

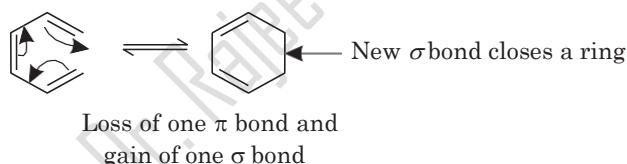
Pericyclic Reactions

INTRODUCTION

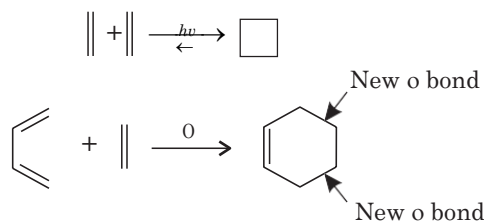
Pericyclic reactions are defined as the reactions that occur by a concerted cyclic shift of electrons. This definition states two key points that characterise a pericyclic reaction. First point is that reaction is concerted. In concerted reaction, reactant bonds are broken and product bonds are formed at the same time, without intermediates. Second key point in pericyclic reactions involves a cyclic shift of electrons. The word pericyclic means around the circle. Pericyclic word comes from cyclic shift of electrons. Pericyclic reactions thus are characterised by a cyclic transition state involving the π bonds.

The energy of activation of pericyclic reactions is supplied by heat (Thermal Induction), or by UV light (Photo Induction). Pericyclic reactions are stereospecific and it is not uncommon that the two modes of induction yield products of opposite stereochemistry.

We shall concern with four major types of pericyclic reactions. The first type is the *electrocyclic reaction*: a reaction in which a ring is closed (or opened) at the expense of a conjugated double (or triple bond) bond.

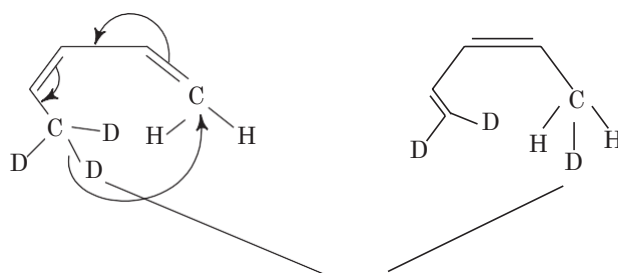


The second type of reaction is *cycloaddition reaction*: a reaction in which two or more π electron systems react to form a ring at the expense of one π bond in each of the reacting partners.



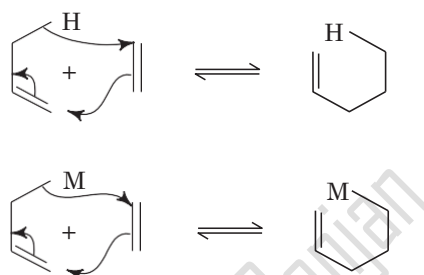
In this reaction formation of two new *sigma* bonds takes place which close a ring. Overall there is loss of two *pi* bonds in reactants and gain of two *sigma* bonds in a product.

The third type of reaction is the *sigmatropic rearrangement* (or reaction): a reaction in which a *sigma* bond formally migrates from one end to the other end of *pi* electron system and the net number of π bonds remains the same.



σ Bonded group moved from end to the other end of the π electron system.

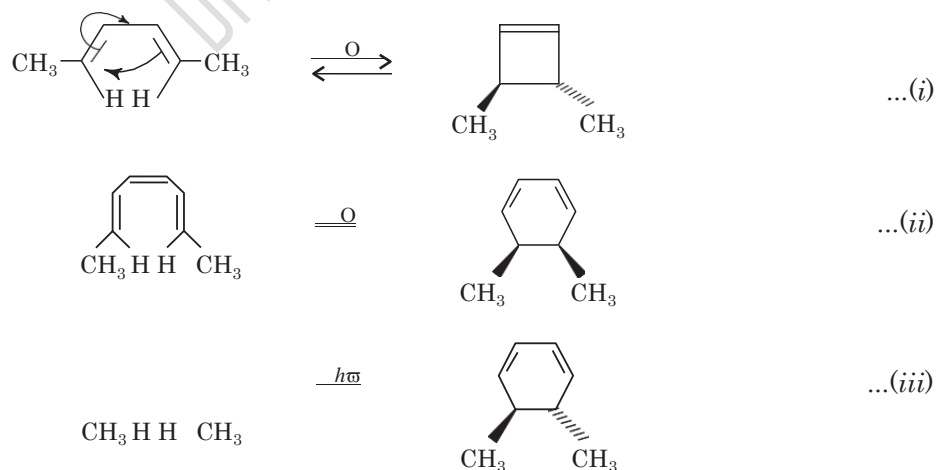
The fourth type of reaction is the *group transfer reaction*: a reaction in which one or more groups or atoms transfer from one molecule to another molecule. In this reaction both molecules are joined together by *sigma* bond.



Three features of any pericyclic reaction are intimately interrelated. These are:

1. **Activation:** Pericyclic reactions are activated either by thermal energy or by UV light. However, many reactions that require heat are not initiated by light and vice-versa.
2. The number of *pi* bonds involved in the reaction.
3. The stereochemistry of the reaction.

Consider the following three reactions:



First two reactions are thermal reactions activated by heat and third reaction is photochemical reaction activated by light. The relationship between the mode of activation

and the stereochemistry is exemplified by a comparison of reactions (ii) and (iii). When starting material is heated it gives *cis* product and when starting material is irradiated the product is *trans*.

These results had been observed for many years but the reasons for them were not known. Several theories have been developed to rationalise these pericyclic reactions. *R.B. Woodward* and *R. Hoffmann* have proposed explanation based upon the symmetry of the molecular orbitals of the reactants and products. The theory proposed is known as *Conservation of Orbital Symmetry*. *K. Fukui* proposed another explanation based upon the frontier molecular orbitals. The theory proposed is known as *Frontier Molecular Orbital (FMO)* method. The *Woodward-Hoffmann* rule and *Hückel-Mobius* (H-M) methods are also used for the explanation of pericyclic reactions. These four theories make the same predictions for pericyclic reactions. These four are the alternate ways for looking at the same reaction.

