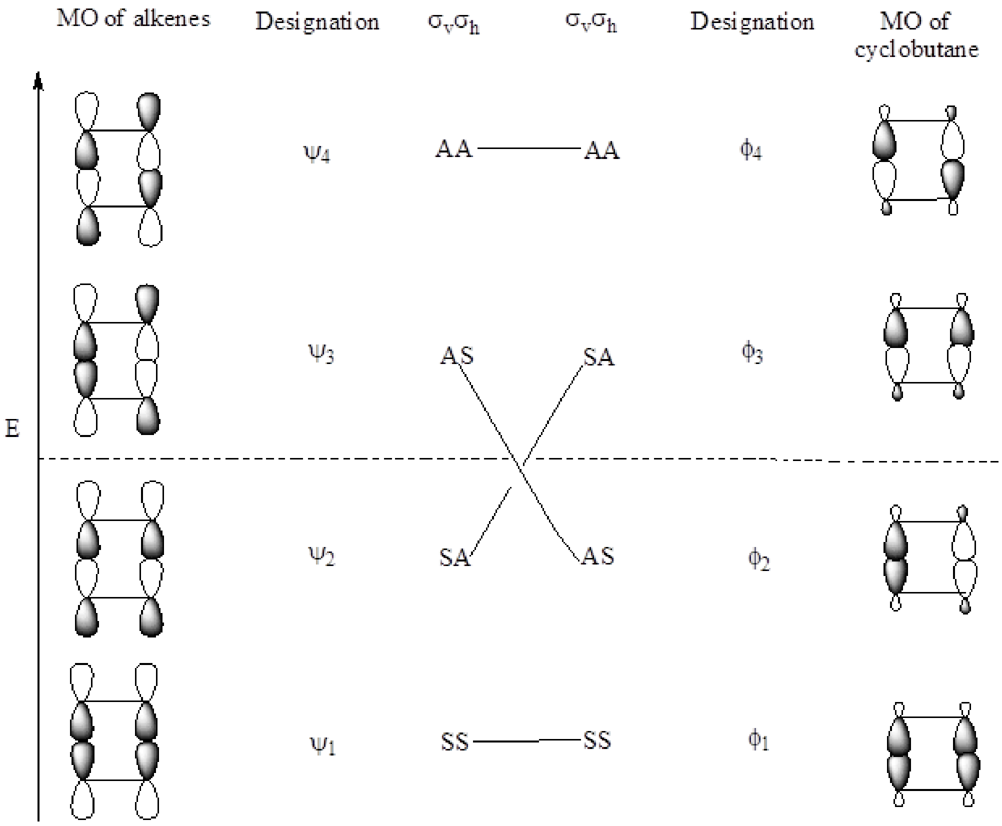


Conclusions from orbitals symmetry correlation diagram for [π2s+π2s] cycloadditions:

I. Bonding molecular orbitals of reactants do not correlate with Bonding molecular orbitals of the product

$$\underset{\text{GS of reactants}}{\psi_1^2\psi_2^2} \longleftrightarrow \underset{\text{UES of product}}{\phi_1^2\phi_3^2}$$

$$\underset{\text{GS of product}}{\phi_1^2\phi_2^2} \longleftrightarrow \underset{\text{UES of reactants}}{\psi_1^2\psi_3^2}$$

In other words

$$\underset{\text{GS of reactants}}{\psi_1^2\psi_2^2} \not\longleftrightarrow \underset{\text{GS of product}}{\phi_1^2\phi_2^2}$$

Therefore, [π2s+π2s] cycloaddition is symmetry forbidden under thermal conditions.

II. First excited state of reactants correlates with the First excited state of product

$$\underset{\text{FES of reactants}}{\psi_1{}^2\psi_2{}^1\psi_3{}^1} \longleftrightarrow \underset{\text{FES of product}}{\phi^2\,\phi_3{}^1\phi_2{}^1 \text{ or } \phi_1{}^2\phi_2{}^1\phi_3{}^1}$$

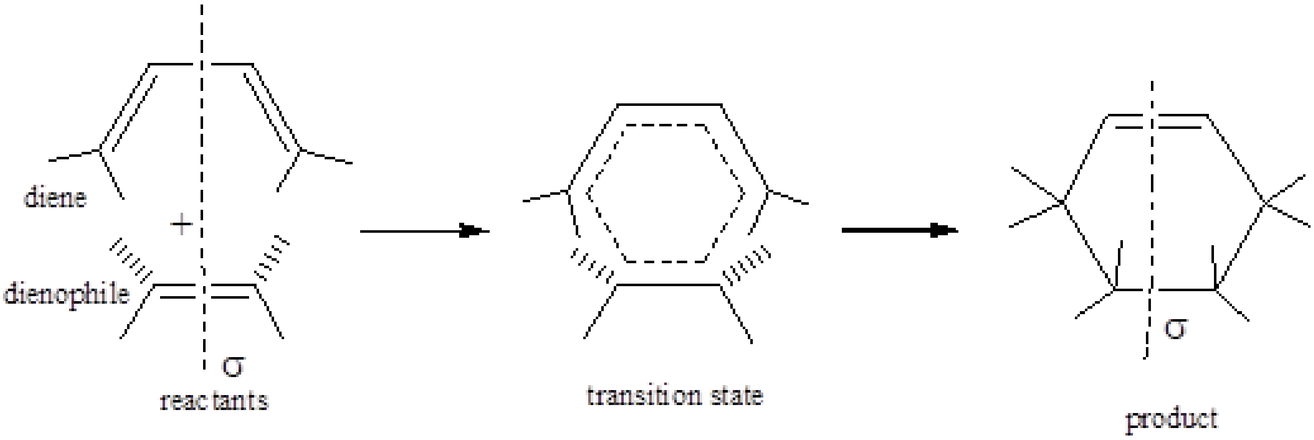
$$\underset{\text{FES of product}}{\phi_1{}^2\phi_2{}^1\phi_3{}^1} \longleftrightarrow \underset{\text{FES of reactants}}{\psi_1{}^2\psi_3{}^1\psi_2{}^1 \text{ or } \psi_1{}^2\psi_3{}^1\psi_3{}^1}$$

In other words

$$\underset{\text{FES of reactants}}{\psi_1{}^2\psi_2{}^1\psi_3{}^1} \longleftrightarrow \underset{\text{FES of product}}{\phi_1{}^2\phi_2{}^1\phi_3{}^1}$$

Therefore, [π2s+π2s] cycloaddition is symmetry allowed under photochemical conditions.

Orbital symmetry correlation diagram for [π4s+π2s] cycloadditions:
Example for [π4s+π2s] cycloaddition:



In this reaction, the reactants, transition state and product all posses only vertical plane of symmetry (σv). Therefore, the molecular orbitals of reactants and products are classified with respect to vertical plane of symmetry (σv). in this transformation we have to consider the symmetry of six molecular orbitals of reactants (ψ1 to ψ4 of diene and π and π* of dienophile) and the symmetry of six molecular orbitals of the product that is cyclohexene derivative (ϕ1 to ϕ4 of the two new sigma bonds and π and π* of the double bond).

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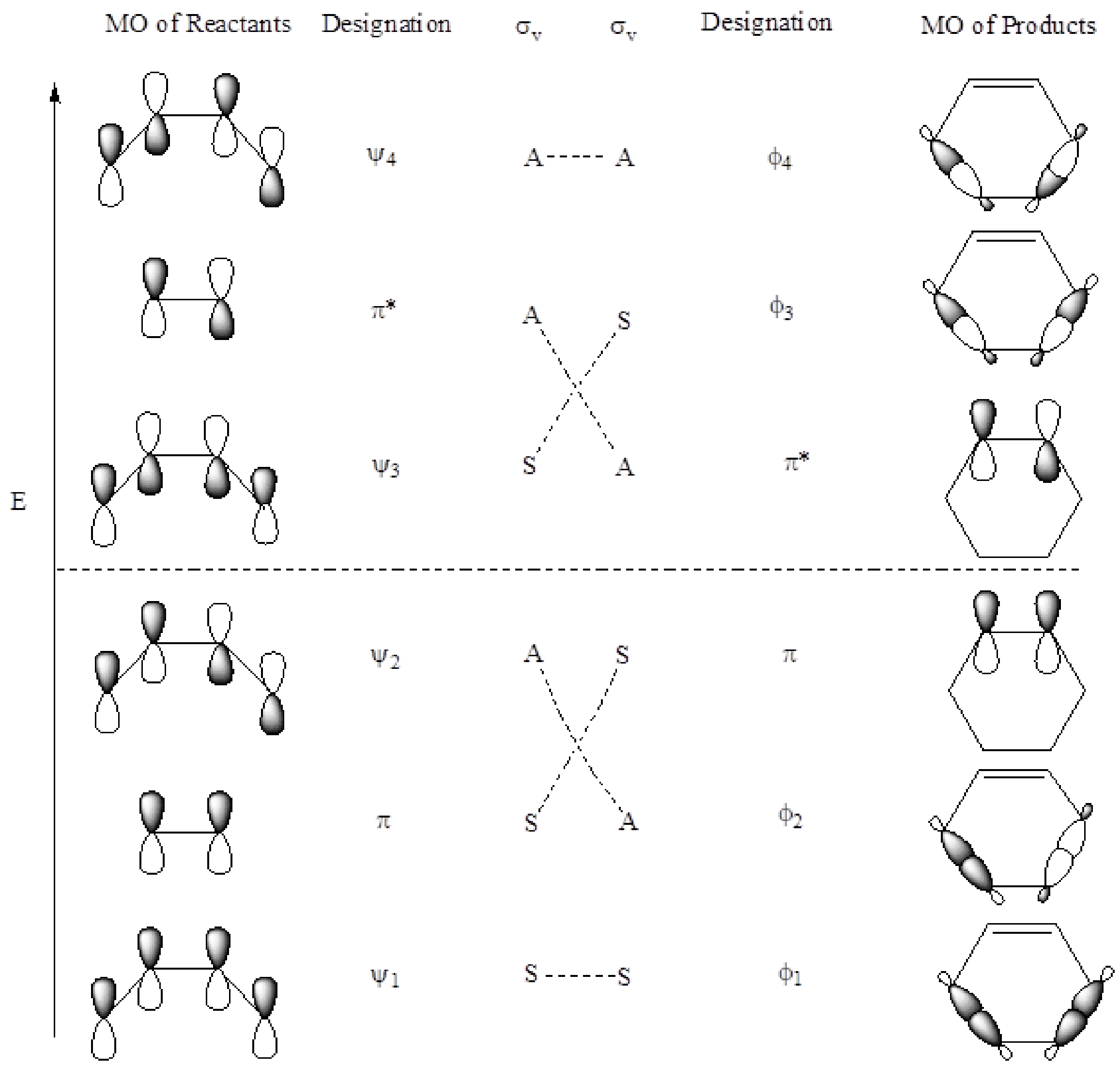

Orbital symmetry correlation diagram for [π4s+π2s] cycloaddition

i. Bonding molecular orbitals of the reactants correlates with bonding molecular orbitals of the product.

$$\underset{\text{GS of reactant}}{\psi_1^2\pi^2\psi_2^2} \longrightarrow \underset{\text{GS of reactant}}{\phi_1^2\pi^2\phi_2^2 \text{ or } \phi_1^2\phi_2^2\pi^2}$$

$$\underset{\text{GS of product}}{\phi_1^2\phi_2^2\pi^2} \longrightarrow \underset{\text{GS of reactant}}{\psi_1^2\psi_2^2\pi^2 \text{ or } \psi_1^2\pi^2\psi_2^2}$$

In other words,

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$$\psi_1^2\pi^2\psi_2^2 \longleftrightarrow \phi_1^2\phi_2^2\pi^2$$

$\therefore$ $[\pi^4{}_s+\pi^2{}_s]$ cycloaddition is symmetry allowed under thermal conditions.

i. First excited state of reactants does not correlates with the first excited state of products.

$$\psi_1^2\pi^2\psi_2^1\psi_3^1 \longrightarrow \phi_1^2\pi^2\phi_2^1\phi_3^1 \text{ or } \phi_1^2\phi_2^1\pi^2\phi_3^1$$

FES of reactant — UES of product

$$\phi_1^2\phi_2^2\pi^1\pi^{*1} \longrightarrow \psi_1^2\psi_2^2\pi^1\pi^{*1} \text{ or } \Psi_1^2\pi^1\Psi_2^2\pi^{*1}$$

FES of product — UES of reactants

In other words,

$$\psi_1^2\pi^2\psi_3^1\psi_3^1 \not\longleftrightarrow \phi_1^2\phi_2^2\pi^1\pi^{*1}$$

FES of reactant — FES of product

[π4s+π2s] cycloaddition is symmetry forbidden under photochemical conditions.

Sigmatropic Reactions:

Perturbational Molecular Orbital (PMO) method:

This is simpler method, following are the steps in the application of Perturbational Molecular Orbital method for the analysis of sigmatropic reactions

i.Depict the transition state of a stereochemical mode of any [i,j] shift, a cyclic array of atomic orbitals. In the transition state, show the transition state bond in the substrate as pairs of p-orbitals, the migrating C-H bond as a p orbital and s orbital of H. Assign one electron to each orbital.

ii. Assign signs in the wave functions in the transition state in the best manner for overlap.

iii. Connect the number of nodes in the transition state.

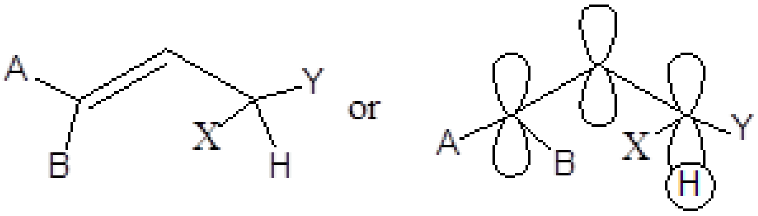
iv. Count the number of electrons participating in the reaction.

v. Classify the transition state as aromatic or antiaromatic.

