

# Pericyclic Reactions

## 1.1: INTRODUCTION:

Pericyclic reactions involve the continuous flow of electrons in cyclic transition state (TS) by breaking and making of bonds in concerted process, without formation of an intermediate. Hence, these reactions are known as concerted reaction.

- ◆ The word pericyclic means, the movement of electrons in a cyclic manner or around the cyclic.

i.e. Peri = around, cyclic = circle or ring.

Pericyclic reactions involve, reactions proceeds in concerted process. The word concerted means reactant bonds are broken and product bonds are formed synchronously.

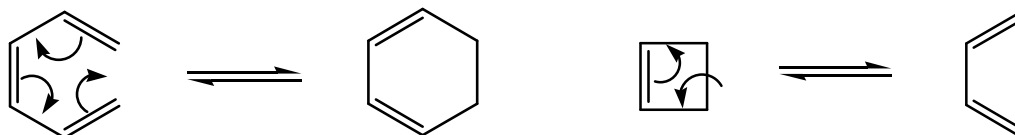
- ⇒ Pericyclic reactions are insensitive to solvent polarity.
- ⇒ Pericyclic reactions are free from free radical initiators or inhibitors.
- ⇒ No any reactive intermediate formed (Carbocation, Carbanion, free radical, Carbene etc.) in pericyclic reactions.
- ⇒ Pericyclic reactions activated by heat (thermal) or light (photochemical).
- ⇒ Pericyclic reactions are stereospecific in nature.

### Classification of pericyclic reactions:

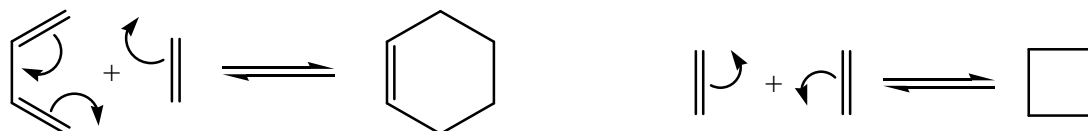
Pericyclic reactions are mainly classified into the four most common types of reactions

- |                             |                              |
|-----------------------------|------------------------------|
| (1) Electrocyclic reactions | (2) Cycloaddition reactions  |
| (3) Sigmatropic reactions   | (4) Group transfer reactions |

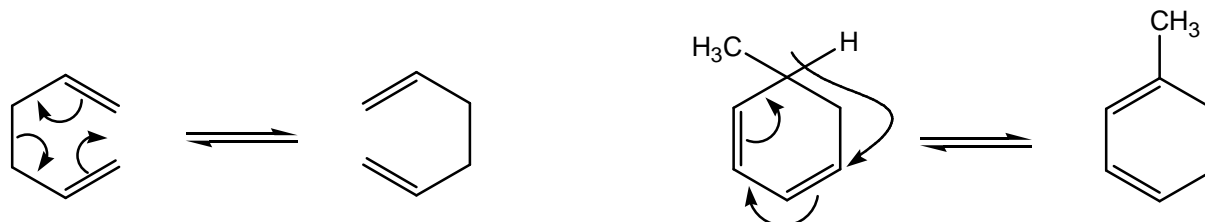
- ◆ In an electrocyclic reaction a cyclic system is formed through the formation of a  $\sigma$  bond from an open chain conjugated polyene system at the cost of a multiple bond and vice-versa.



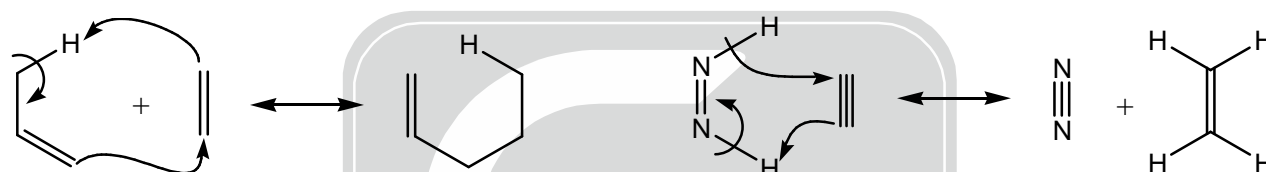
- ◆ In cycloaddition reactions two or more components containing  $\pi$  electrons come together to form a cyclic system through the formation of two or more new bond at the cost of overall two or more  $\pi$  bonds respectively.



- ◆ Sigmatropic rearrangements are the unimolecular isomerization reactions in which  $\sigma$  bond moves from one position to another over an unsaturated system. In such reaction, rearrangement of the  $\pi$ -bonds takes place to accommodate the new  $\sigma$  bond, but the total number of  $\pi$  bonds remains the same.



- ◆ Group transfer reaction involve the transfer of one or more atoms or groups from one component to another in a concerted manner. In these reactions two components join together to form a single molecule through the formation of a  $\sigma$  bond.



## 1.2: MOLECULAR ORBITALS AND THEIR SYMMETRY PROPERTIES:

In pericyclic reactions, the reactivity of the reactions can be explained on the basis of perturbational Molecular Orbital (PMO) theory. The basic postulate of PMO theory is that a chemical reaction takes place by the perturbation of molecular orbitals (MOs) of reactants on heating and on irradiation with light. The degree of perturbation is a function of degree of overlapping interactions of the atomic orbitals in an MOs. These orbital overlapping interaction produce degenerate MOs of different energies. The suitable degenerate MOs take part in the reactions to give products through cyclic transition state in a concerted process. The linear combination of atomic orbitals is known as LCAO theory or PMO theory.