In order to understand the theories of pericyclic reactions, we must first understand molecular orbitals of compound containing *pi* bonds.

CONSTRUCTION OF π MOLECULAR ORBITALS OF ETHYLENE AND 1, 3-BUTADIENE

We know that the number of molecular orbitals is always equal to the number of atomic orbitals that combine to form them. The same principle applies to π molecular orbitals. A π electron system derived from the interaction of a number of m of p orbitals contain m molecular orbitals, that differ in energy. Half of the molecular orbitals are bonding molecular orbitals and remaining half are antibonding molecular orbitals. π molecular orbitals of ethylene from the two p atomic orbitals of the two carbons can be constructed as follows :

Each p orbital consists of two lobes, with opposite phases of the wave function of the two lobes. The plus and minus signs used in drawing these orbitals indicate the phase of the wave function.

In the bonding orbital of ethylene, there is overlap of similar signs (+ with + and - with -) in the bonding region between the nuclei. This reinforcement of the wave function is called *constructive* overlap. In the antibonding orbital there is cancelling of opposite signs (+ and -) in the bonding region. This cancelling of the wave function is called *destructive* overlap (Fig. 1).

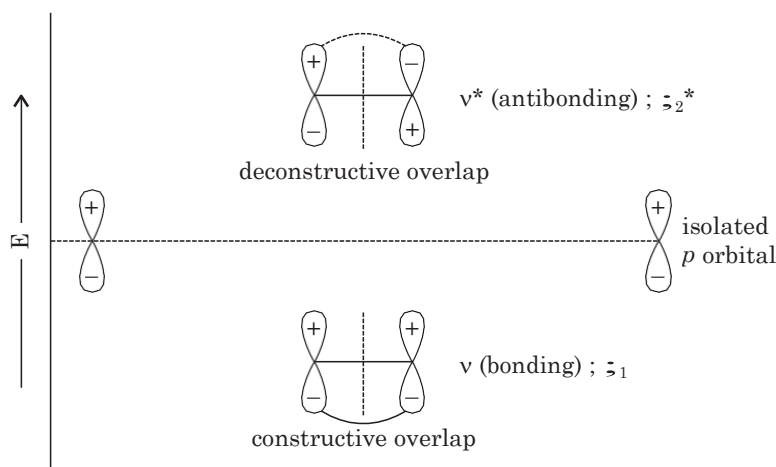


Fig. 1 The combination of two p orbitals results in the formation of two molecular orbitals.

In 1,3-butadiene, we have a system of four p orbitals on four adjacent carbons. These four p orbitals will overlap to produce four π molecular orbitals. We can get four new MOs in a number of equivalent ways. One of the ways to obtain four new molecular orbitals is by linear combination of two molecular orbitals of ethylene. Linear combination of orbitals is also known as *perturbation theory* or *perturbation molecular orbital (PMO) theory*. Linear combination always takes place between two orbitals (two atomic orbitals, two molecular orbitals or one atomic and one molecular orbitals) having minimum energy difference. This means that we need to look only at the results of the $\pi \pm \pi$ and $\pi^* \pm \pi^*$ interactions and do not have to consider $\pi \pm \pi^*$ (Fig. 2).

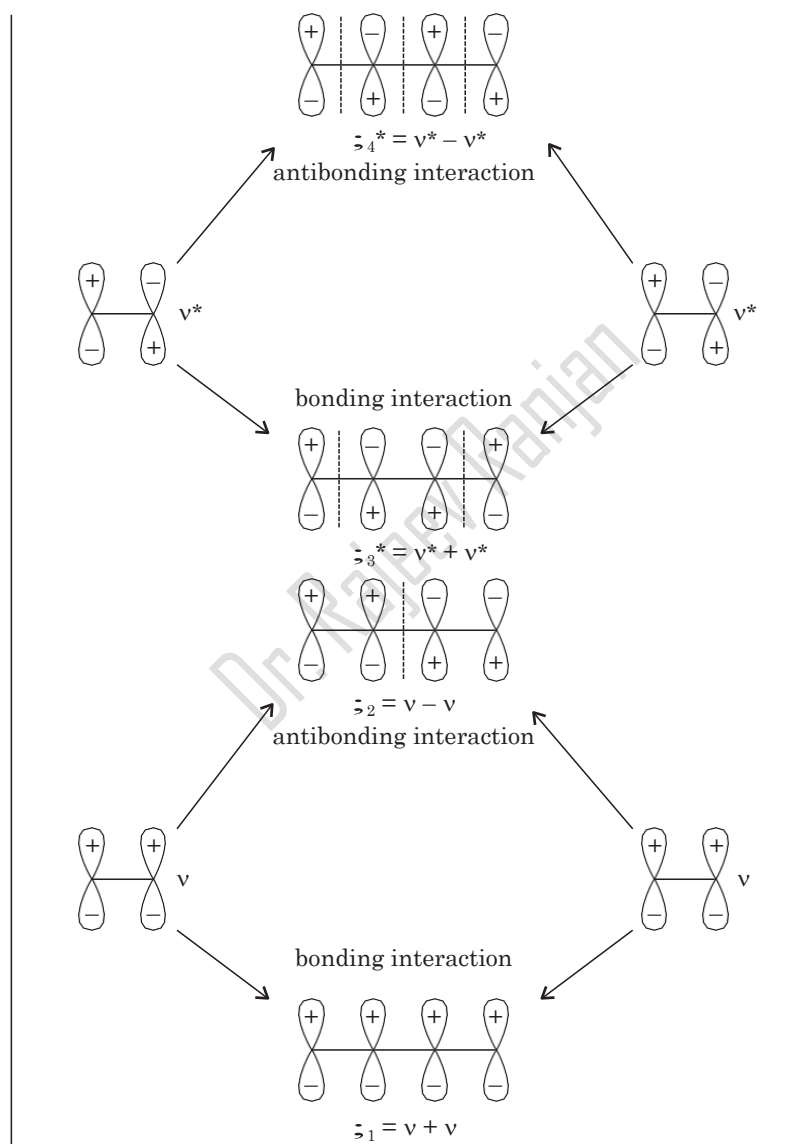


Fig. 2 The schematic formation of the π molecular orbitals of 1,3-butadiene from the π molecular orbitals of ethylene.