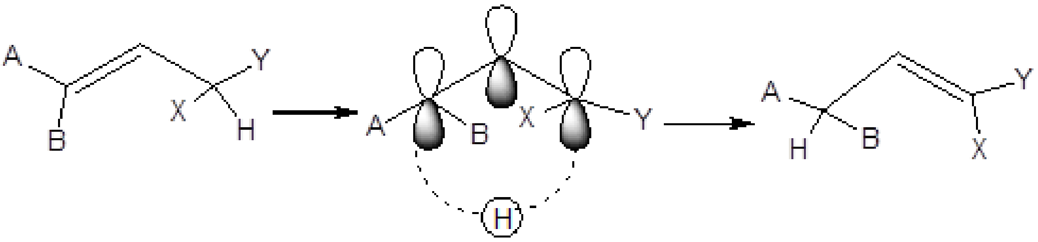
vi. Predict the allowed reaction conditions for [i,j] shift.

[i,j] sigmatropic shift of a H involving 4nπe-:
Ex: [1,3] sigmatropic shift of a H

For writing the transition state, the double bond in the substrate is shown as a pair of p-orbitals and the migrating C-H bond as a p-orbital of C and an s-orbital of H. Four electrons participate in the reaction.



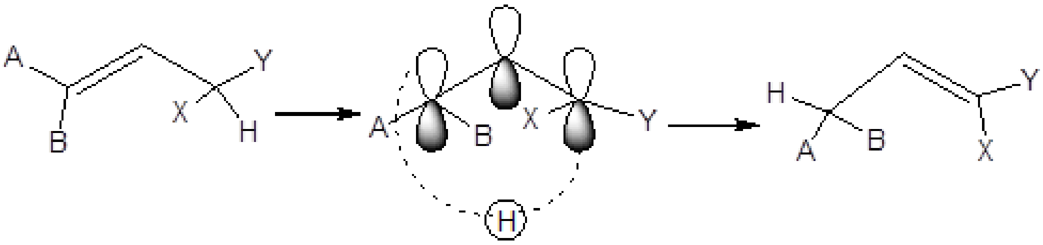
a) [1,3] sigmatropic shift of a H



transition state
zero node
4e$^-$ or 4πe$^-$ (n=1)
Huckel anti aromatic transition state

Therefore, [1,3] suprafacial shift of a H is photochemically allowed and thermally forbidden

b)[1,3] Antarafacial shift of H



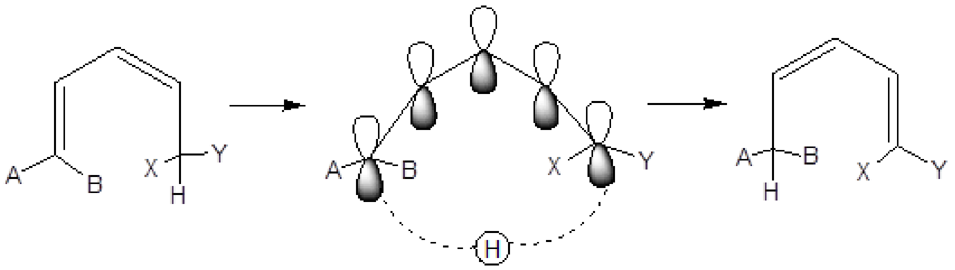
transition state
one node
4πe$^-$ (n=1)
Mobius aromatic transition state

Therefore, [1,3] antarafacial shift of H is thermally allowed and photochemically forbidden.

[i,j] sigmatropic shift of H involving 4n+2πe-:

a) [1,5] sigmatropic shift of H

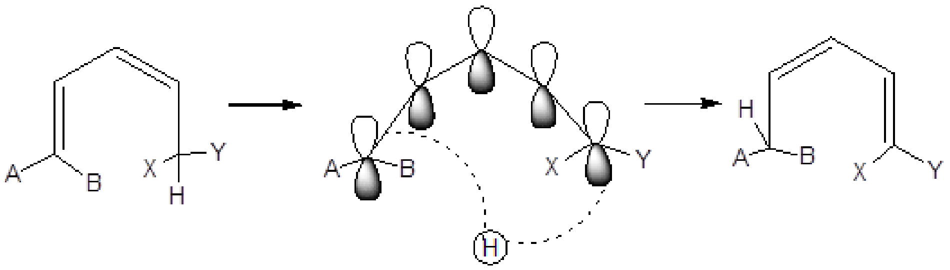
Two double bonds are shown as four p orbitals, the migrating C-H bond as a p orbital of carbon and as an s orbital of H. six electrons are participating in the reaction.



transition state
zero node
$6e^-$ or $4n+2e^-$ (n=1)
Huckels aromatic transition state

Therfore, [1,5] suprafacial shift of a H is thermally allowed and photochemically forbidden

b) [1,5] Antarafacial shift of H



transition state
one node
$6e^-$ or $4n+2e^-$ (n=1)
Mobius anti aromatic transition state

Therefore, [1,5] antarafacial shift of a H is photochemically allowed and thermally forbidden.

[i,j] Sigmatropic shift of a group involving 4ne-:

[1,3] sigmatropic shift of a group:

For writing the transition state, the double bond and the migrating C-C bond in the substrate are shown as two pairs of p orbitals. Therefore, four electrons participates in the reaction.

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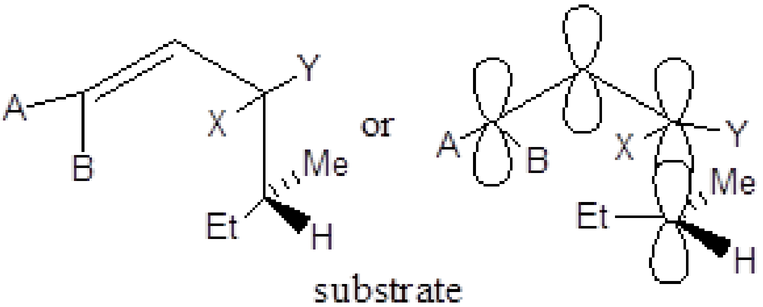
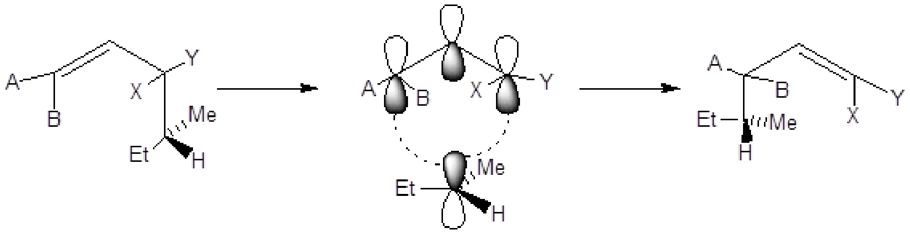


substrate

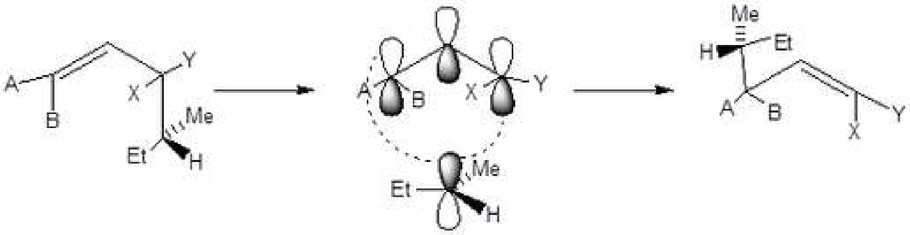
a) [1,3] suprafacial shift of a group with retention of configuration:



transition state
zero node
4e$^-$ or 4ne$^-$(n=1)
Huckel anti aromatic transition state

Therefore, [1,3] suprafacial shift of a group with retention of configuration is photochemically allowed and thermally forbidden.

b) [1,3] antarafacial shift of a group with retention of configuration:



transition state
one node
4e$^-$or4ne$^-$(n=1)
Mobius aromatic transition state

Therefore, [1,3] antarafacial shift of a group with retention of configuration is thermally allowed photochemically forbidden.

c) [1,3] suprafacial shift of a group with inversion of configuration:

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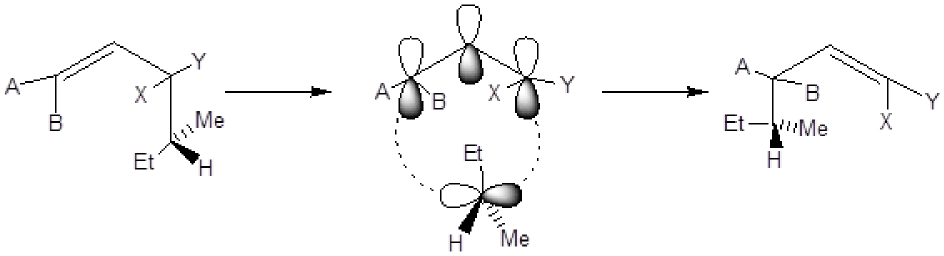
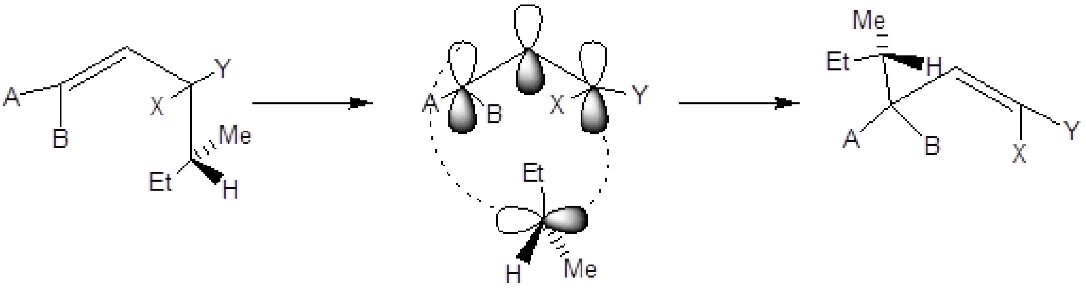


transition state
one node
$4e^-$ or $4ne^-(n=1)$
Mobius aromatic transition state

Therefore, [1,3] suprafacial shift of a group with inversion of configuration is thermally allowed photochemically forbidden.

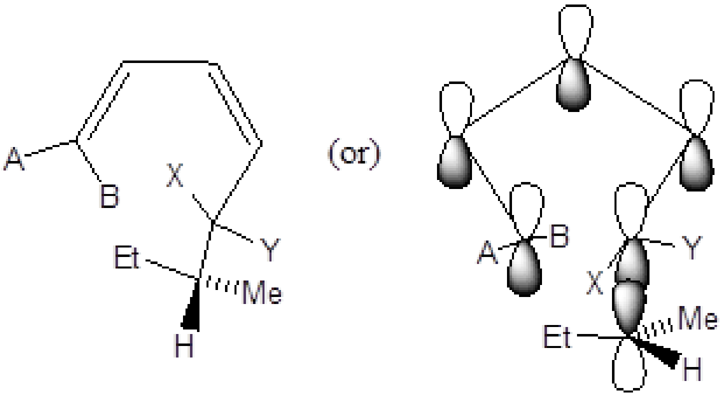
d) [1,3] antarafacial shift of a group with inversion of configuration



transition state
zero node
$4e^-$ or $4ne^-(n=1)$
Huckels anti aromatic transition state

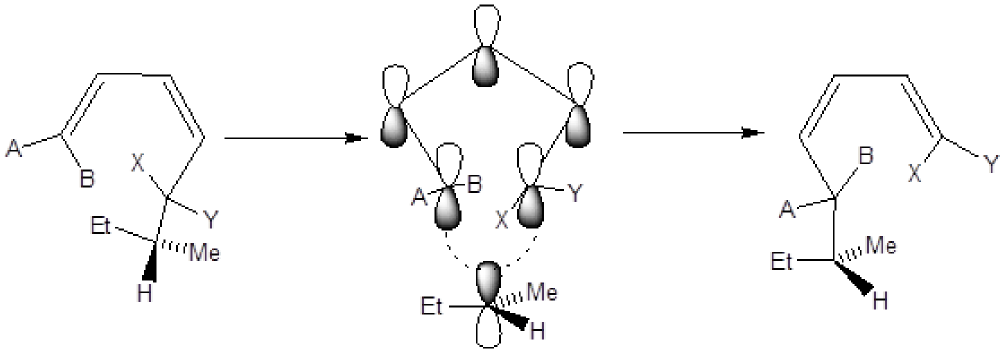
Therefore, [1,3] antarafacial shift of a group with inversion of configuration is photochemically allowed thermally forbidden.