The shapes of the MOs that are formed by the linear combination of atomic orbitals (LCAO) are related to the shapes of atomic orbitals.

### Generalized considerations:

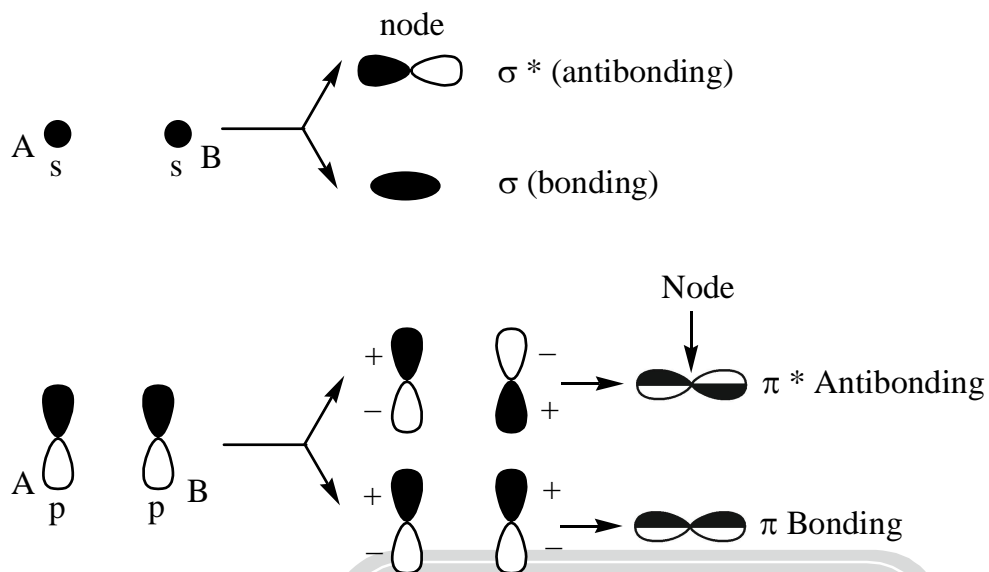
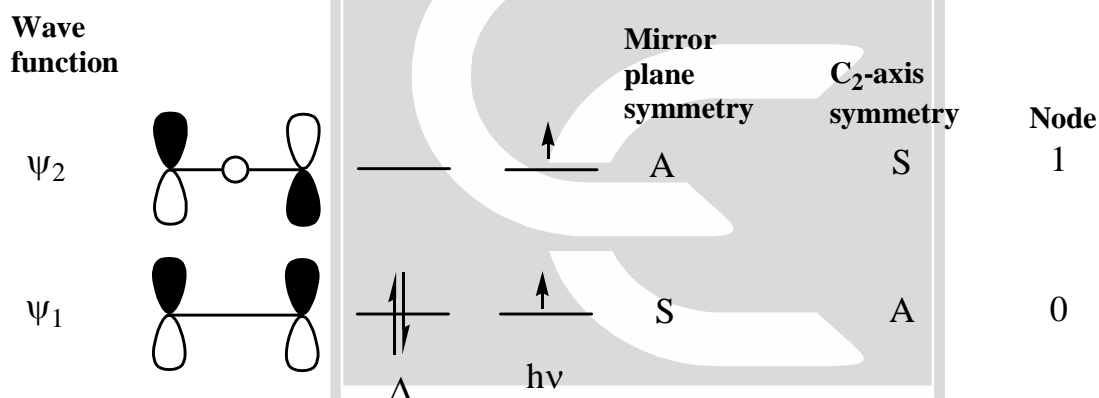
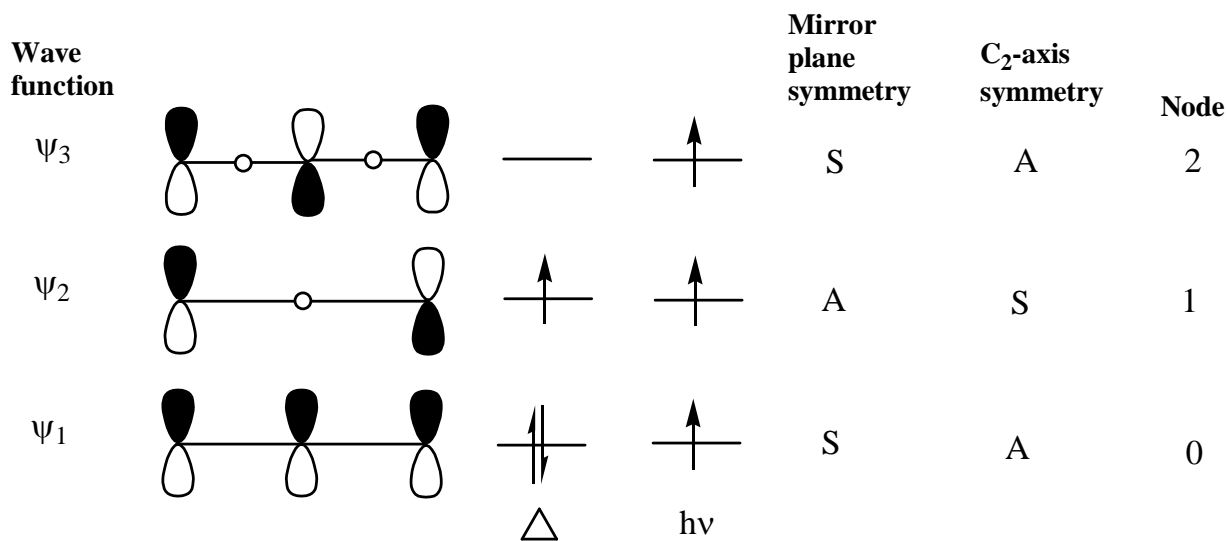
- Number of p-orbitals equal to number of carbon atom upto conjugation
- The molecular orbital of any molecule shows two types of symmetry i.e. mirror plane ( $m$ ) and centre of symmetry ( $c_2$ )