The lowest energy orbital (ψ_1) of 1,3-butadiene is exceptionally stable for two reasons : there are three bonding interactions, and the electrons are delocalised over four nuclei (Fig. 3).

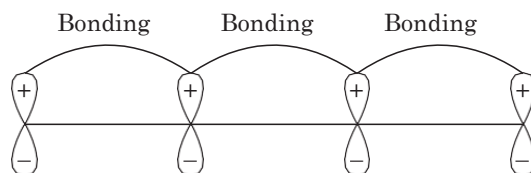


Fig. 3 $\psi_1 = \pi + \pi$ (bonding interaction between two ethylene bonding MOs)

The second molecular orbital ψ_2 of 1,3-butadiene is obtained from the antibonding interaction between two bonding molecular orbitals of ethylene. The ψ_2 orbital has two bonding and one antibonding interaction, so we would expect it to be a bonding orbital (two bonding – one antibonding = one bonding). Thus energy of ψ_2 is more than that of ψ_1 . ψ_2 molecular orbital has one node between $C_2 - C_3$. A node is a plane where the wave function drops to zero (Fig. 4).

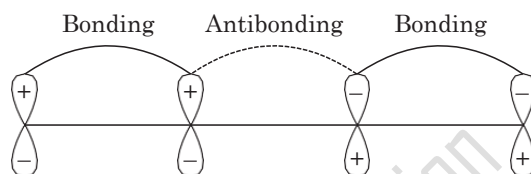


Fig. 4 $\psi_2 = \pi - \pi$ (antibonding interaction between two ethylene π molecular orbitals)

The third butadiene MO, ψ_3^* has two nodes. This molecular orbital is obtained from the bonding interaction between π^* and π^* of two ethylene molecules. There is a bonding interaction of the $C_2 - C_3$ bond and there are two antibonding interactions : one at $C_1 - C_2$ bond and the other at the $C_3 - C_4$ bond. This is an antibonding orbital (one bonding – two antibonding = one antibonding) having two nodes. Thus energy of this ψ_3^* orbital is more than the energy of ψ_2 MO (Fig. 5).

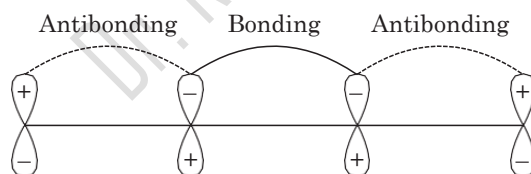


Fig. 5 $\psi_3^* = \pi^* + \pi^*$ (bonding interaction between two antibonding MOs of ethylene)

The fourth molecular orbital (ψ_4^*) is obtained from the antibonding interaction between π^* and π^* of two ethylene molecules. This molecular orbital has three nodes and is totally antibonding. This MO has the highest energy (Fig. 6).

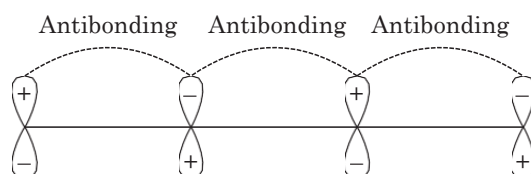


Fig. 6 $\psi_4^* = \pi^* - \pi^*$ (antibonding interaction between π^* and π^* of ethylene)

Following generalisations can be made to construct the molecular orbitals of the conjugated polyenes from the π molecular orbitals of ethylene and 1,3-butadiene :

1. A π electron system derived from the interaction of a number of m of p orbitals contain m molecular orbitals (MOs) that differ in energy. Thus the number of π MOs are always equal to the number of atomic p orbitals. In 1,3-butadiene, four p orbitals are used in the formation of the π MOs, thus four π MOs results, which we shall abbreviate as ψ_1 , ψ_2 , ψ_3 and ψ_4 (or π_1 , π_2 , π_3 and π_4).
2. Half of the molecular orbitals (*i.e.* $m/2$) have lower energy than the isolated p orbitals. These are called bonding molecular orbitals (BMOs). The other half have energy higher than the isolated p orbitals. These are called antibonding molecular orbitals (ABMOs). To emphasise this distinction, antibonding MOs will be indicated with asterisks. Thus, 1,3-butadiene has two bonding MOs (ψ_1 and ψ_2) and two antibonding MOs (ψ_3^* and ψ_4^*).
3. The bonding MO of lowest energy ψ_1 has no node. Each molecular orbital of increasingly higher energy has one additional node. Thus, in 1,3-butadiene ψ_1 has zero node, ψ_2 has one node, ψ_3^* has two nodes and ψ_4^* has three nodes.
4. The nodes occur between atoms and are arranged symmetrically with respect to the centre of the π electron system.

The node in ψ_2^* of ethylene is between two carbons atoms, in the centre of the π system (Fig. 1). The node in ψ_2 of 1,3-butadiene is also symmetrically placed in the centre of the π system. The two nodes in ψ_3^* are placed between carbon-1 and carbon-2 and between carbon-3 and carbon-4 respectively—equivalent distance from the centre of the π system. Each of the three nodes in ψ_4^* , the orbital of highest energy, must occur between carbon atoms. Thus the highest level has a node between each adjacent carbon pair (Fig. 2).

The next generalisation relates to the symmetry of the molecular orbitals. Various molecular orbitals are classified according to their two independent symmetrical properties.