[i,j] Sigmatropic shift of a group involving 4n+2e-:



Two double bonds in the substrate are shown as four p orbitals, the migrating C-C bond is shown as p orbitals. Six e- participate in the reaction.

a) [1,5] suprafacial shift of a group with retention of configuration



transition state

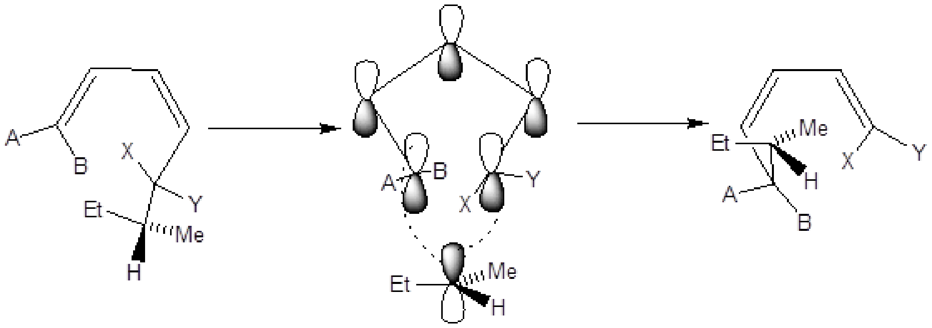
zero node

6e$^-$ or 4n+2e$^-$ (n=1)

Huckel aromatic transition state

Therefore, [1,5] suprafacial shift of a group with retention of configuration is thermally allowed and photochemically forbidden.

b) [1,5] antarafacial shift of a group with retention of configuration:



transition state

one node

6e$^-$ or 4n+2e$^-$ (n=1)

Mobius anti aromatic transition state

Therefore, [1,5] antarafacial shift of a group with retention of configuration is allowed photochemically and thermally forbidden.

c) [1,5] suprafacial shift of a group with inversion of configuration:

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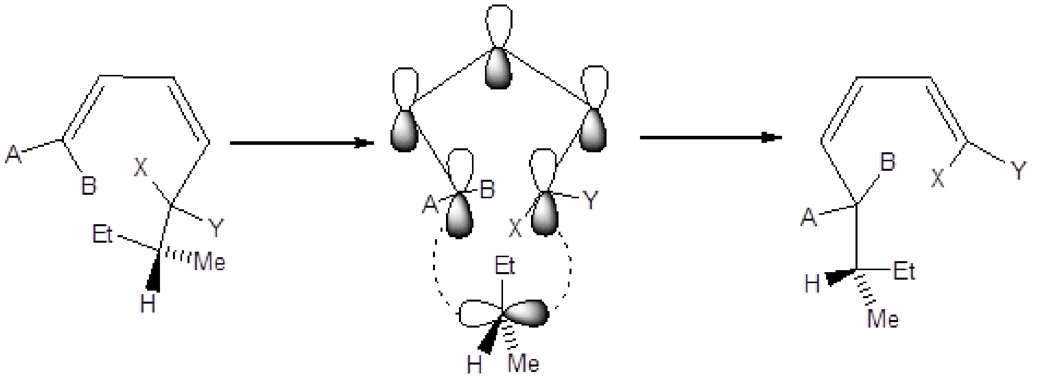
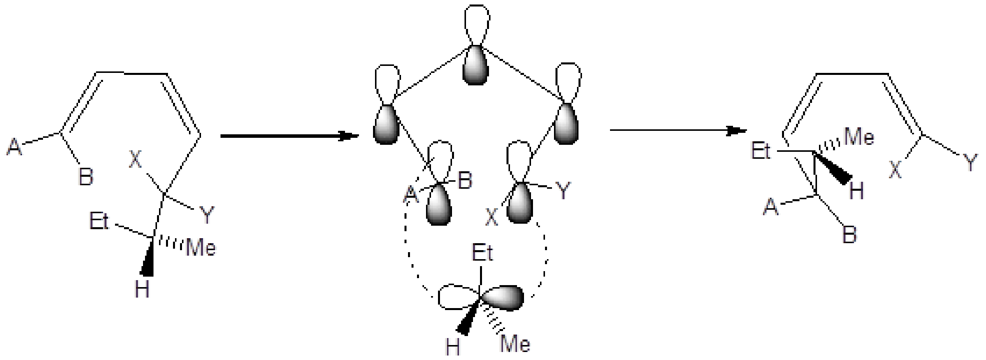


transition state
one node
$6e^-$ or $4n+2e^-$ (n=1)
Mobius anti aromatic transition state

Therefore, [1,5] suprafacial shift of a group with inversion of configuration is photochemically allowed and thermally forbidden.

d) [1,5] antarafacial shift of a group with inversion of configuration:



transition state
zero node
$6e^-$ or $4n+2e^-$ (n=1)
Huckels aromatic transition state

Therefore, [1,5] antarafacial shift of a group with inversion of configuration is thermally allowed photochemically forbidden.

[i,j] Sigmatropic shift where both i and j are greater than one:

[3,3], [3,5] and [5,5] shifts are some of the examples of this group of reactions. We shall discuss the [3,3] sigmatropic shifts. In [3,3] sigmatropic shifts, [i,j] corresponds to 6e- or 4n+2e- (n=1).

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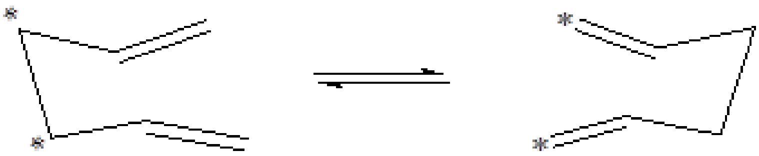
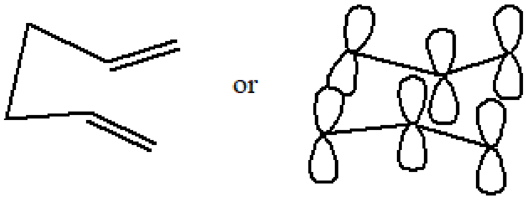
[3,3] Sigmatropic shifts:



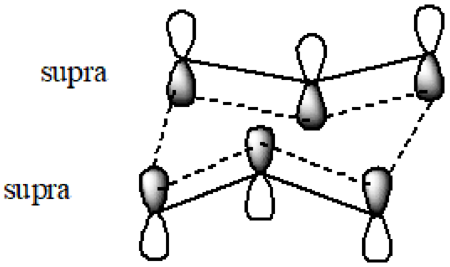
1,5-hexadiene
(with c^{14} label at 3,4-positions)

1,5-hexadiene
(with c^{14} label at 1,6-positions)

Stereochemically there can be four types of [3,3] shifts viz supra-supra, supra-antara, antara-supra and antara-antara shifts. In the transition state of [3,3] shifts, two double bonds are shown as four p orbitals and the migrating C-C bond as a pair of p orbitals. So, total six electrons participate in this reaction.



a) [3,3] supra-supra shift

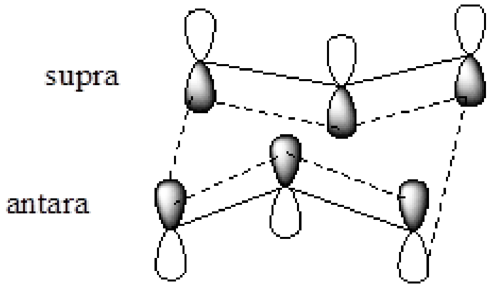


transition state
zero node
$6e^-$
Huckel aromatic transition state

Therefore, [3,3] supra-supra shift is thermally allowed and photochemically forbidden.

Cope rearrangement and Claisen rearrangement are examples of thermally allowed of [3,3] supra-supra shifts. The transition state for the thermally allowed supra-supra [3,3] sigmatropic can have two configurations, chair and boat. The chair shape transition state is favoured over the boat shape transition state.

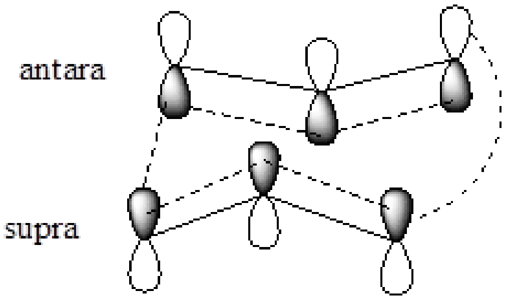
b) [3,3] supra-antara shift :



transition state
one node
$6e^-$
Mobius anti aromatic transition state

Therefore, [3,3] supra-antara is photochemically allowed and thermally forbidden.

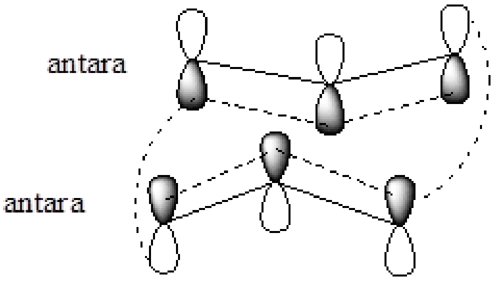
c) [3,3] antara-supra shift:



transition state
one node
$6e^-$
Mobius anti aromatic transition state

Therefore, [3,3] antara-supra shift is photochemically allowed and thermally forbidden.

d) [3,3] antara-antara shift:



transition state
zero node
$6e^-$
Huckel aromatic transition state

Therefore, [3,3] antara-antara shift is thermally allowed and photochemicallyforbidden.

Identical results are obtained in [5,5] sigmatropic shifts when (i+j) corresponds to 10e- (4n+2(n=2)), where as in [3,5] sigmatropic shifts (where i+j=8 or 4n(n=2), exactly opposite conclusions are derived.

Selection rules for sigmatropic reactions of order (i,j) by PMO method

Reaction	No. of in the T.S	Stereochemistry		Reaction conditic	
[1,3] shift of H	4ne	supra	-	hυ	D
	4ne	antara	-	D	hυ
[1,5] shift of H	4n+2e-	supra	-	D	hυ
	4n+2e-	antara	-	hυ	D
[1,3] shift of group	4ne-	supra	Retention	hυ	D
	4ne-	antara	Retention	D	hυ
	4ne-	supra	Inversion	D	hυ
	4ne-	antara	Inversion	hυ	D
[1,5] shift of group	4n+2e-	supra	Retention	D	hυ
	4n+2e-	antara	Retention	hυ	D
	4n+2e-	supra	Inversion	hυ	D
	4n+2e-	antara	Inversion	D	hυ
[3,3] sigmatriopic shift	4n+2e	supra-supra	-	D	hυ
	4n+2e	supra-antara	-	hυ	D
	4n+2e	antara-supra	-	hυ	D
	4n+2e	antara-antara	-	D	hυ

Frontier molecular orbital (FMO) method

In this approach it is assumed that the migrating bond undergoes homolytic cleavage, resulting in the formation of a pair of radicals.

[i,j] Sigmatropic shift of an H involving 4ne-:

Ex: In [1,3] Sigmatropic shift of H, the substrate is considered as an allylradical (π-system) and a H atom (migrating species).

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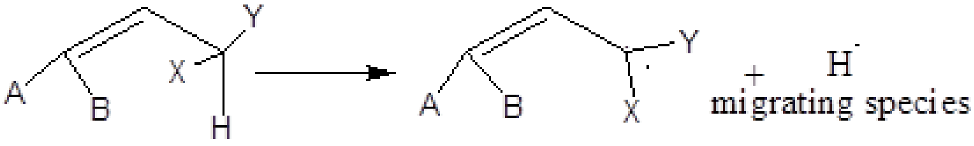
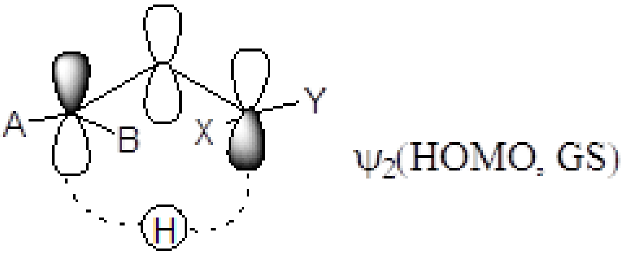


Under thermal conditions, the symmetry of HOMO of the π-system in ground state and under photochemical conditions, the symmetry of HOMO of the π-system in first excited state are examined. Under both the conditions the symmetry of HOMO of the migration species in the ground state is considered. If the interaction between the HOMO of two species in a sigmatropic reaction leads to bonding interaction, the reaction is symmetry allowed when the interaction is antibonding, the reaction is symmetry forbidden. The conclusions obtained by the applications of Frontier Molecular Orbital method to various sigmatropic shifts, are same as those derived by Perturbational Molecular Orbital method.

In [1,3] Sigmatropic shift of a H, Under thermal conditions ψ2 transition state the HOMO of allyl radical in ground state and ψ3 is the HOMO in the first excited state.

a). [1,3] suprafacial shift of a H:

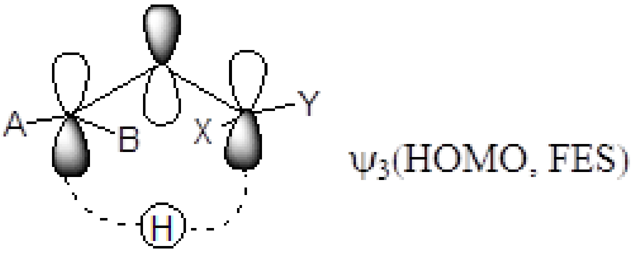
i)Under thermal conditions:



antibonding interaction

Therefore, [1,3] suprafacial shift of H is thermally forbidden.

ii) Under photochemical conditions:



bonding interaction

Therefore, [1,3] suprafacial shift of H is photochemically allowed.

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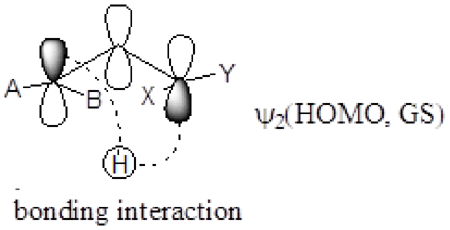
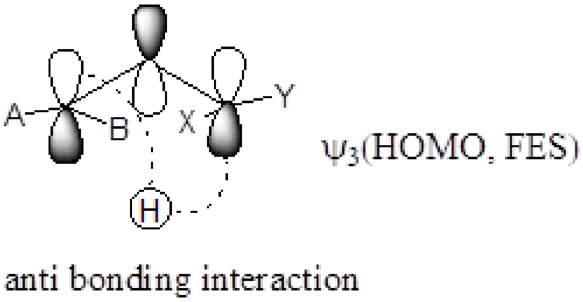
b). [1,3] antarafacial shift of a H:

i) Under thermal conditions



Therefore, [1,3] antarafacial shift of H is thermally allowed.

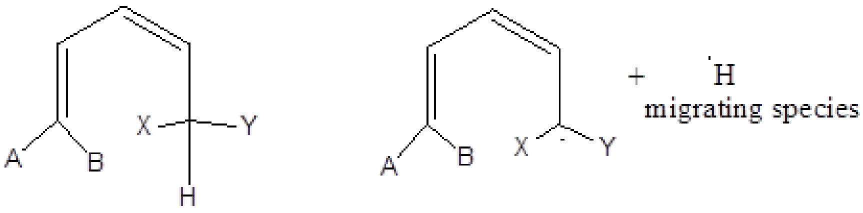
ii) Under photochemical conditions



Therefore, [1,3] antarafacial shift of H is photochemically forbidden.