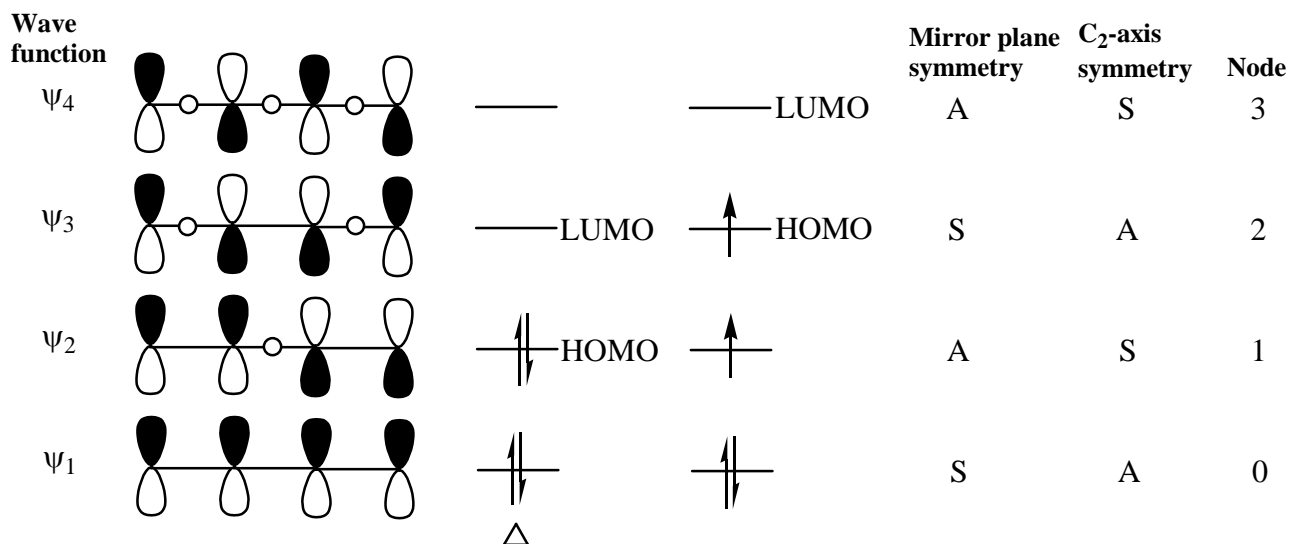
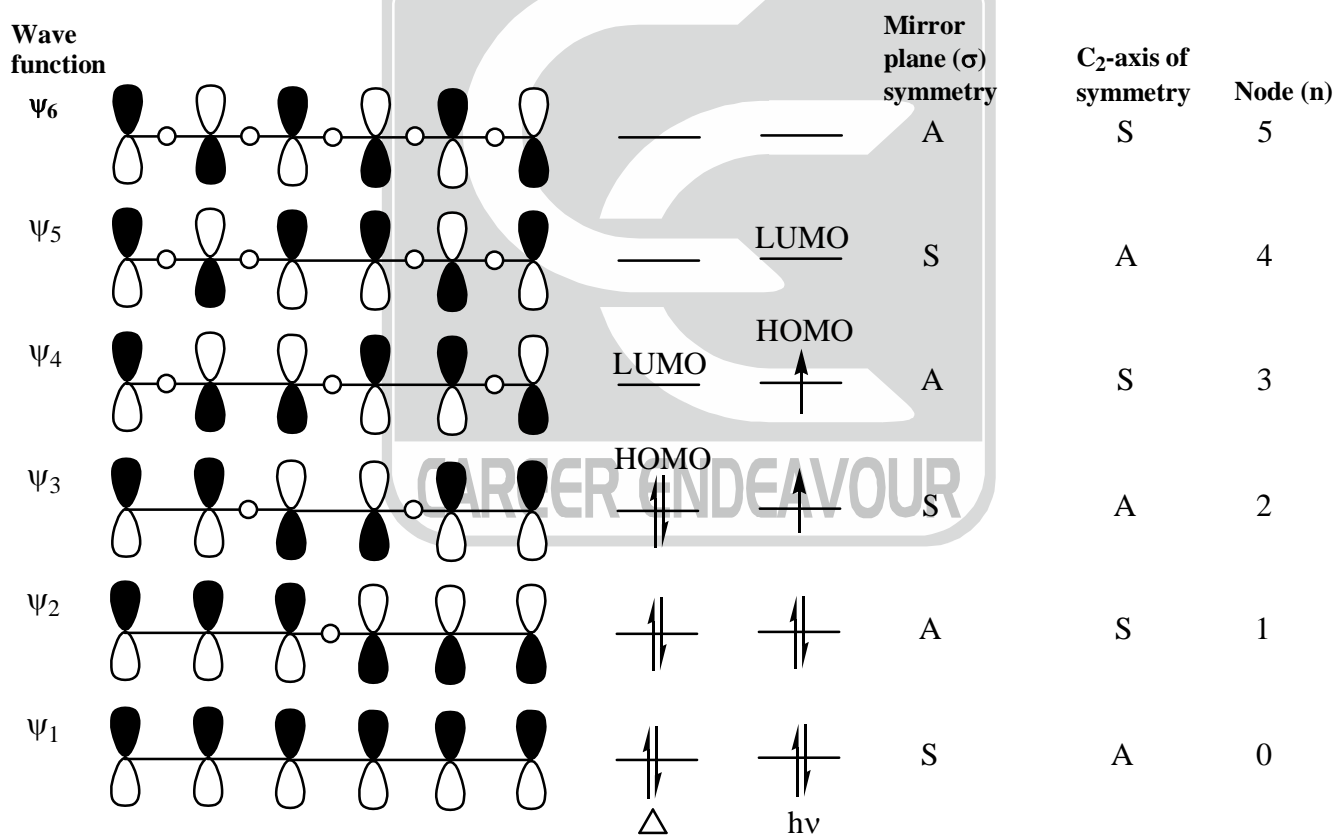