SYMMETRY IN π MOLECULAR ORBITAL

A π molecular orbital possesses either mirror plane symmetry or centre of symmetry. Both symmetries are not present together in a given π molecular orbital.

m-Symmetry. Some molecular orbitals have the symmetry about the mirror plane (m) which bisects the molecular orbitals and is perpendicular to the plane of the molecule (Fig. 7).

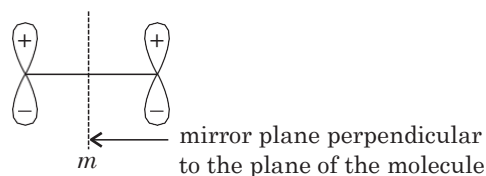


Fig. 7

Both orbitals in Fig. 7 are mirror images to each other hence in this MO there is mirror plane symmetry, abbreviated as $m(S)$.

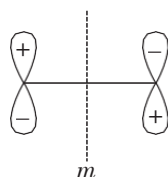


Fig. 8 (a)

In Fig. 8 (a) both orbitals are not mirror images to each other. Thus in this MO there is mirror plane asymmetry, abbreviated as $m(A)$.

C_2 -Symmetry. The centre of symmetry is a point in the molecular axis from which if lines are drawn on one side and extended an equal distance on the other side, will meet the same phases of the orbitals (Fig. 8 (b)).

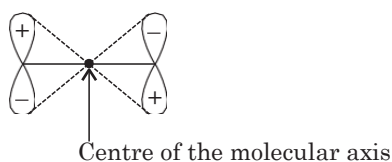
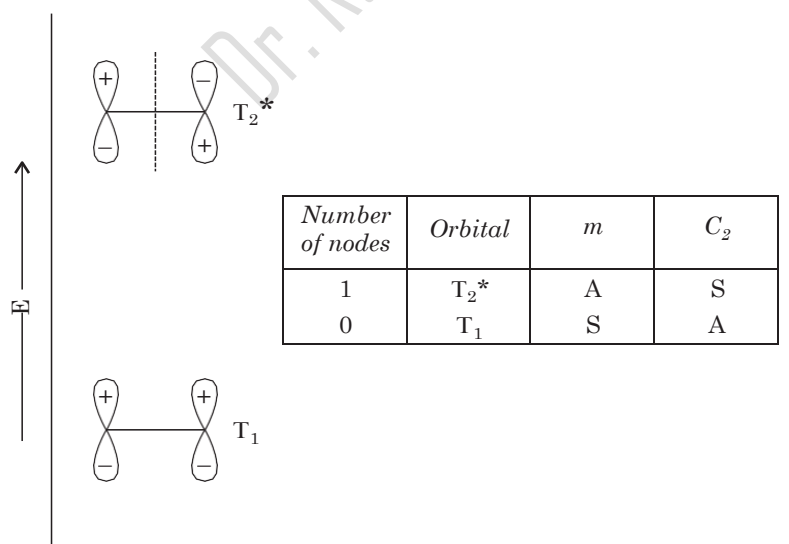


Fig. 8 (b)

Both orbitals in Fig. 8 (b) are symmetrical with respect to centre of the molecular axis. Thus in this MO there is centre of symmetry, abbreviated as $C_2(S)$.

$m(S)$ means plane of symmetry.
 $C_2(S)$ means centre of symmetry.

Let us take examples for the purpose of symmetry properties in ethylene (Fig. 9) and 1,3-butadiene (Fig. 10).

Fig. 9 Symmetries in the π molecular orbitals of ethylene

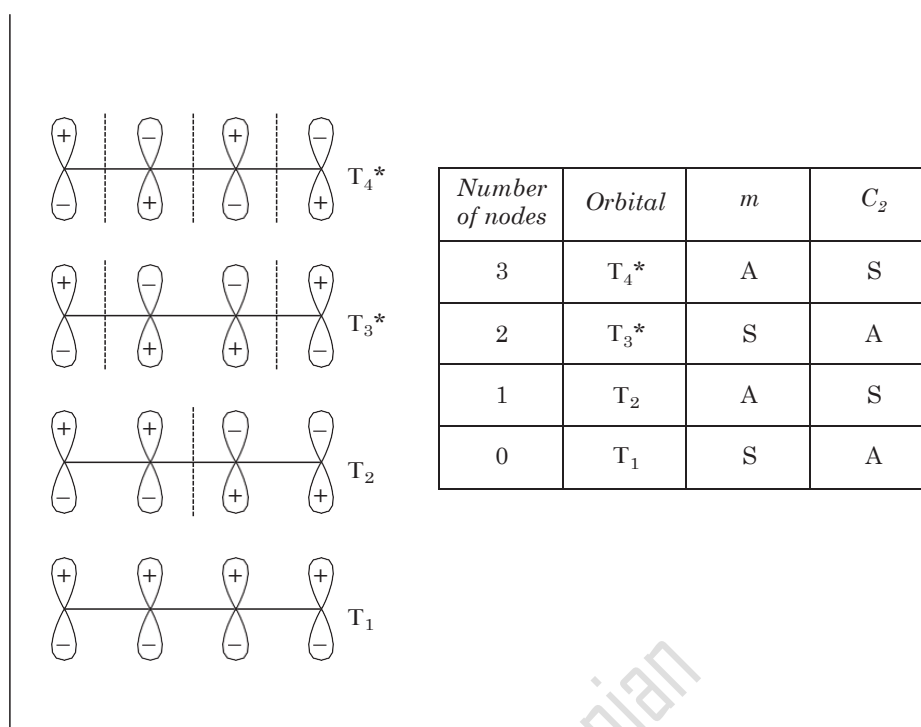


Fig. 10 Symmetries in the π molecular orbitals of 1,3-butadiene

On the basis of the above two examples we can conclude the following *very important points* for linear conjugated π systems :

1. The wave function ψ_n will have $(n - 1)$ nodes.
2. When n is odd, ψ_n will be symmetric with m and asymmetric with C_2 .
3. When n is even, ψ_n will be symmetric with C_2 and asymmetric with m . Table-1.