[i, j] sigmatropic shift of a H involving 4n+2e-:

Ex: In [1,5] sigmatropic shift of H, the substrate is considered as an 2,4-pentadienyl radical (π-system) and a H atom (migrating species).



Under thermal conditions, the symmetry of HOMO of the π-system in ground state and under photochemical conditions, the symmetry of HOMO of the π-system in first excited state are examined. Under both the conditions the symmetry of HOMO of the migration species in the ground state is considered. If the interaction between the HOMO of two species in a sigmatropic reaction leads to bonding interaction, the reaction is symmetry allowed when the interaction is antibonding, the reaction is symmetry forbidden. The conclusions obtained by the applications of

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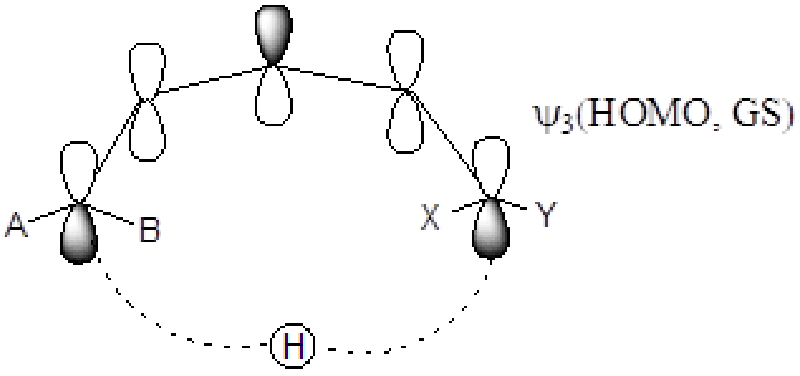
Frontier Molecular Orbital method to various sigmatropic shifts, are same as those derived by Perturbational Molecular Orbital method.

In [1,5] sigmatropic shift of a H, Under thermal conditions ψ3 transition state the HOMO of allyl radical in ground state and ψ4 is the HOMO in the first excited state.

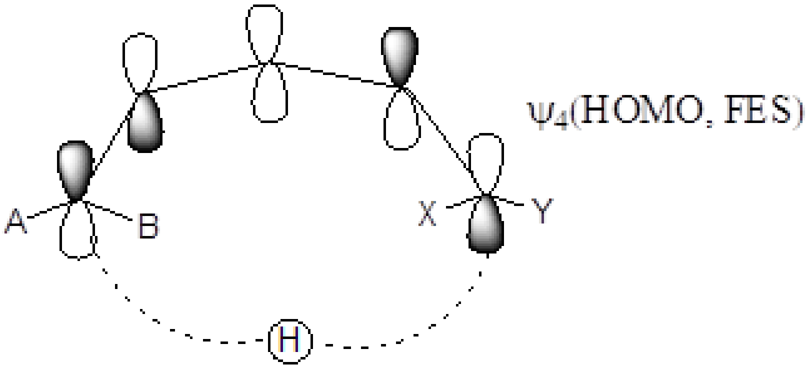
a) [1,5] Suprafacial shift of a H:
i) Under thermal conditions:



bonding interaction

Therefore, [1,5] suprafacial shift of H is thermally allowed

ii) Under photochemical conditions:



anti bonding interaction

Therefore,[1,5] suprafacial shift of H is photochemically forbidden.

b) [1,5] antarafacial shift of a H:

i) Under thermal conditions:

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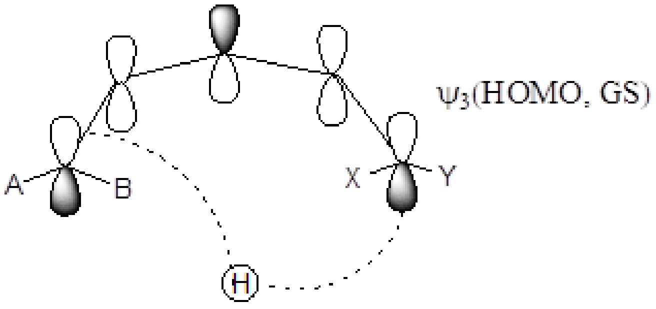
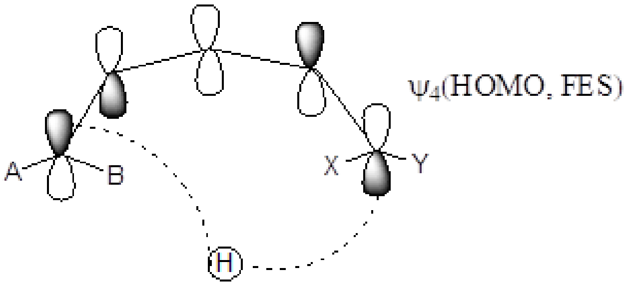


anti bonding interaction

Therefore, [1,5] antarafacial shift of H is thermally forbidden.

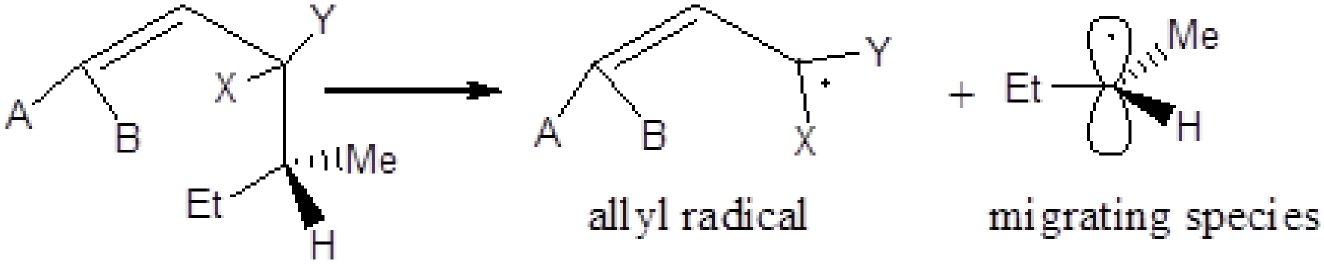
ii) Under photochemical conditions:



bonding interaction

Therefore, [1,5] antarafacial shift of H is photochemically allowed.

[i,j] Sigmatropic shift of a group involving 4ne-:
Ex: In [1,3] sigmatropic shift of group, the substrate is considered as an allylradical (π-system) and a goup (migrating species).



a) [1,3] Suprafacial shift of a group with retention of configuration:
i. Under thermal conditions

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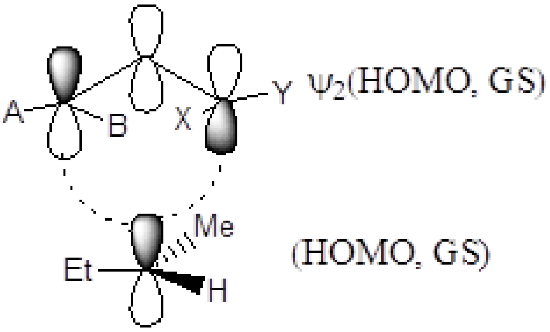
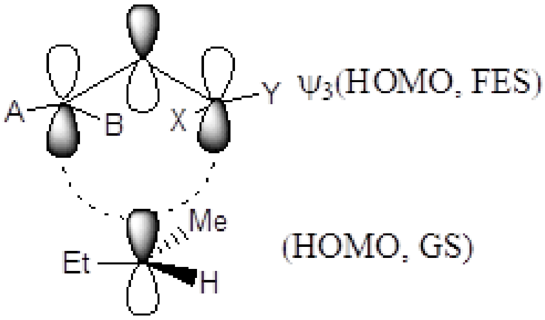


antibonding interaction

Therefore, [1,3] suprafacial shift of a group with retention of configuration under thermal conditions is forbidden.

iii. Under phototchemical conditions:

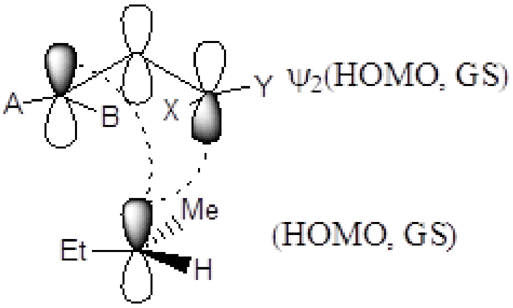


bonding interaction

Therefore, [1,3] suprafacial shift of a group with retention of configuration under photochemical conditions is allowed.

b) [1,3] antarafacial shift of a group with retention of configuration:

i. Under thermal conditions:



bonding interaction

Therefore, [1,3] antarafacial shift of a group with retention of configuration under thermal conditions is allowed.

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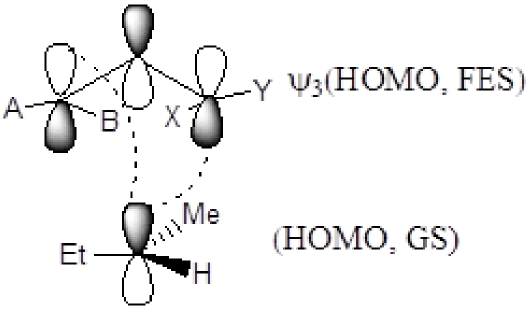
ii. Under photochemical conditions:

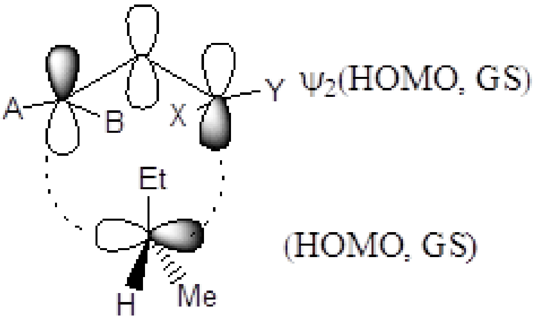


anti bonding interaction

Therefore, [1,3] antarafacial shift of a group with retention of configuration under photochemical conditions is forbidden.

c). [1,3] suprafacial shift of a group with inversion of configuration:

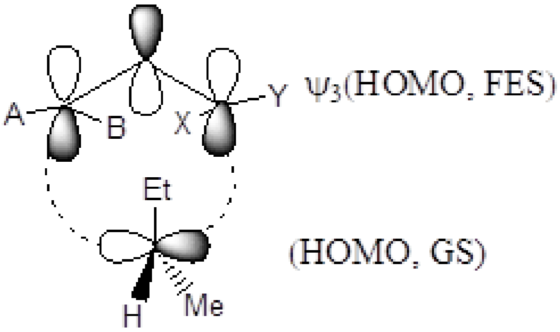
i. Under thermal conditions:



bonding interaction

Therefore, [1,3] suprafacial shift of a group with inversion of configuration under thermal conditions is allowed.

ii. Under photochemical conditions:



anti bonding interaction

Therefore, [1,3] suprafacial shift of a group with inversion of configuration under photochemical conditions is forbidden.

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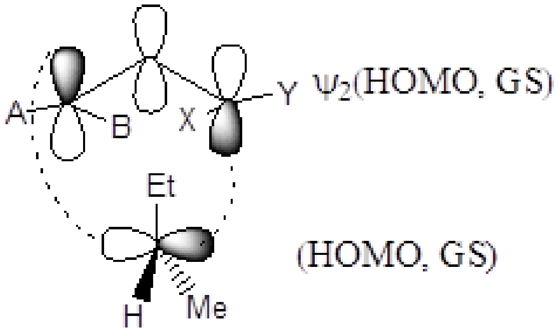
d). [1,3] antarafacial shift of a group with inversion of configuration

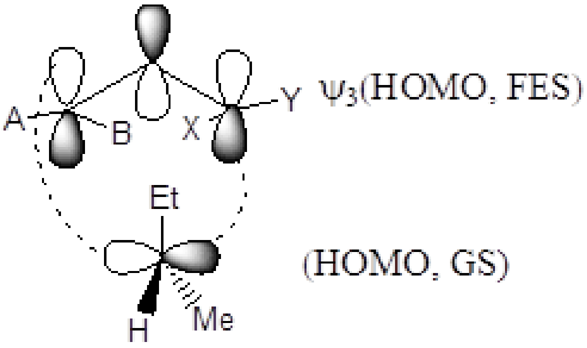
i. Under thermal conditions:



anti bonding interaction

Therefore, [1,3] antarafacial shift of a group with inversion of configuration under thermal conditions is forbidden.

ii. Under photochemical conditions:

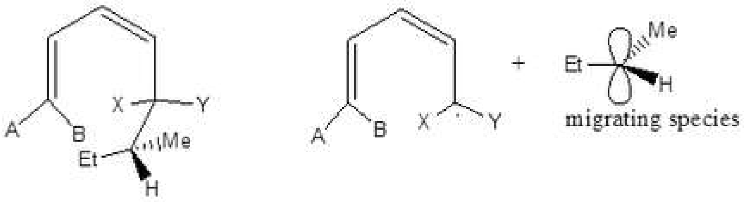


bonding interaction

Therefore, [1,3] antarafacial shift of a group with inversion of configuration under photochemical conditions is allowed.