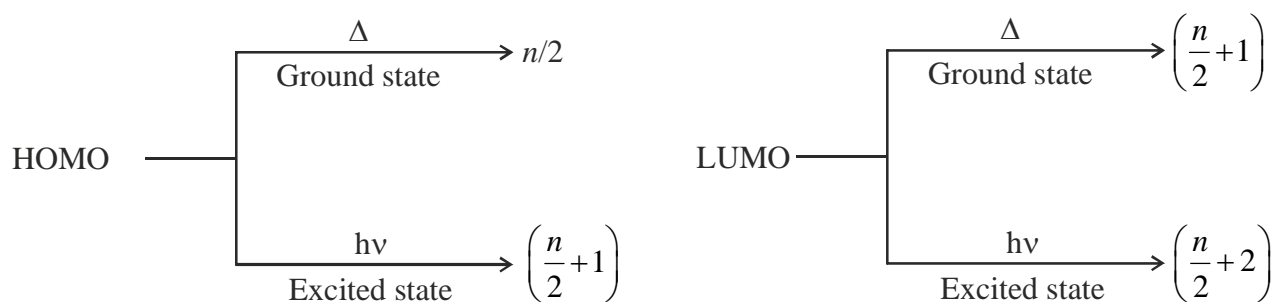
- Molecular orbital having same sign at terminal contain  $m$ .
- Molecular orbital having opposite sign at terminal contain  $c_2$ .
- If any molecular orbital contain  $m$  (mirror plane) i.e. molecular orbital is symmetric with  $m$  otherwise antisymmetric with  $m$ .
- If any molecular orbital contain  $c_2$  i.e. molecular orbital is symmetric with  $c_2$  otherwise antisymmetric with  $c_2$ .
- Node is the position where lobes changes its sign.

HOMO = Highest Occupied Molecular Orbital

LUMO = Lowest Unoccupied Molecular Orbital

**Formation of bonding and antibonding orbitals:****Symmetry properties of Ethene ( $\text{CH}_2 = \text{CH}_2$ ):****Molecular orbitals formation in allyl systems ( $\text{CH}_2 = \text{CH} - \text{CH}_3$ )**

Molecular orbitals of 1, 3-butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ )Molecular orbital symmetry of 1, 3, 5-hexatriene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ )**Symmetry properties of the orbital  $\psi_n$  of a linear conjugated:** $\psi$  = Wave functionNode =  $\psi_n - 1$ HOMO  $\Rightarrow$  Highest occupied molecular orbitalsLUMO  $\Rightarrow$  Lowest unoccupied molecular orbitalsSOMO  $\Rightarrow$  Singly occupied molecular orbitals