Table 1 Symmetry elements in the orbital ψ_n of a linear conjugated polyene

Wave function	nodes $(n - 1)$	m	C_2
$\Psi_{\text{odd}} ; \Psi_1, \Psi_3, \Psi_5 \dots$	0 or even	S	A
$\Psi_{\text{even}} ; \Psi_2, \Psi_4, \Psi_6 \dots$	odd	A	S

FILLING OF ELECTRONS IN π MOLECULAR ORBITALS IN CONJUGATED POLYENES

Conjugated polyenes always contain even number of carbon atoms. These polyenes contain either $(4n)\pi$ or $(4n + 2)\pi$ conjugated electrons. The filling of electrons in the π molecular orbitals of a conjugated polyene is summarised below :

1. Number of bonding π MOs and antibonding π MOs are same.
2. Number of electrons in any molecular orbital is maximum two.

3. If a molecular orbital contains two electrons then both electrons are always paired.
4. Molecular orbitals follow Aufbau principle and Hund's rule.
5. Energy of the π molecular orbital is directly proportional to the number of the nodal planes.
6. There will be no degenerate molecular orbitals in any energy level, *i.e.*, each and every energy level contains one and only one molecular orbital.

CONSTRUCTION OF MOLECULAR ORBITALS OF CONJUGATED IONS AND RADICALS

Conjugated unbranched ions and radicals have an odd number of carbon atoms. For example, the allyl system (cation, anion or radical) has three carbons and three p orbitals—hence, three molecular orbitals. We can get three new molecular orbitals by linear combination of one molecular orbital of ethylene and an isolated p orbital. As already mentioned that the linear combination always takes place between two orbitals having minimum energy difference. In allylic system linear combination takes place between one ethylene MO and an isolated p orbital. This means that we need to look at the results of the $\pi \pm p$ and $\pi^* \pm p$ interactions (Fig. 11).

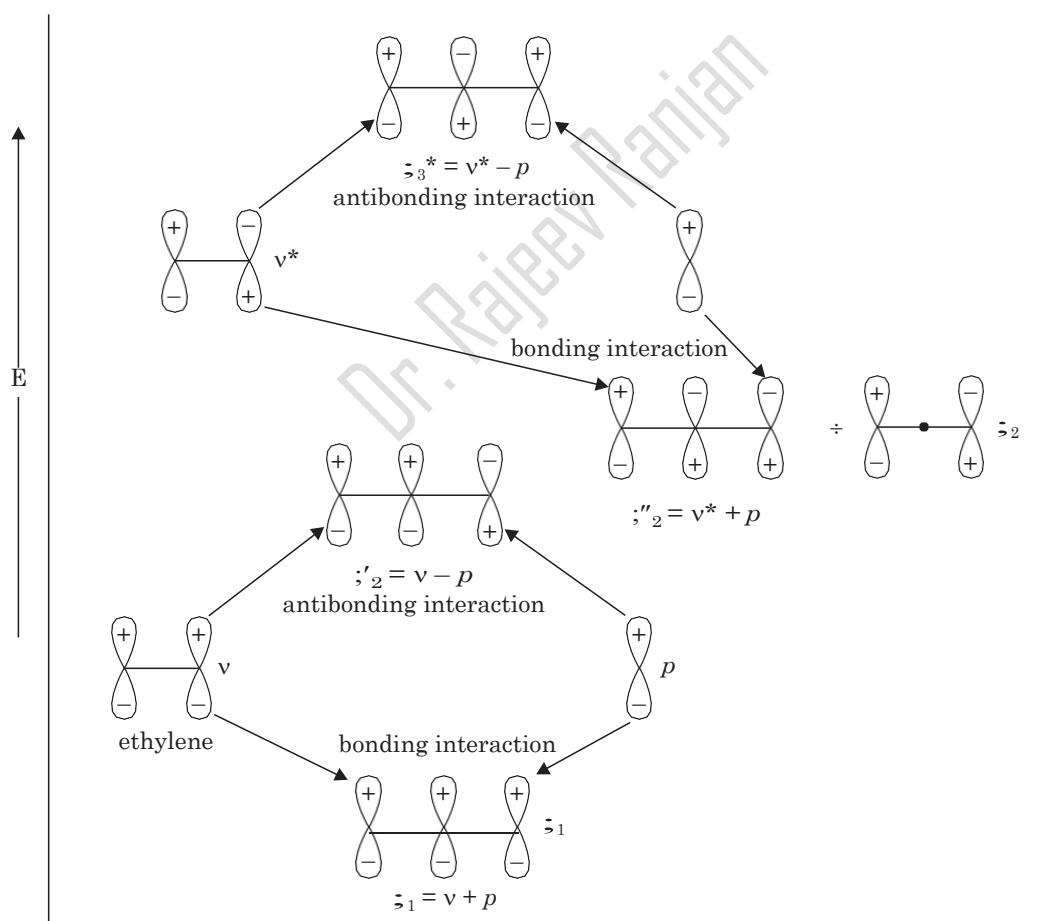


Fig. 11

- (i) The ethylene bonding orbital, π gives linear combination with the p orbital in a bonding way and moving down in energy to give ψ_1 .
- (ii) The ethylene antibonding orbital (π^*) gives linear combination with p orbital in an antibonding way and moving up in energy to give ψ_3^* .
- (iii) The p orbital mixes with the both bonding and antibonding orbitals of ethylene. Thus there is double mixing for the p orbital. The lower energy ethylene bonding orbital (π) mixing in an antibonding way to push the p orbital up in the energy ($\psi_2' = \pi - p$) but the ethylene antibonding orbital mixing in a bonding way to push to p orbital down in energy ($\psi_2'' = \pi^* + p$). Thus the net result in the energy change is zero. Under this situation a nodal plane always passes through the central carbon of the chain. This means an electron in ψ_2 has no electron density on the central carbon. Thus the ψ_2 , *i.e.*, central molecular orbital must be non-bonding molecular orbital. Thus the molecular orbitals of the allylic system is represented as follows (Fig. 12).