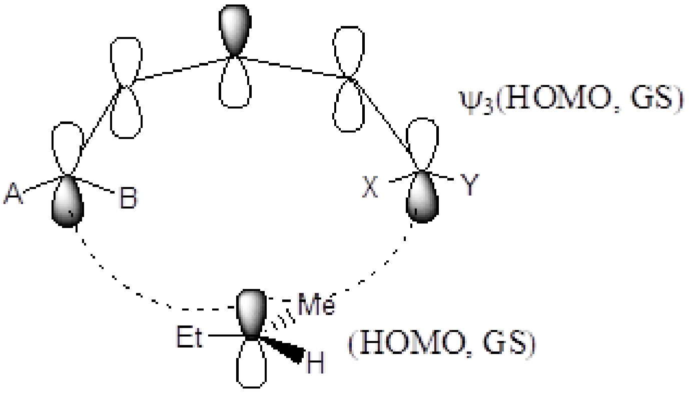
[i,j] Sigmatropic shift of a group involving 4n+2e-:

Ex: In [1,5] sigmatropic shift of group, the substrate is considered as an 2,4-pentadienyl radical (π-system) and a group (migrating species).



a). [1,5] suprafacial shift of a group with retention of configuration:

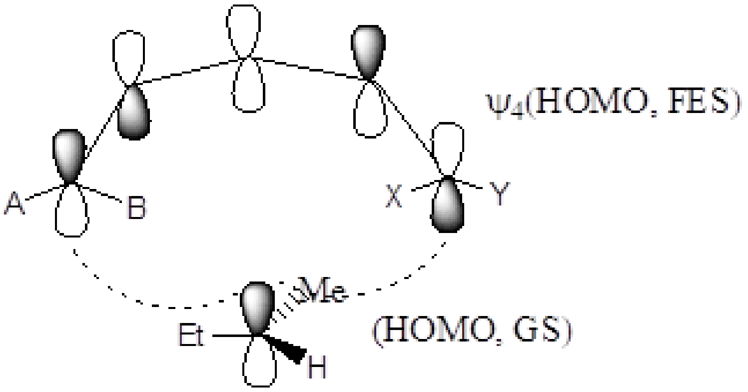
i. Under thermal conditions



bonding interaction

Therefore, [1,5] suprafacial shift of a group with retention of configuration is thermally allowed.

iii. Under photochemical conditions:



anti bonding interaction

Therefore, [1,5] suprafacial shift of a group with retention of configuration is photochemically forbidden.

b). [1,5] antarafacial shift of a group with retention of configuration:

i. Under thermal conditions:

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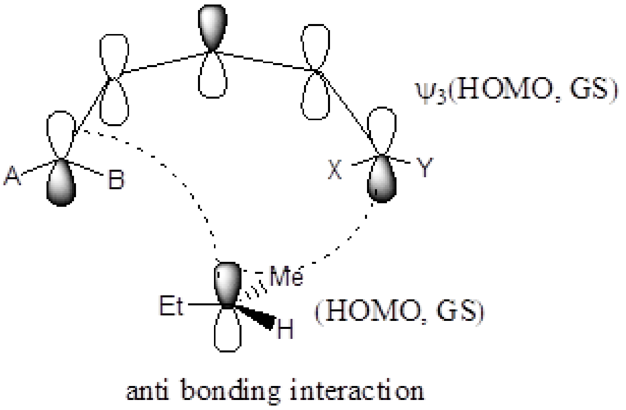
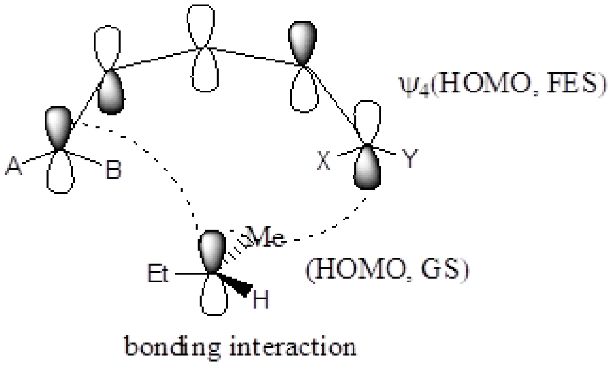


anti bonding interaction

Therefore, [1,5] antarafacial shift of a group with retention of configuration is thermally forbidden.

iii. Under photochemical conditions:

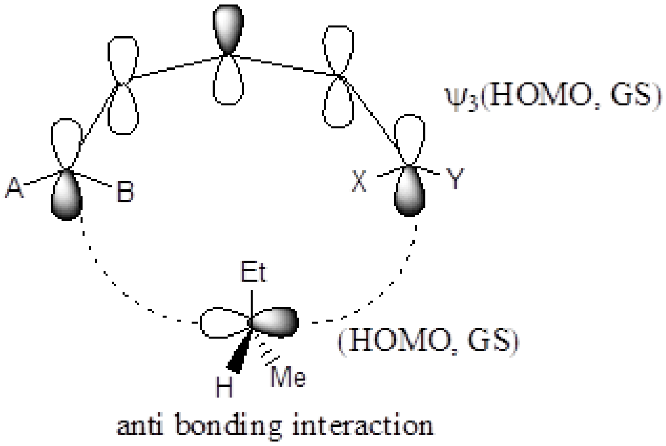


bonding interaction

Therefore, [1,5] antarafacial shift of a group with retention of configuration is photochemically allowed.

c). [1,5] suprafacial shift of a group with inversion of configuration:

i. Under thermal conditions :



anti bonding interaction

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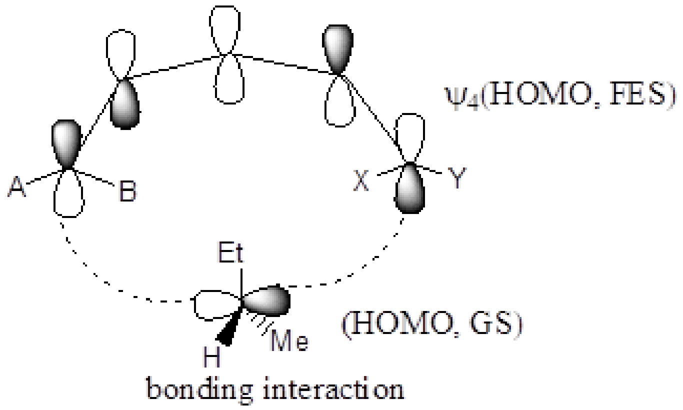
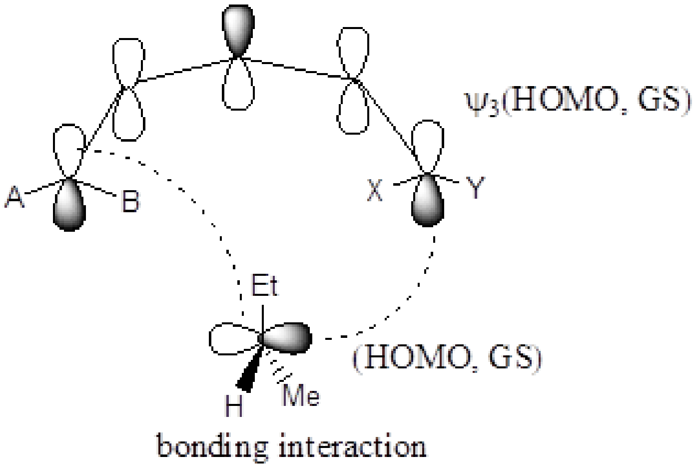
Therefore, [1,5] suprafacial shift of a group with inversion of configuration is thermally forbidden.

ii. Under photochemical conditions:



Therefore, [1,5] suprafacial shift of a group with inversion of configuration is photochemically allowed.

d). [1,5] antarafacial shift of a group with inversion of configuration:
i. Under thermal conditions:



Therefore, [1,5] antarafacial shift of a group with inversion of configuration is thermally allowed.

iii. Under photochemical conditions:

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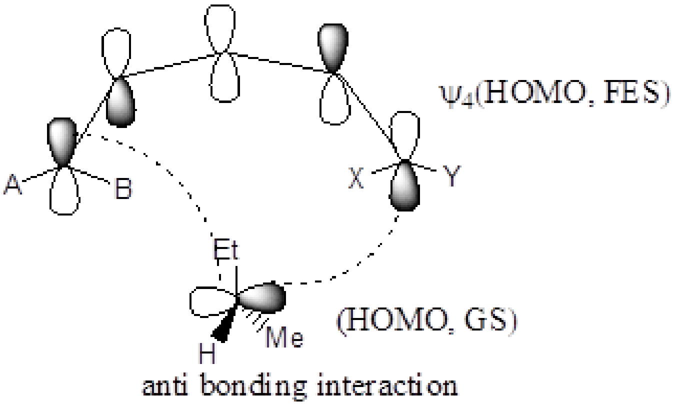
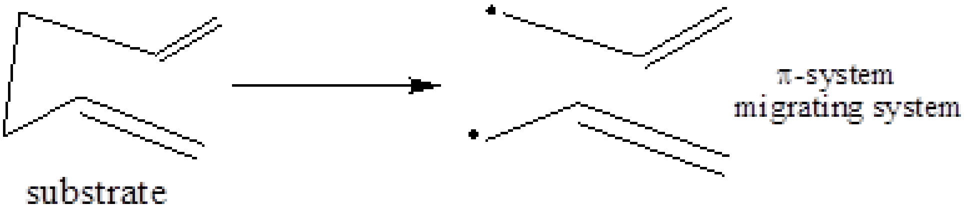


Therefore, [1,5] antarafacial shift of a group with inversion of configuration is photochemically forbidden.

[i,j] sigmatropic shifts where both i and j are greater than one:

[3,3] Sigmatropic shifts:

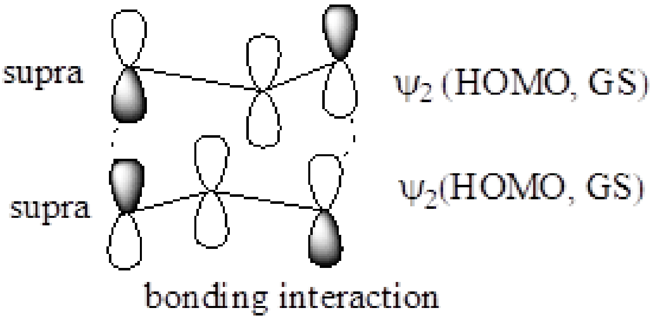
Ex



In [3,3] sigmatropic shifts,the substrate may be assumed to be homolytically cleaved into two allyl radicals, one of which is considered as π system and the other as migrating group. In the ground state of allyl radical ψ2 is the HOMO and in the first excited state ψ3 is the HOMO.

a) [3,3] supra-supra shift:

i. Under thermal conditions:



Therefore, [3,3] supra-supra shift is thermally allowed.

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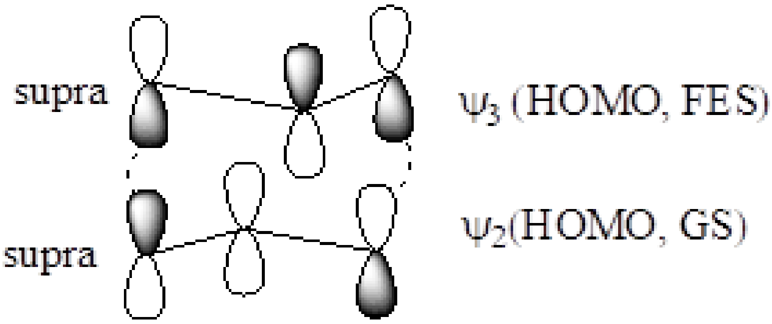
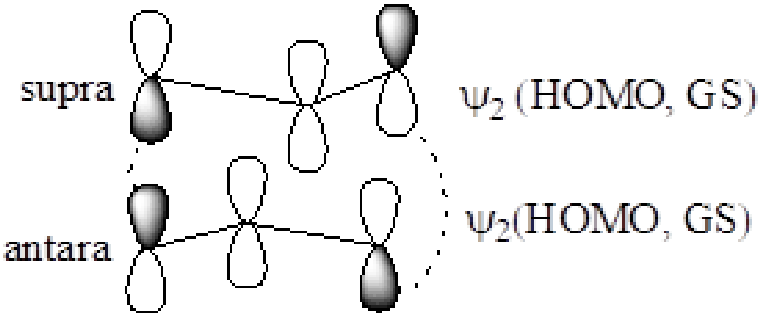


anti bonding interaction

Therefore, [3,3] supra-supra shift is photochemically forbidden.

b) [3,3] supra-antara shift :

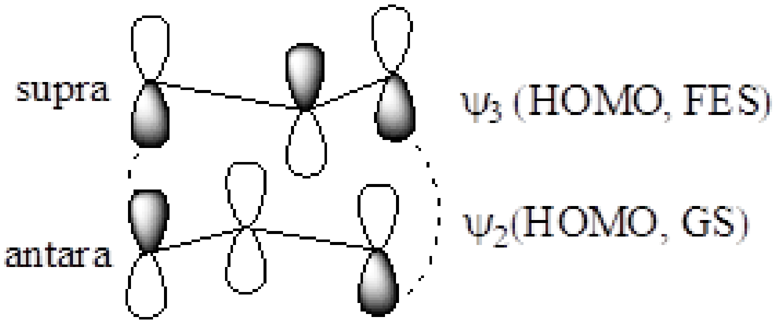
i. Under thermal conditions:



anti bonding interaction

Therefore, [3,3] supra-antara shift is thermally forbidden.

iii. Under photochemical conditions:



bonding interaction

Therefore, [3,3] supra-antara shift is photochemically allowed.

c) [3,3] antara-supra shift:

i. Under thermal conditions:

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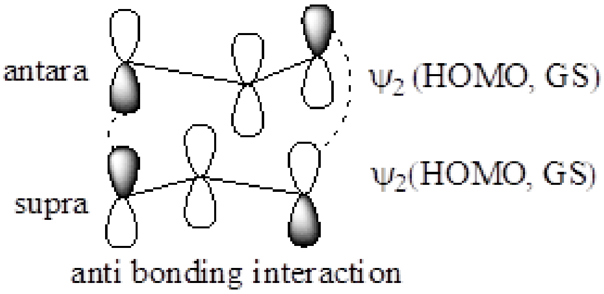
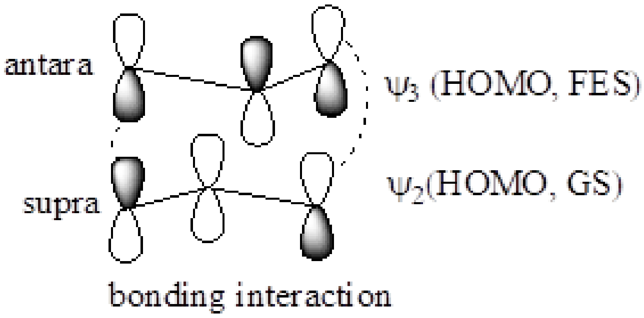


Therefore, [3,3] antara-supra shift is thermally forbidden.