$n$  = Number of conjugated  $\pi$  electrons

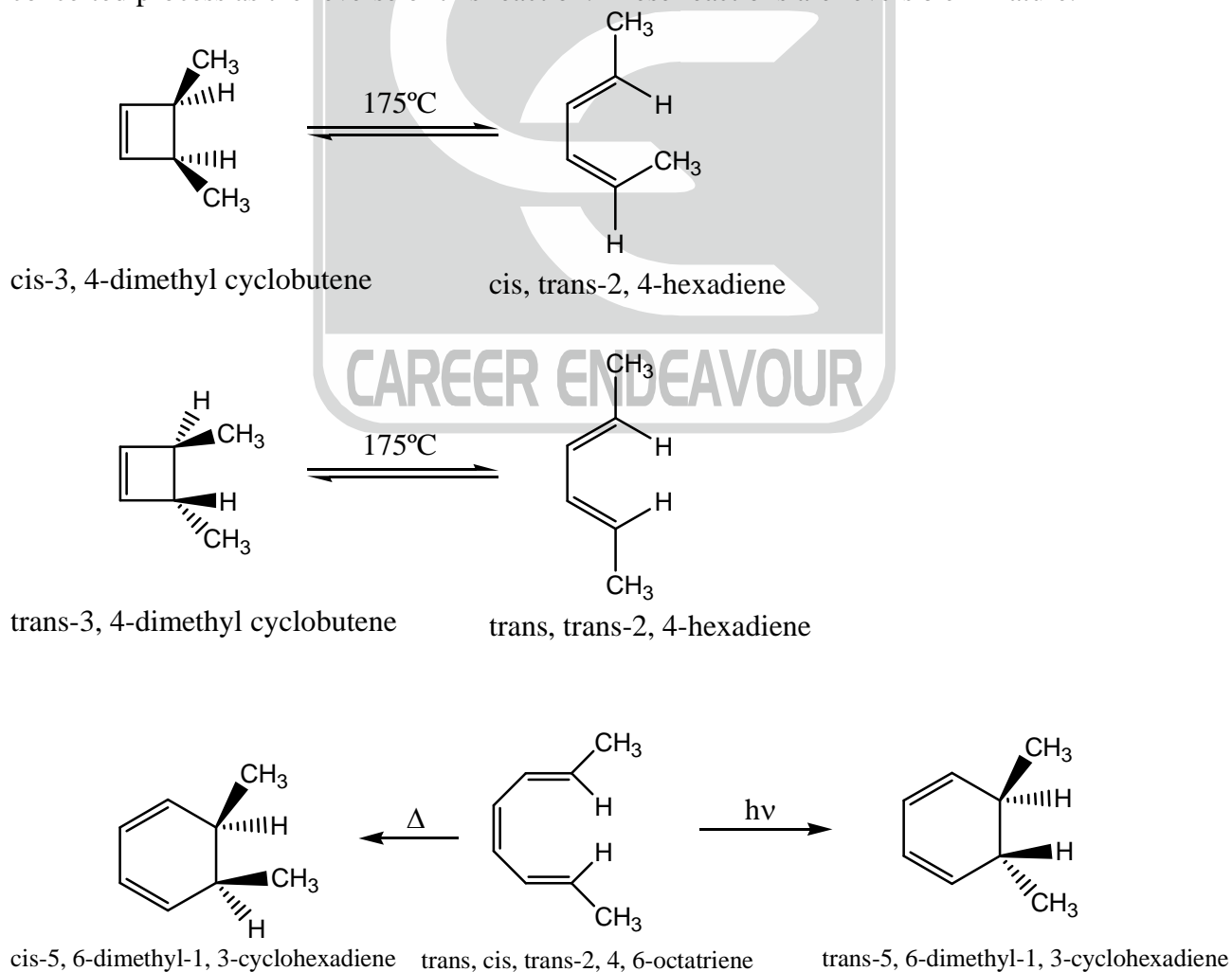
\* If  $\psi_n$  is odd, then sign of terminal lobes will be symmetric (same)

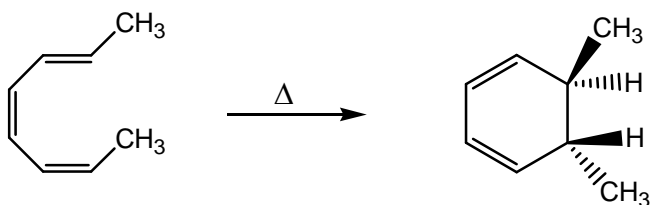
\* If  $\psi_n$  is even, then sign of terminal lobes will be antisymmetric (opposite)

### 1.3: ELECTROCYCLIC REACTIONS

#### 1. 3.1: INTRODUCTION:

An electrocyclic reaction are characterised by thermal or photochemical conversion of an acyclic conjugated system into a ring system by formation of a  $\sigma$  bond between the ends of the conjugated system in a concerted process as the reverse of this reaction. These reactions are reversible in nature.





trans, cis, cis-2, 4, 6-octatriene

trans-5, 6-dimethyl-1, 3-cyclohexadiene

### 1.3.2: ORBITAL SYMMETRY BASIS FOR STEREOSPECIFICITY:

The motion of the substituents in the same direction clockwise or anti-clockwise is known as conrotatory mode of motion, while the motion of the substituents in opposite direction is known as disrotatory mode of motion.

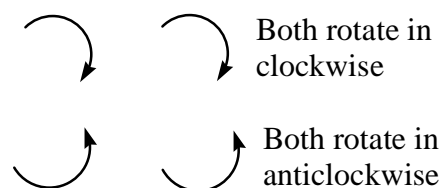
For thermal reaction of  $4n\pi$  electrons conjugated system,  $\psi_2$  would be HOMO because it contains lowest number of node (one node). While for photochemical reactions of  $4n\pi$  electron system,  $\psi_3$  would be HOMO because it is the first excited state of ground state  $\psi_2$ . Therefore, in thermal reactions of  $4n\pi$  electrons systems, conrotatory motion of the groups in the terminal carbon of the open chain  $\pi$  system brings the lobes of the same phase for bonding with a mobius type TS and orbital symmetry allowed process. While disrotatory motion brings the lobes of the opposite phase for anti-bonding formation and is said to be orbital symmetry forbidden process. While for photochemical reactions of  $4n\pi$  electron systems, disrotatory motion brings the lobes of same phase, and hence the reaction will proceed with low activation energy and is said to be orbital symmetry allowed process. On the other hand, conrotatory motion bring the lobes of opposite phase and hence reaction is unfavourable for its high activation energy and is referred as symmetry forbidden reaction path.