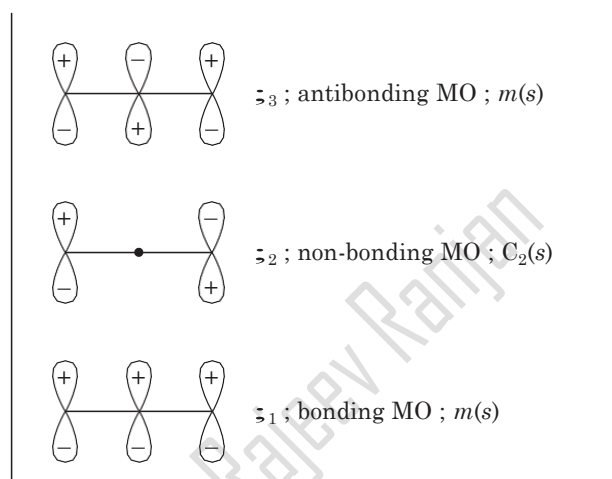


Fig. 12 π molecular orbitals of allyl system.

From the example of allyl system following generalisation can be made to construct the molecular orbitals of the conjugated open chain system (cation, anion and radical) containing odd number of carbon atoms :

- Number of conjugated atoms (or p orbitals) are always odd. For example, allyl system has three orbitals and 2,4-pentadienyl system has five orbitals.
- These systems have always one non-bonding molecular orbital whose energy is always equal to the unhybrid p orbital. Non-bonding molecular orbital is always central molecular orbital of the system (Fig. 12).
- If system has m (which is always odd) atomic p orbitals then it has :
 - $\frac{m-1}{2}$ bonding molecular orbitals,
 - $\frac{m-1}{2}$ antibonding molecular orbitals, and
 - one non-bonding molecular orbital.
- In non-bonding molecular orbital all the nodal planes (*i.e.*, $n - 1$ nodal planes for ψ_n wave function) pass through the carbon nucleus (or nuclei) (Fig. 13).

5. When ψ_n is odd ($\psi_1, \psi_3, \psi_5, \dots$), all nodal planes pass between two carbon nuclei (Fig. 13).
6. When ψ_n is even ($\psi_2, \psi_4, \psi_6, \dots$), one nodal plane passes through the central carbon atom and remaining nodal planes pass between two carbon atoms (Fig. 13).

Fig. 13 illustrates schematically the forms of the molecular orbitals for chains upto seven carbon atoms in length with symmetries and nodal planes.

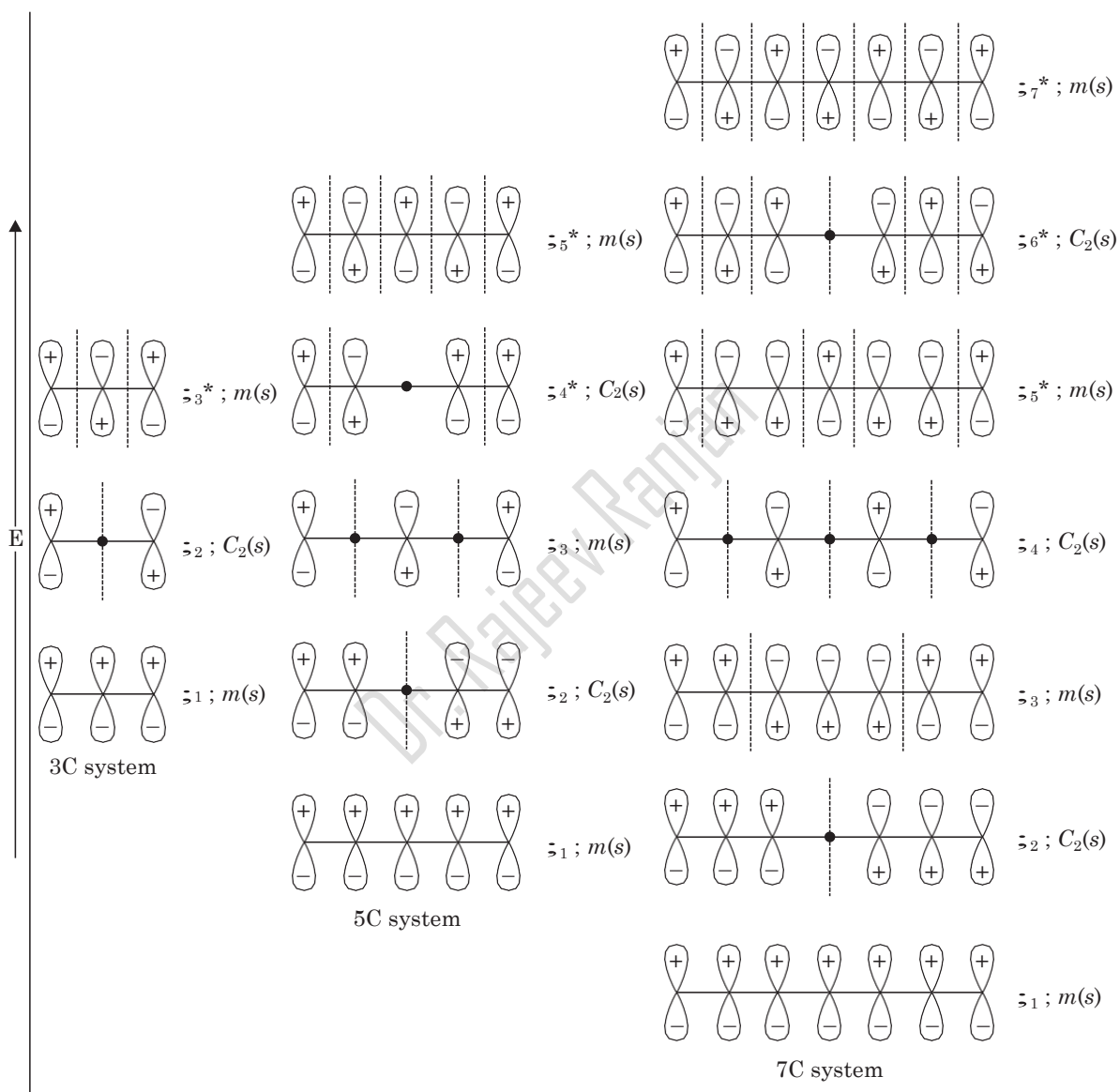


Fig. 13 π molecular orbitals of allyl 2,4-pentadienyl and 2,4,6-heptatrienyl system.