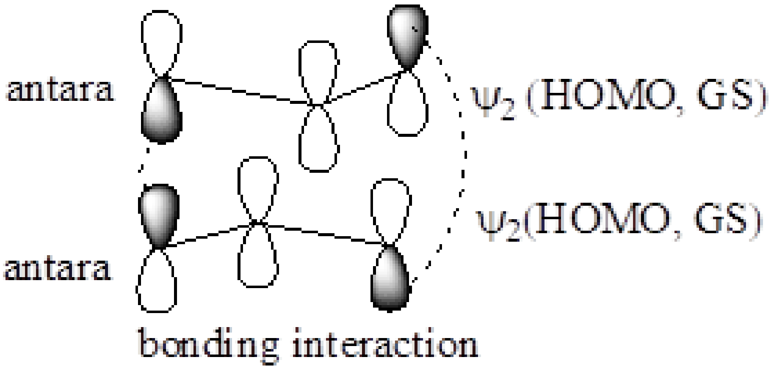
ii. Under photochemical conditions:



Therefore, [3,3] antara-supra shift is photochemically allowed.

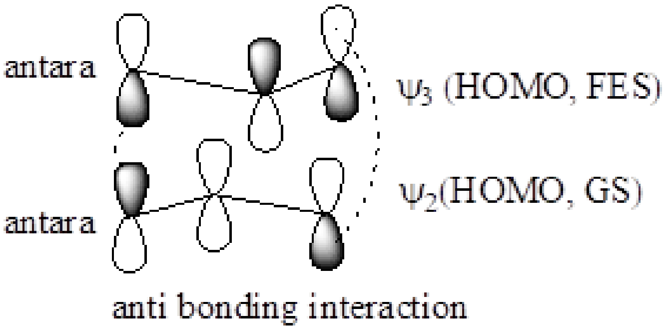
d) [3,3] antara-antara shift:

i. Under thermal conditions:



Therefore, [3,3] antara-antara shift is thermally allowed.

ii. Under photochemical conditions:



Therefore, [3,3] antara-antara shift is photochemically forbidden.

Aromaticity

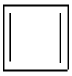
Aromatic compounds are planar, monocyclic and polycyclic conjugated polyenes containing (4n+2)π electrons (n=0,1,2,3….) which are delocalized in the conjugated frame work. The main characteristic features of aromatic compounds are:

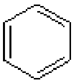
1. Greater thermodynamic stability compared to their corresponding acyclic conjugated polyenes and cyclic conjugated polyenes with 4nπ electrons.

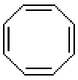
2. Their chemical reactivity characterized by substitution reactions rather than additions, with retention of the aromatic ring system and

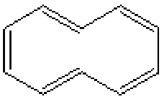
3. In their 1H-NMRspectrum, the aromatic protons are desheilded viz benzene, the six protons resonate at δ7.2 down field compared to acyclic olefins and conjugated polyenes which resonate in the region of δ5.0 – 6.0.

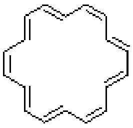
Completely conjugated monocyclic polyenes of the general formula CnHn are also known as annulenes.


[4] annulene

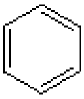

[6] annulene

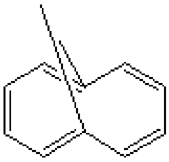

[8] annulene

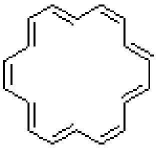

[10] annulene


[18] annulene

Planar, monocyclic conjugated polyenes having (4n+2) electrons in the conjugated system 9n=0,1,2,3) are thermodynamically more stable than corresponding acyclic conjugated polyenes are said to be aromatic. The delocalization of the π electrons in these rings is the reason for their greater stability in benzene, 1,6-methano-[10]-annulene.


[6] annulene


1,6-methano-[10]-annulene


[18] annulene

In contrast, planar cyclic monocyclic conjugated polyenes having 4n electrons in the conjugated system eg; [4] annulene, [8] annulene are thermodynamically less stable than the corresponding acyclic polyenes and are said to be anti aromatic. These systems prefer the cyclic alternate single and double bonds and delocalization of the pi electrons in these rings increase the energy.

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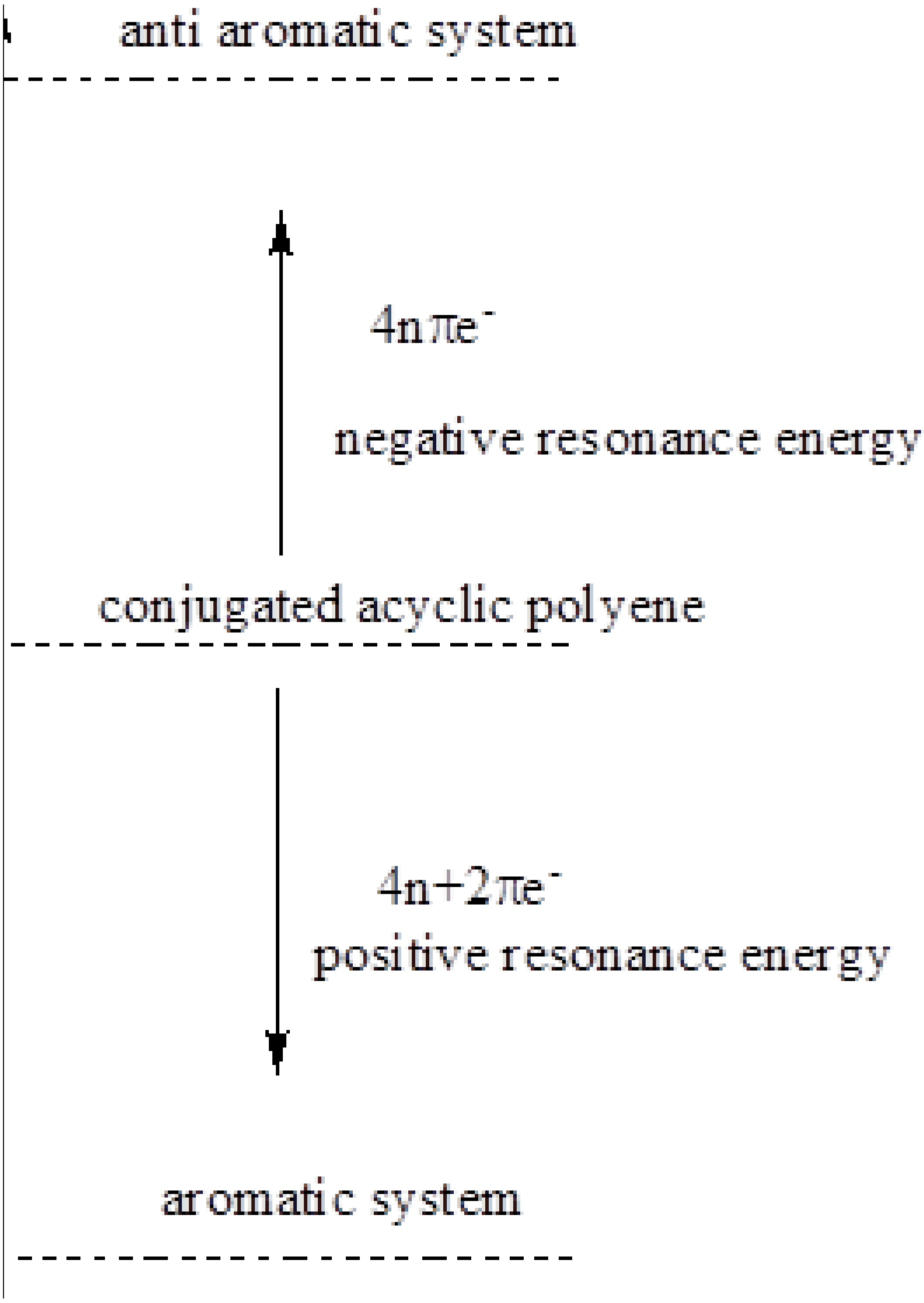
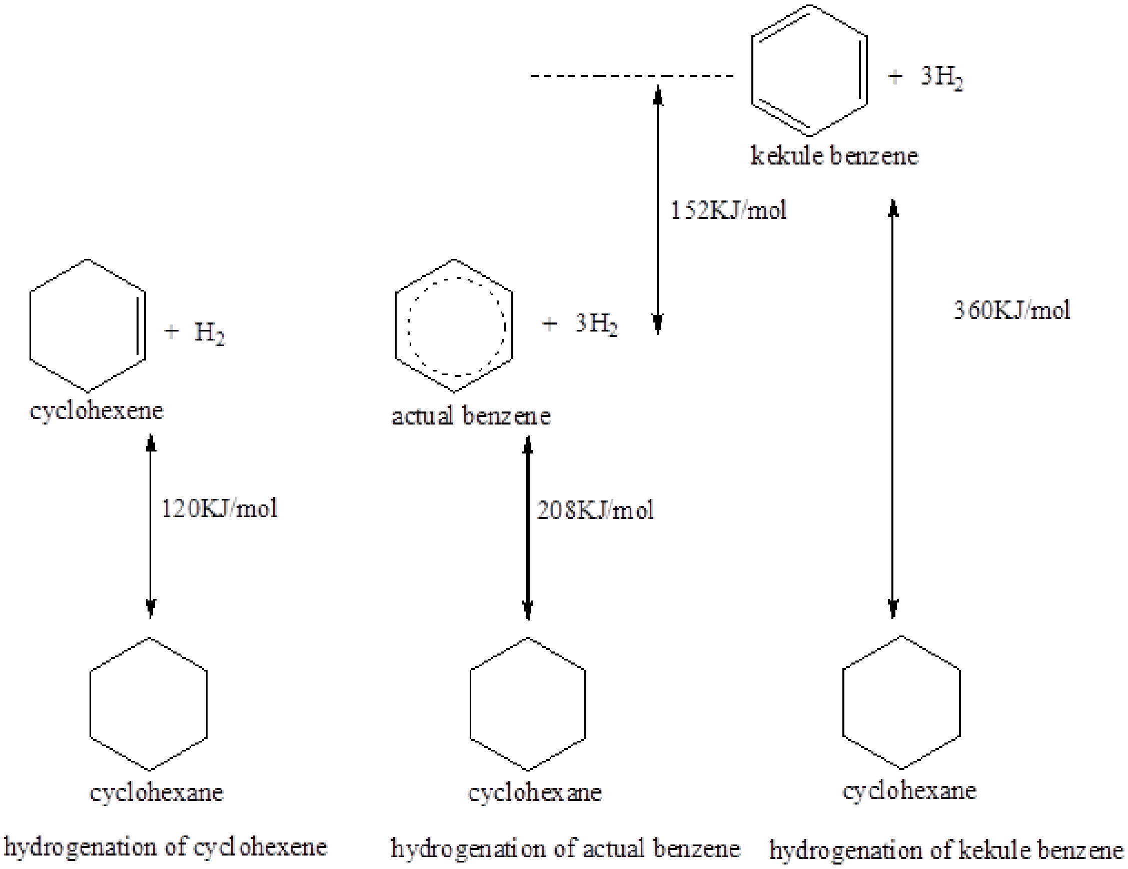
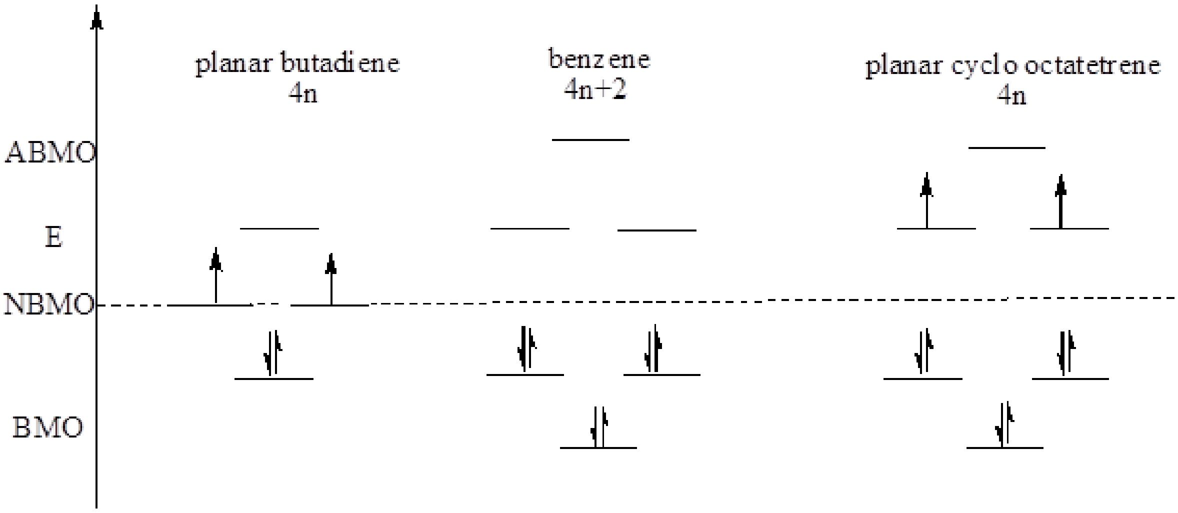


Larger annulenes irrespective of whether they have 4n or 4n+2 π electrons in the conjugated rings have a stability which is of the same order as that of a corresponding conjugated acyclic polyene. These annulenes are said to be non-aromatic eg; annulenes with greater than 26 ring carbons. The difference is expected that of heat of hydrogenation and observed heat of hydrogenation is called or delocalization energy.