Disrotatory motion of the groups of terminal carbons brings the lobes of same phase for bonding, involving a Huckel type transition state and is said to be symmetry allowed path.

#### Orbital motions:

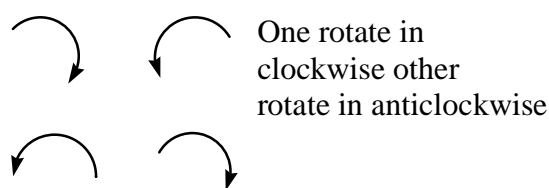
##### Conrotatory motions

Motion of orbitals in same direction

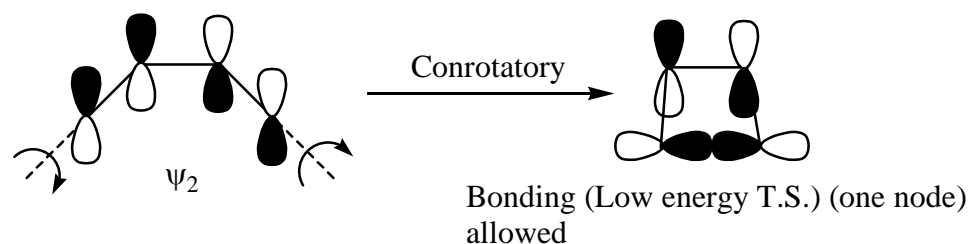


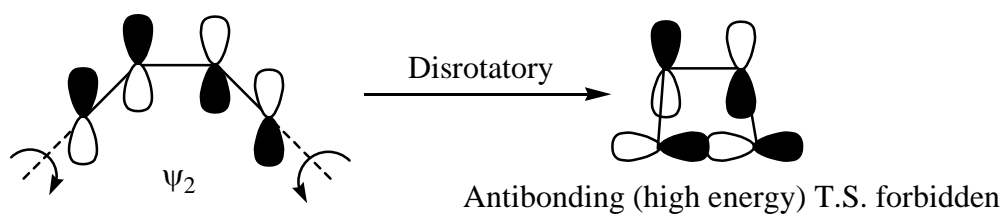
##### Disrotatory motions

Motion of orbitals in opposite direction

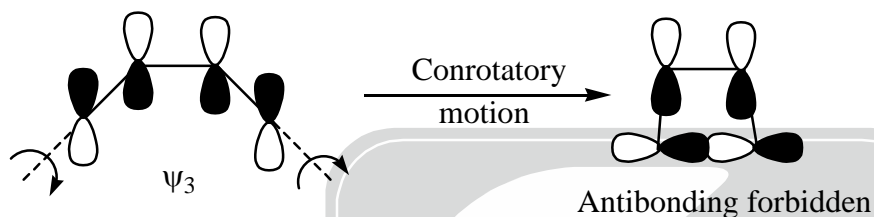
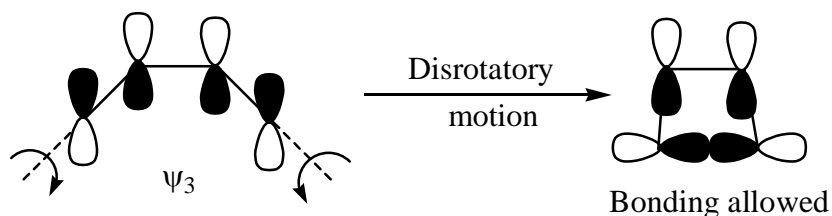


Thermal electrocyclic ring closure of  $4n\pi$  electron conjugated system

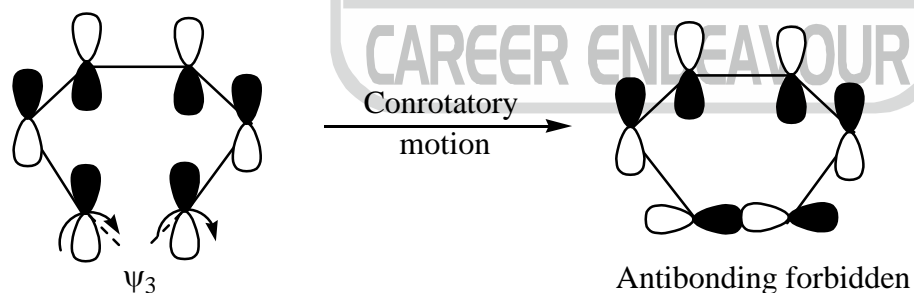
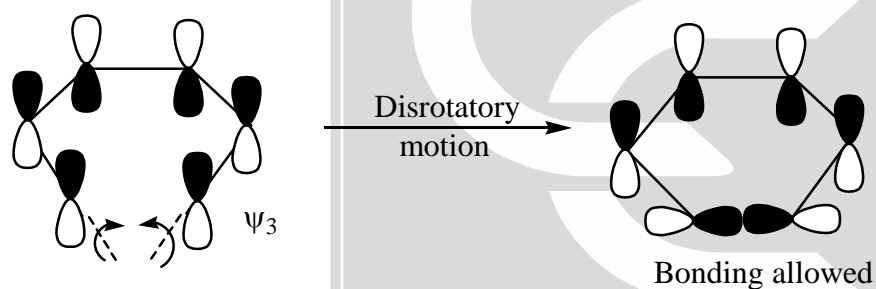