Electron occupancy of allyl carbocation, allyl free radical and allyl carbanion is shown in Fig. 14.

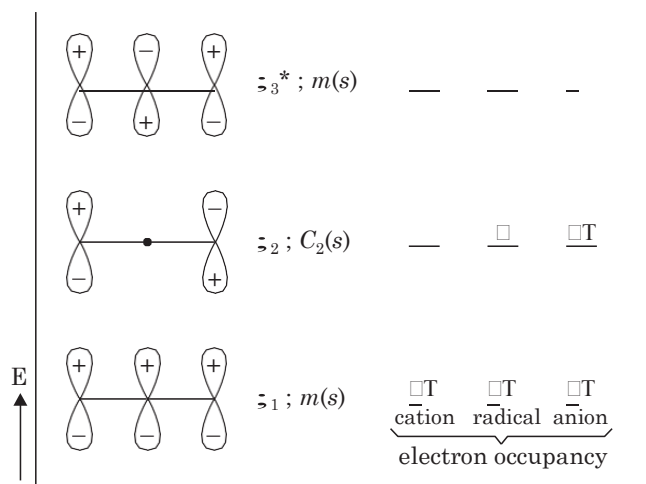


Fig. 14 π molecular orbitals with electron occupancy of the allyl system

Similarly, electron occupancy of 2,4-pentadienyl systems are shown in Fig. 15.

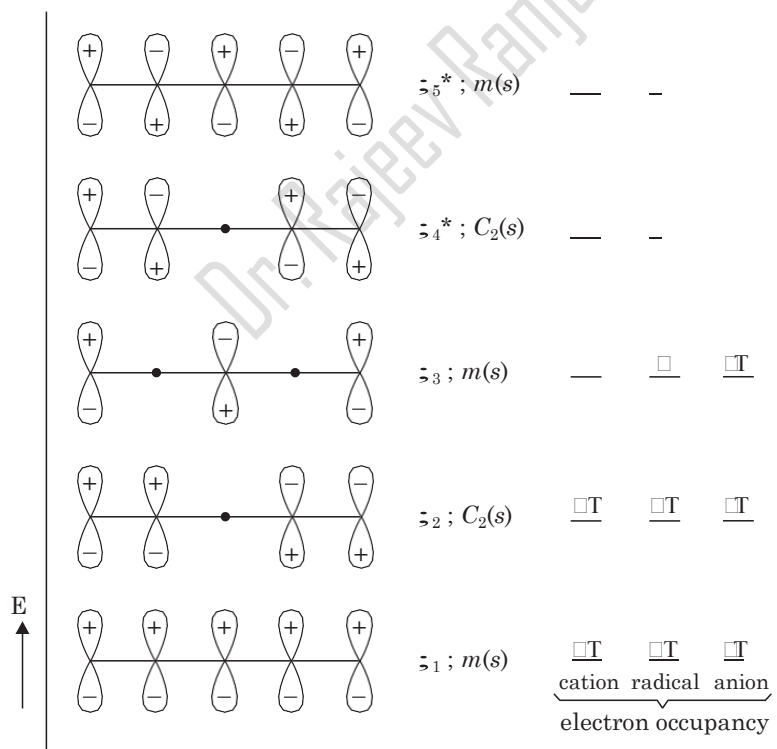


Fig. 15 π molecular orbitals with electron occupancy of the 2,4-pentadienyl system

Notice that cations, radicals and anions involving the same π system have the same molecular orbitals. For example, the MOs of the allyl system apply equally well to the allyl cation, allyl radical and allyl carbanion because all the three species contain the same p orbitals. These species differ only in the *number* of π electrons, as shown in the “*electron occupancy*” column of Fig. 14.

FRONTIER MOLECULAR ORBITALS

Two π molecular orbitals are of particular importance in understanding pericyclic reactions. One is the occupied molecular orbital of highest energy, known as *highest occupied molecular orbital* (HOMO). The other is the unoccupied molecular orbital of lowest energy known as *lowest unoccupied molecular orbital* (LUMO). HOMO and LUMO of any given compound have opposite symmetries (Fig 16). HOMO and LUMO are referred to as *frontier molecular orbitals*.

–	ψ_4^*	–	$C_2(s)$	
–	ψ_3^*	–	$m(s)$	LUMO or ground state LUMO
–	ψ_2	$\square\uparrow$	$C_2(s)$	HOMO or ground state HOMO
–	ψ_1	$\square\uparrow$	$m(s)$	

Fig. 16 Electronic state of ground state of 1,3-butadiene

HOMO of the ground state species is also known as ground state HOMO. Similarly, LUMO of the ground state of the species is known as ground state LUMO.

Why are the LUMO and HOMO so important in determining the course of a concerted reaction? The electrons in the HOMO of a molecule are like the outer shell electrons of an atom. They can be removed with the least expenditure of energy because they are already in a highest energy level than any of the other electrons in the molecule. The LUMO of a molecule is the orbital to which electrons can be transformed with the least expenditure of energy.

The higher is the energy of HOMO of a molecule, the more easily electrons can be removed from it. The lower is the energy of the LUMO of the molecule, the more easily electrons can be transferred into it. Therefore, the interaction between a molecule with a high HOMO and are with a low LUMO is particularly strong.

In general, the smallest the difference in energy between HOMO of one molecule and the LUMO of another with which it is reacting, the stronger is the interaction between the two molecules.