Criteria for Aromaticity, the 4n+2 Rule:
Huckel Molecular orbitals



The set of molecular orbitals generated by this method are such that there is always one

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molecular orbital is lowest in energy and one highest in energy and the other molecular orbitals are located between these two in pairs.

Non benzonoid aromatic compounds:

Members of this class of compounds which unlike benzene have odd number of carbon atoms eg; 3,5,7 and have aromatic character. These exist as cations eg; cyclopropenium ions, tropylium cation and anions like cyclopentadienyl anion or dipolar compounds eg; tropanone.

Ring size	Cation	Anion
3	aromatic	antiaromatic
5	antiaromatic	aromatic
7	aromatic	antiaromatic
9	antiaromatic	aromatic

The sextet of pi electrons which has taken as a criteria for aromatic compounds is also observed in the non benzonoid compounds. The non benzonoid compounds are charaterised by equal ring c-c bond lengths, planar ring, high resonance energy and a diamagnetic ring current in their 1H-NMR spectra.

Frost Muslin Diagrams:

Frost - Muslim method gives simplified representations of the Huckel molecular orbitals in all cyclic fully conjugated monocyclic system. This method considers the cyclic conjugated as a regular m-sided polygon (m= number of carbons in the ring).

The systems are considered to be planar and in each of the ring system the c-c bond lengths and bond angles are the same. The polygon is inserted into a circle which is divided equally by a vertical and horizontal axis. The polygon is inserted into this circle in such a way that one of thwe carbons coincides with the vertical axis at the bottom. This point represents the lowest energy molecular orbital, which is a bonding molecular orbital. The other molecular orbital are located where ever the carbons of the polygon touch the circle and these molecular orbitals will be in the pairs.

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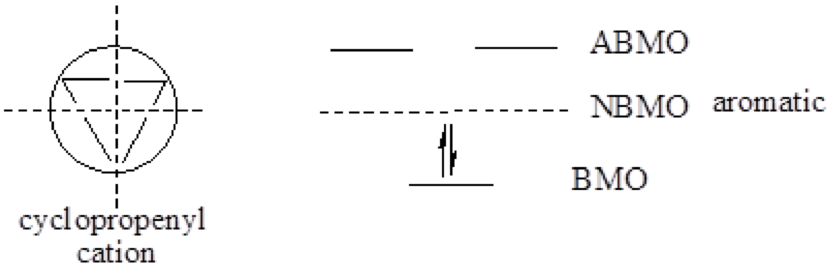
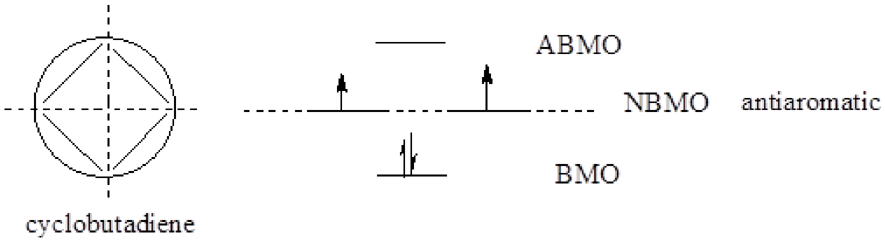
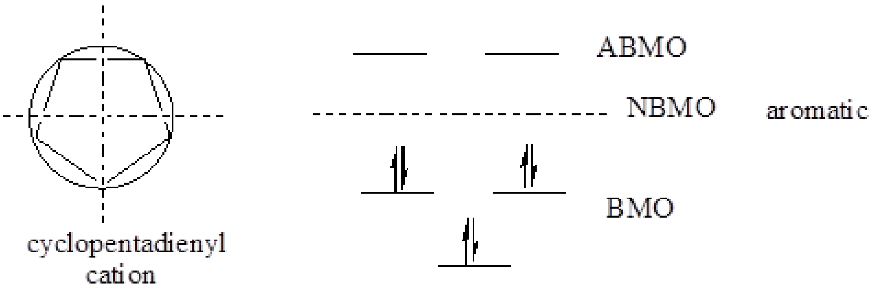
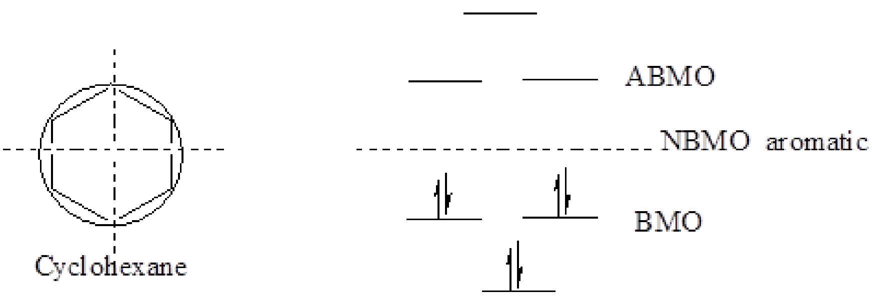
When the carbons of the polygon coincide with the horizontal axis of the circle, two molecular orbitals are located at this energy level. These are anti aromatic systems and are non bonding molecular orbitals (NBMO). Molecular orbitals located below the horizontal line are bonding molecular orbitals (BMO). While those are located above the non bonding molecular orbital (NBMO) are non bonding molecular orbitals (NBMO). In cyclic systems with (4n+2)π electrons.

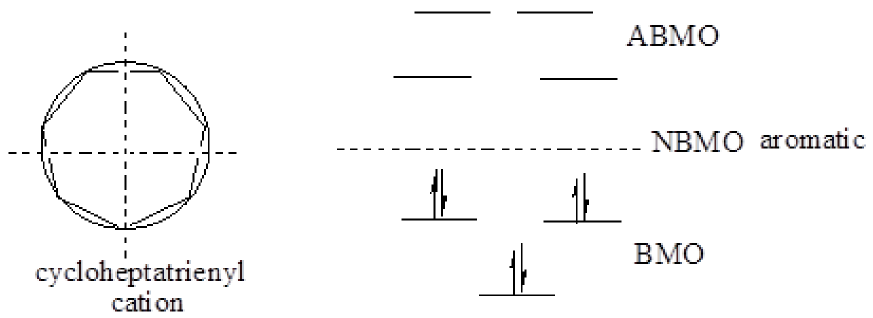
All the π electrons are in bonding molecular orbital in a paired, closed shell configuration. In cyclic systems with 4nπ, two electrons invariably are located one each in the two non bonding molecular orbitals. In 4n+2 and 4nπ electron system there are no electrons in the anti bonding molecular orbitals in the ground state.

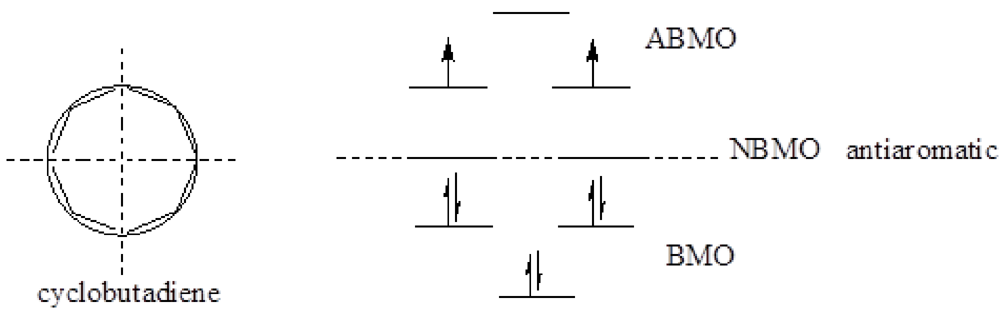








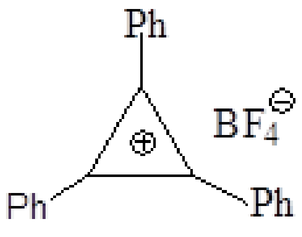


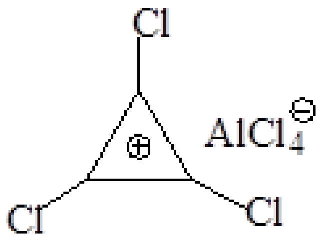


2π – electron system

Cyclopropenium ion, the smallest 4n +2 π electron ring system (n=0) is in the cyclopropenium ion C3H3+ which has two electron delocalized in a 3- membered ring.

Triphenylcyclopropeniumtetrafluoroborate & trichlorocyclopropeniumtetrachloroaluminate are the examples for 2π electron aromatic cations. Inspite of the large bond angle strain these compounds are stable indicating their aromatic character.





6π – electron system

Cyclopentadienyl anion and cycloheptatrienyl cation containing six π electrons are stable and aromatic. Cyclopentadienyl anion obtained by the deprotonation of cyclopentadiene has six π electrons delocalized over acompletely conjugated planar monocyclic array of five sp2 hybridised

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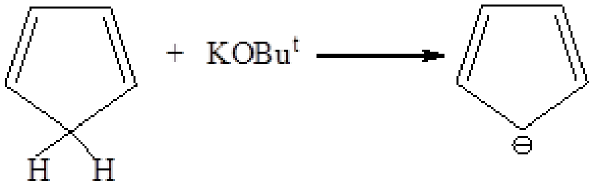
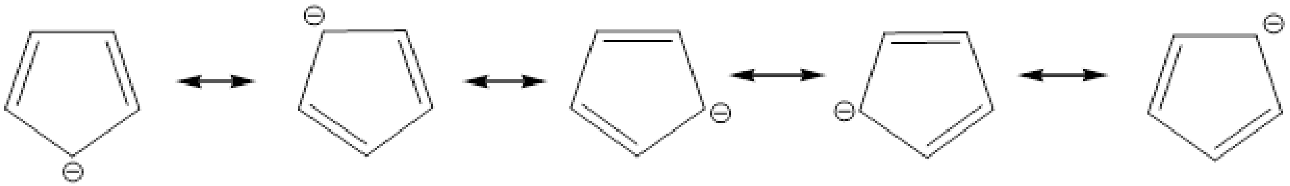
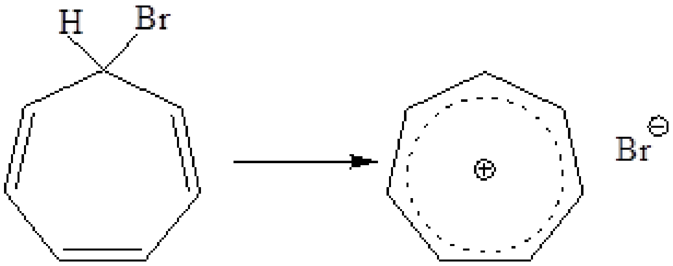
carbon atoms obeys Huckel rule. Cyclopentadiene is gratly acidic, pka=16 since the conjugate base cyclopentadienyl anion is highly resonance stabilized.





Cycloheptatrienyl cation contains a six π electron system with closed shell configuration similar of benzene. The six π electrons are delocalized over seven carbons. Tropylium bromide is a fully ionic compound since in the ionic form; the seven memebered ring is an aromatic cation.



Azulene:

Azulenes are aclass pf bicyclic nonbenzenoid hydrocarbons. The development of blue colors in cetain essential oils; for example, Oil of chamomile after asimple operation such as steam distillation or treatment with acids or oxidizing agents is well known. Many such oils contain hydrogenated azulene derivatives and the development of the blue colour is due to the dehydrogenation of these compounds.

Azulene may be regarded as an aromatic hydrocarbon having a cyclic conjugated cyclopentadiene fused with conjugated cycloheptatriene ring, containing 10π electrons. The dipole moment of azulene, 1.08 D though not large contributes to the dipolar from significantly. The resonance energy of 205 KJ/Mol indicates considerable aromatic stabilization.

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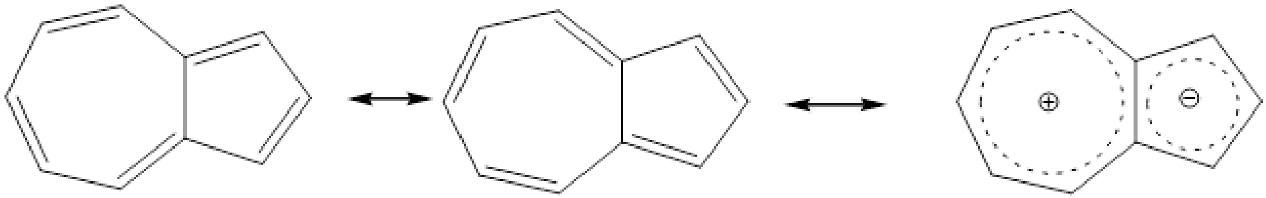
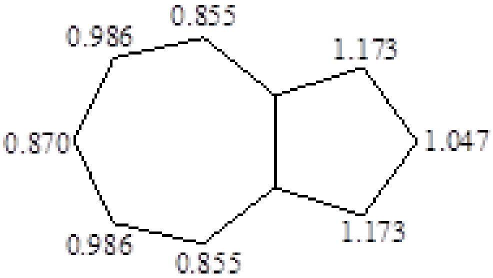


Electron Densities in Azulene: The proton NMR spectrum of azulene shows an AB2 pattern for the five membered ring and AB2X2 pattern for the seven membered ring. Azulene is thus an aromatic system with the unusal feature that two positions 1 and 3 possess a high electron density balanced by decrease of the π electron density in the seven membered rings at 4, 6 and 8 positions. The electron density, 1H-NMR and UV spectral data, the C-C bond length of 1.39A0 and the resonance energy (205KJ/Mol) confirms the aromatic and dipolar nature of azulene. The UV spectrum of azulene is also in agreement with this structure. Azulene shows a strong absorption in the range of 230-245nm which is responsible for its blue color.



ANNULENES:

Huckel rule of aromaticity is applicable to larger annulenes [10], [14], [18] and [22] annulenes provided there are no intramolecular steric interactions that result in the loss of planarity in these rings.