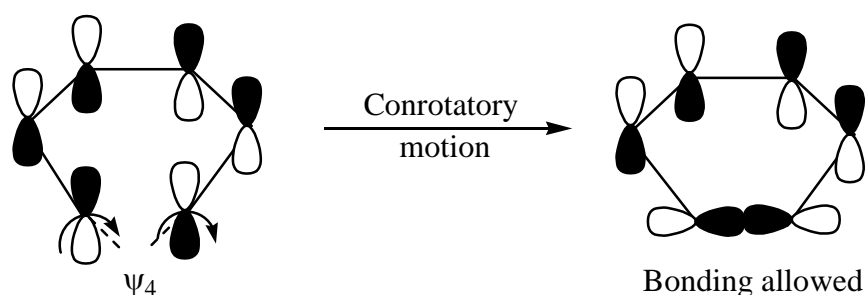
Photochemical electrocyclicization of  $4n\pi$  electron conjugated system

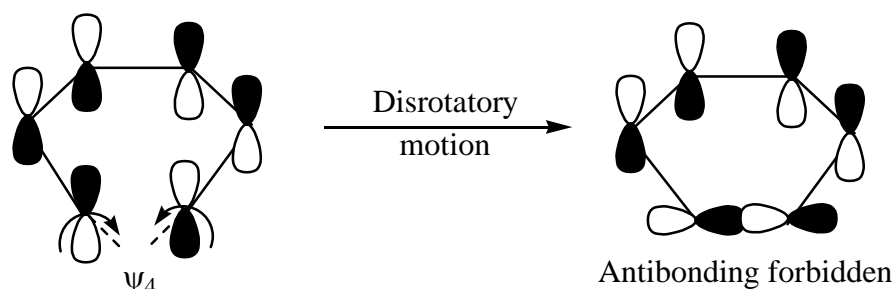


Thermal electrocyclicization of  $(4n + 2)\pi e^-$ s conjugated system



Photochemical electrocyclicization of  $(4n + 2)\pi e^-$ s conjugated system

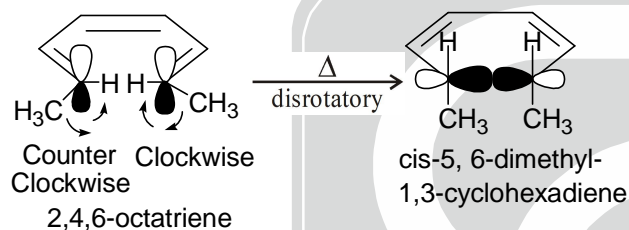




**(A) Thermal Electrocyclic Reaction:** To explain the stereochemistry observed in electrocyclic reactions, we must examine the symmetry of the molecules orbital that contains the most loosely held  $\pi$  electrons. In a thermal reaction, we consider the HOMO of the ground state electronic configuration. Rotation occurs in a disrotatory or conrotatory fashion so that like phases of the  $p$ -orbital on the terminal carbons of this molecular orbital combine.

The number of double bonds in the conjugated polyene determines whether rotation will be conrotatory or disrotatory.

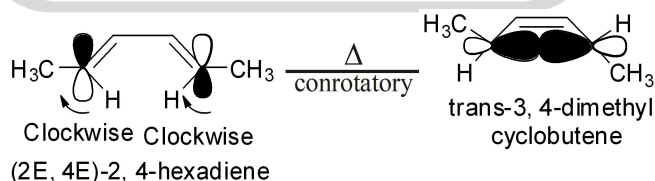
**For example:** Thermal electrocyclic ring closure of (2E, 4Z, 6E)-2, 4, 6-octatriene yield a single product with cis-methyl group on the ring.



Cyclization occurs in a disrotatory fashion because the HOMO of a conjugated triene has like phases of the outermost  $p$ -orbitals on the same side of molecules. A disrotatory ring closure is symmetry allowed because like phases of the  $p$ -orbitals overlap to form the new  $\sigma$  bond of the ring.

**Thermal electrocyclic reactions occur in a disrotatory fashion for a conjugated polyene with odd number of  $\pi$ -bonds.**

**For example:** Thermal electrocyclic ring closure of (2E, 4E)-2, 4-hexadiene forms a cyclobutene with trans methyl group.

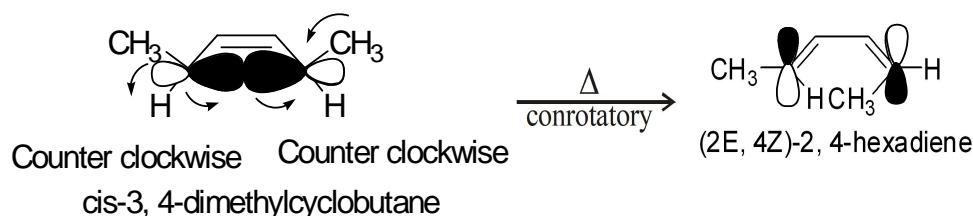


Cyclization occurs in a conrotatory fashion because the HOMO of a conjugated diene has like phase of the outermost  $p$ -orbitals on opposite sides of molecule. A conrotatory ring closure is symmetry allowed because like phase of the  $p$ -orbitals overlap to form the new  $\sigma$  bond of the ring.