EXCITED STATES

The molecules and ions we have been discussing can absorb energy from electromagnetic radiation of certain wavelengths. This process is shown schematically in Fig. 17 for 1,3-butadiene. Let us refer to the normal electronic configuration of 1,3-butadiene as the *ground state*. When 1,3-butadiene absorbs a photon of proper wavelength *an electron* is promoted from

the HOMO (ψ_2) to the LUMO (ψ_3^*). The species with the promoted electron is an *excited state* of 1,3-butadiene. The orbital ψ_3^* becomes HOMO and ψ_4^* becomes LUMO of the excited state. HOMO of excited state is termed as excited state HOMO or photochemical HOMO. Similarly, LUMO of the excited state is termed as excited state LUMO or photochemical LUMO (Fig. 17).

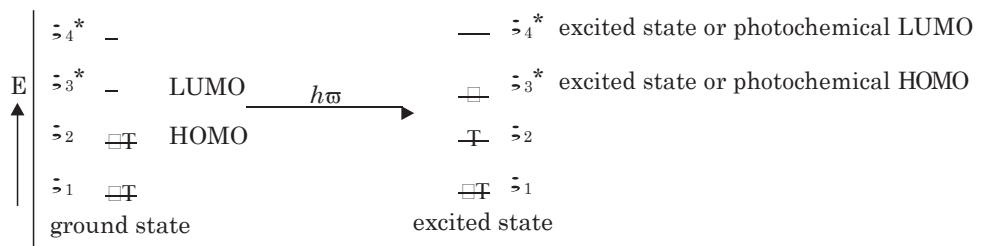
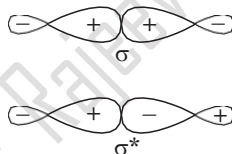


Fig. 17

Notice that the HOMO of ground state and excited state have opposite symmetries. Similarly, LUMO of the ground state and excited state also have opposite symmetries.

SYMMETRIES IN CARBON-CARBON SIGMA BOND

The sigma orbital of a carbon-carbon covalent bond has a mirror plane symmetry, and since a rotation of 180° through its midpoint regenerates the same sigma orbital, it also has a C_2 symmetry. A sigma antibonding molecular orbital is asymmetric with respect to both m and C_2 (Table 2).

Table 2 Symmetric properties of σ and σ^* molecular orbitals.

Orbital	m	C_2
σ^*	A	A
σ	S	S

THEORY OF PERICYCLIC REACTIONS

Pericyclic reactions are defined as reactions that occur by concerted cyclic shift of electrons. According to the Woodward and Hoffmann symmetry of the molecular orbitals that participate in the chemical reaction determines the course of the reaction. They proposed what they called the principle of the *conservation of orbital symmetry*; in the concerted reactions. In the most general terms, the principle means that in concerted pericyclic reactions, the molecular orbitals of the starting materials must be transformed into the molecular orbitals of the product in

smooth continuous way. This is possible only if the orbitals have similar symmetry, *i.e.*, orbitals of the reactant and product have similar symmetries.

In concerted reaction product formation takes place by formation of cyclic transition state. The transition state of pericyclic reactions should be intermediate between the electronic ground states of the starting material and product. Obviously, the most stable transition state will be one which conserves the symmetry of the reactant orbitals in passing to product orbitals. In other words, a symmetric (S) orbital in the reactant must transform into a symmetric orbital in the product and that an asymmetric (A) orbital must transform into an asymmetric orbital. If the symmetries of the reactants and product orbitals are not the same, the reaction will not take place in a concerted manner.

If symmetry is conserved during the course of the reaction then reaction will take place and process is known as *symmetry allowed* process. If symmetry is not conserved during the course of the reaction, the reaction is known as *symmetry-forbidden* process. The energy of the transition state (*i.e.*, energy of activation of the transition state) of symmetry allowed process is always lower than the symmetry-forbidden process.

PROBLEMS

- Sketch the π molecular orbitals of
 - 1,3-Butadiene
 - 1,3,5-hexatriene
- Sketch the π molecular orbitals of the allyl system. Give electron occupancy in allyl carbocation, allyl free radical and allyl carbanion.
- Sketch the π molecular orbitals of 2,4-pentadienyl system. Also draw nodal points in molecular orbitals. Show electron occupancy in its carbocation, free radical and carbanion.
- Give symmetric properties of HOMO and LUMO of the following systems :
 - Butadiene
 - Excited state butadiene
 - 1,3,5-Hexatriene
 - Excited state hexatriene.
- Show the electronic configuration of the ground state of 1,3,5-hexatriene. Give symmetric properties of all the molecular orbitals of 1,3,5-hexatriene.
- Show the electronic configuration of the excited state of 2,4-pentadienyl cation. Give symmetric properties of HOMO and LUMO of the system.
- Draw molecular orbitals of 1,3-butadiene from the linear combination of molecular orbitals of two ethylene molecules.
- Draw molecular orbitals of allyl system by the use of the linear combination of molecular orbital of one ethylene molecule and one p -atomic orbital.
- Explain why ψ_3 of butadiene has higher energy than the ψ_2 ?
- Explain why energy of ψ_5 of 1,3,5-hexatriene is less than the ψ_6 .
- What are HOMO and LUMO ? Why these two orbitals are so important in pericyclic reactions ?
- Give classification of pericyclic reactions with one example each.
- Draw the p -orbital array in the π molecular orbitals of the following ions
 - Draw diagrams showing the occupied orbitals of the ground states and indicate the HOMO's.
 - $$\text{CH}_3-\text{CH}=\overset{\oplus}{\text{C}}\text{H}-\text{CH}-\text{CH}_3$$
 - $$\text{CH}_2=\overset{\ominus}{\text{C}}\text{H}-\text{CH}-\text{CH}_3$$
 - $$\text{CH}_3-\overset{\ominus}{\text{C}}\text{H}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$$
- How many approaches have been made to explain the results of pericyclic reactions ?
- What do you understand from Frontier orbital and orbital symmetry ?



**University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi**

Dr. Rajeev Ranjan