[10] Annulene: [10] Annulene (cyclodecapentaene) expected to be aromatic on the basis of Huckel's rule as it has 10 π electrons. Three isomers of [10] annulenes are possible are expected to be aromatic but it is not aromatic dua to a combination of steric and angular strains. For all cis (Z,Z,Z,Z,Z) isomer II, which is a regular decagon the C-C angle would have to be 1440 considerably larger than the normal sp2 carbon 1200 angle. Similarly large bond angle strain is present in the mono-trans (E,Z,Z,Z,Z) isomer III, preventing the molecules with one trans double bond being aromatic. In the other (Z,E,Z,Z,E) isomer I, the C-C bond angles are all 1200 but the hydrogen at 1,6 positions interfere with each other and force the molecule out of planarity. In the 1H-NMR spectra of all these three molecules isomers protons appear in the olefinic region δ5.00 -6.00; indicating they are not aromatic.

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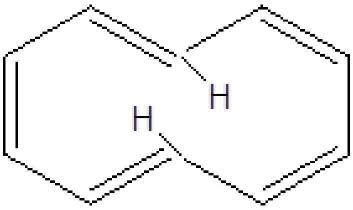
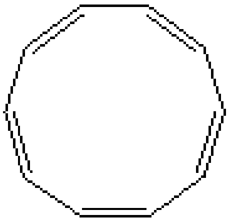
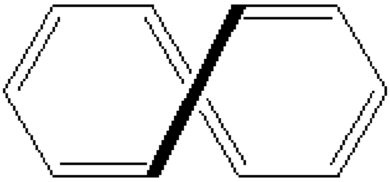


Z,E,Z,Z,E(I)
trans,cic,trans,cis,
cis-cyclodecapentaene

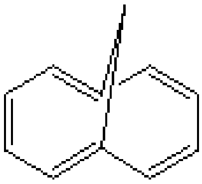


Z,Z,Z,Z,Z(II)
cis,cic,cis,cis,
cis-cyclodecapentaene



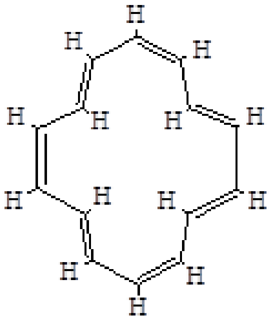
E,Z,Z,Z,Z(III)
trans,cic,cis,cis,
cis-cyclodecapentaene

Emaneul Vogel suggested that when the two inner hydrogens are replaced by -CH2- group, the ring is able to assume a conformation close enough to planar to become aromatic. Its aromatic character is also evident from its 1H-NMR spectrum which shows two sets of signals due to the diamagnetic ring current. Eight protons located outside are deshielded and appear at δ7.10 and the bridge methylene protons which are located above the ring are shielded appear at δ0.50. further, from its heat of hydrogenation it has resonance energy of 72.2 KJ/Mol.



1,6-methano-[10]-annulene

[14] Annulenes: [14] annulene has the vander waals strain from the four inner hydrogens but it is planar. Its 1H-NMR spectrum shows the outer protons at δ7.6 (10 H) and inner protons at δ0.0 (4 H).



[14] Annulene

[12] and [16] Annulenes: [12] and [16] annulenes are antiaromatic 4n (n=3,4). These annulenes show a paramagnetic ring current and are said to be paratopic. Now the inner protons are deshielded and outer protons are shielded in contrast to (4n+2) electron annulenes. In [16] annulene, the conjugated system has alternate single and double bonds C=C 1.34 A0 and C-C 1.46A0 and is non planar.

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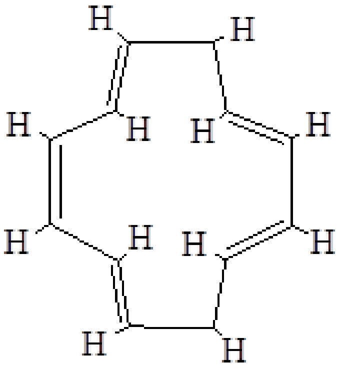
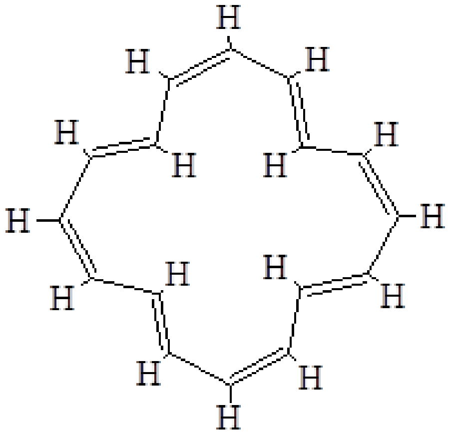
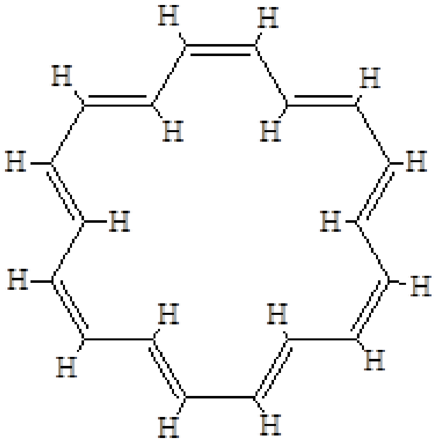


[12] Annulene

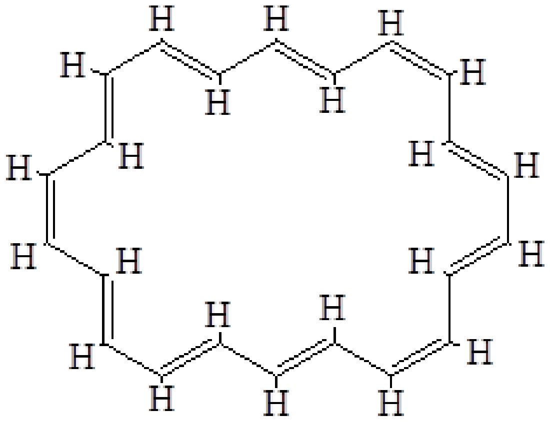


[16] Annulene

[18] and [22] Annulenes: [18] and [22] annulenes are aromatic as evident from their 1H-NMR spectra. [18] Annulene having a D6h symmetry which is planar and has all its C-C bond distance in the range of 1.37-1.43 A0 (which is similar to that of the benzene). In its 1H-NMR spectrum, the twelve outer protons appear at δ 9.30 and the six protons at δ3.00. It has resonance energy of 75.6 KJ/mol. The chemical reactivity of [18] annulene however does not support aromatic nature as it undergoes addition of bromine just as a polyene. In [22] annulene, in its 1H-NMR spectrum at -900C, the inner protons appear at δ0.4 while the other 14 outer protons at δ9.6 confirming its aromatic nature and planarity.

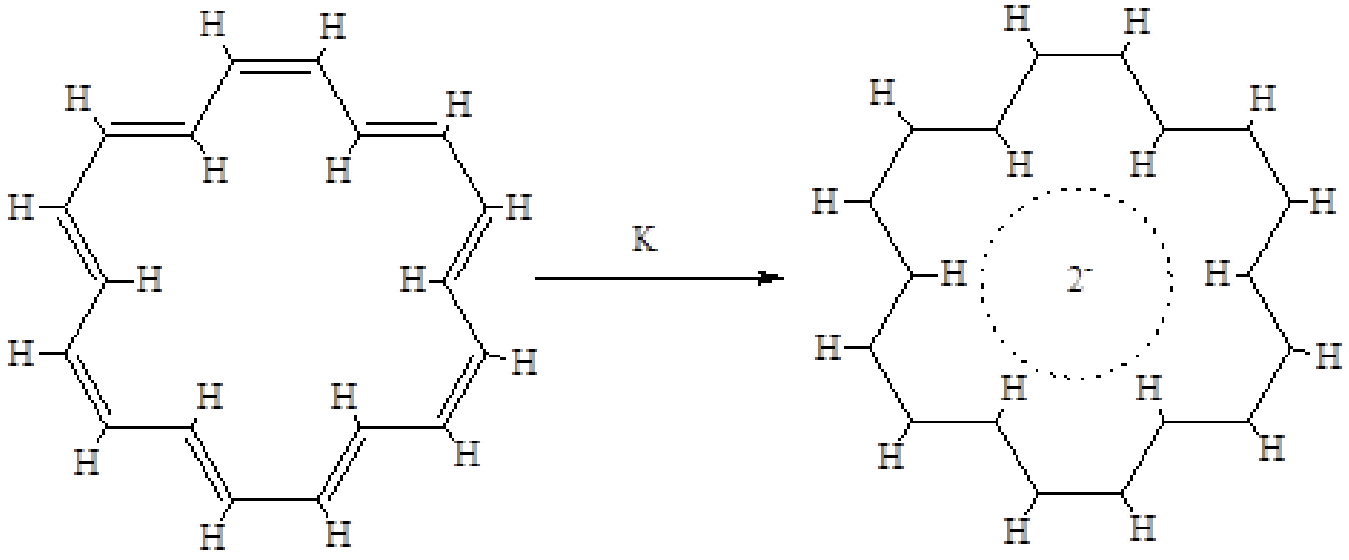


[18] Annulene



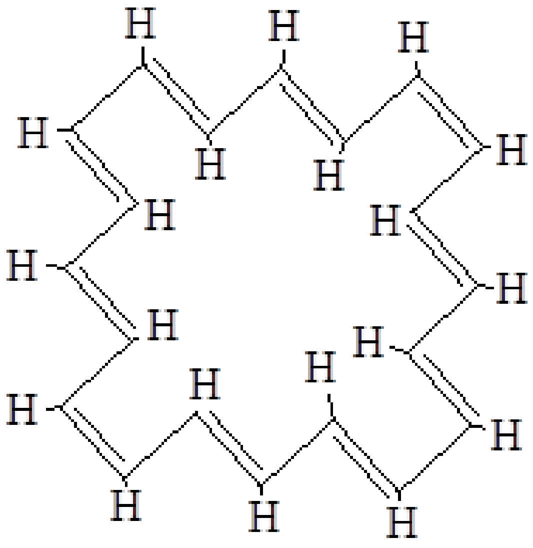
[22] Annulene
Dark purple

[20] and [24] Annulenes: [20] and [24] annulenes exhibit paramagnetic ring current shielding in the 1H NMR Spectrum and hence are antiaromatic. [18] annulene by reaction with potassium is converted to the dianion [18] annulene which is a 20 π electron 4ne- system. In this dianion, the outer protons are shielded and resonate at δ1.0 while the inner protons are deshielded and appear at δ9.0

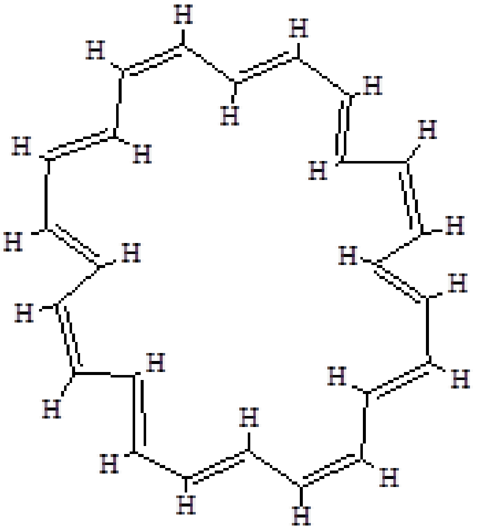


[18] Annulene

dianion of
[18] Annulene



[20]Annulene



[24] Annulene

Craig's Rule: Craig's rule applies to conjugated polycyclic hydrocarbons in which at least two centres lie on a symmetry axis that converts one Kekule type structure to another. This is useful to distinguish the aromatic and nonaromatic conjugated polycyclic hydrocarbons on the basis of the sum of the number of symmetrically related π-centers (not those on the symmetry axis) represented by symbol (f) and the number of interconversions (g) of spin symbols α or β by rotation about the axis. Thus, if the sum of (f) and (g) is even, the hydrocarbon is aromatic and if the sum of (f) and (g) is odd, the hydrocarbon is classified as nonaromatic.

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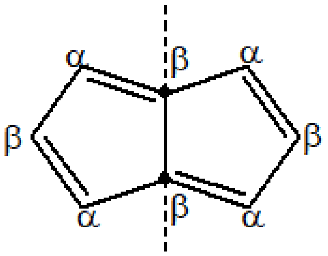
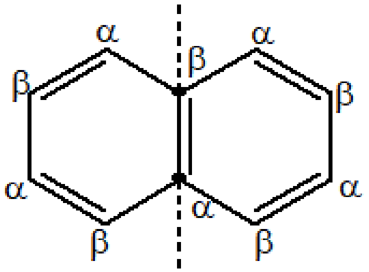
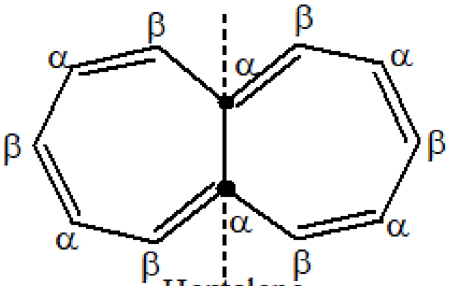


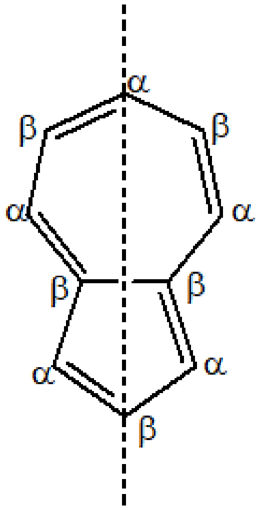
Pentalene
f+g=3+0=3
odd
nonaromatic



Naphthalene
f+g=4+0=4
even
aromatic



Heptalene
f+g=5+0=5
odd
nonaromatic



Azulene
f+g=4+0=4
even
aromatic

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