**Thermal electrocyclic reactions occur in conrotatory fashion for a conjugated polyene with an even number of  $\pi$  bonds.**

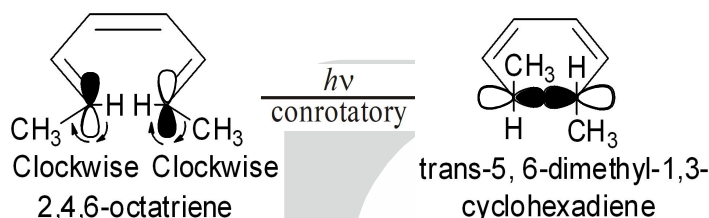
Since electrocyclic reactions are reversible, electrocyclic ring opening reactions follow the same rule as electrocyclic ring closure. Thus, thermal ring opening of cis-3, 4-dimethylcyclobutene gives a diene with even number of  $\pi$  bonds occurs in a conrotatory fashion to form (2E, 4Z)-2, 4-hexadiene as the only product.





**(B) Photochemical Electrocyclic Reaction:** Photochemical electrocyclic reactions follow similar principles as those detailed in thermal reactions with one important difference. In photochemical reactions, we must consider the orbitals of the HOMO of the excited state to determine the course of the reaction. The excited state HOMO has the opposite orientation of the outermost  $p$ -orbitals compared to the HOMO of the ground state. As a result, the method of ring closure of a photochemical electrocyclic reaction will be opposite to that of a thermal electrocyclic reaction for the same number of  $\pi$ -bonds.

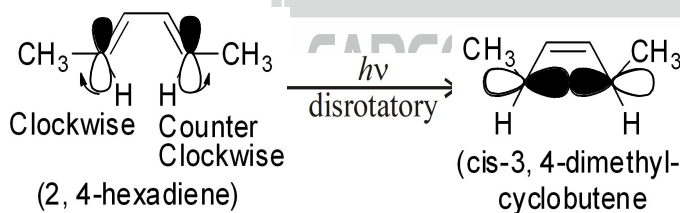
**For example:** Photochemical electrocyclic ring closure of (2E, 4Z, 6E)-2, 4, 6-octatriene yields a cyclic product with trans methyl group on the ring.



Cyclization occurs in a conrotatory fashion because the excited state HOMO of a conjugated triene has like phases of the outermost  $p$ -orbitals on the opposite sides of the molecule.

**Photochemical electrocyclic reactions occur in a conrotatory fashion for a conjugated polyene with odd number of  $\pi$ -bonds.**

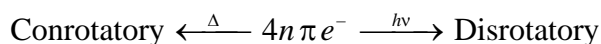
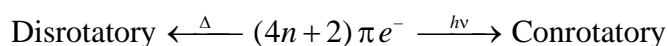
Photochemical electrocyclic ring closure of (2E, 4E)-2, 4-hexadiene forms a cyclobutene with cis-methyl groups.



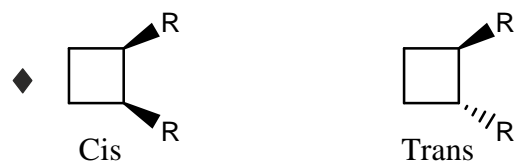
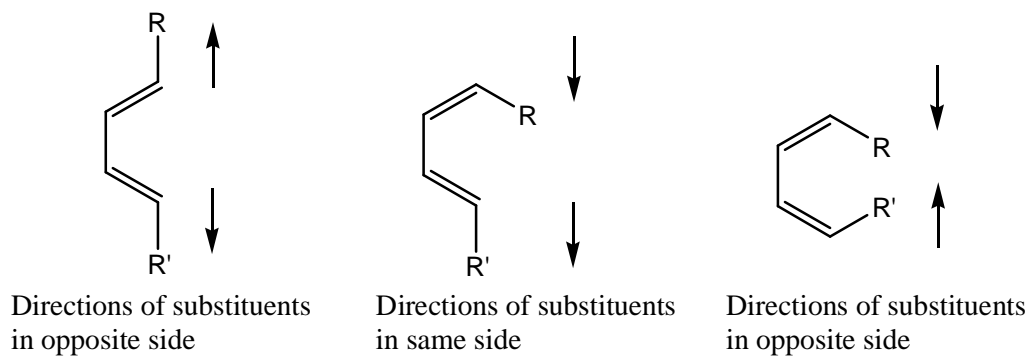
Cyclization occurs in a disrotatory fashion because the excited state HOMO of a conjugated diene has like phase of the outermost  $p$ -orbitals on the same side of the molecule.

**Woodward Hoffmann rules for electrocyclic reactions:**

Acyclic conjugated system	Thermally	Photochemically
$4n \pi e^-$	Conrotatory	Disrotatory
$(4n + 2) \pi e^-$	Disrotatory	Conrotatory



◆ Quick Concept:



Directions of substituents	Rotation	Stereochemistry	
O	D	C	ODC
O	C	T	OCT
S	C	C	SCC
S	D	T	SDT

- ◆ O means : Opposite direction    D means : Disrotatory    C means : Cis (stereochemistry)  
 S means : Same direction        C means : Conrotatory    T means : Trans (stereochemistry)

