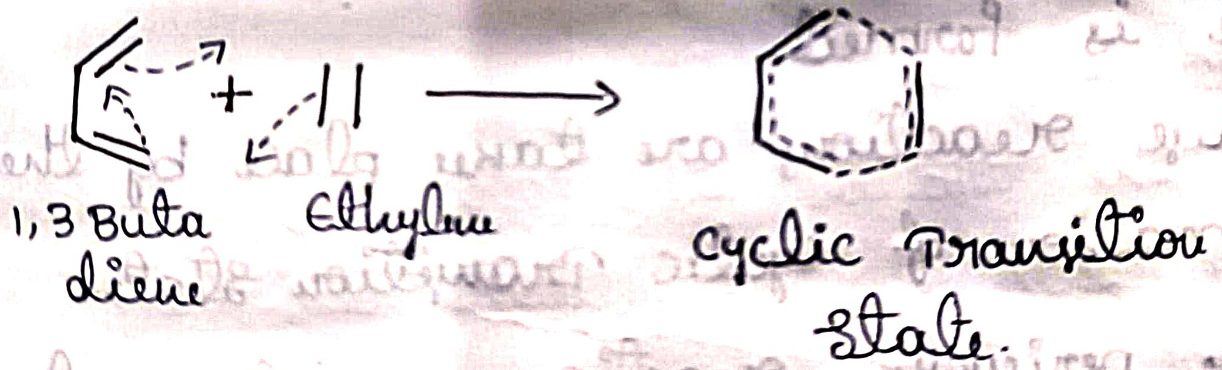
* Pericyclic Reactions *

* The term "pericyclic reactions" was coine by R.B. wood ward. The pericyclic mean arround a cycle.

* The class of organic reactions which takes place in a concerted manner throu-h the formation of a cyclic transition state by the cyclic shift of electrons are called "**Pericyclic Reactions.**"

Ex :- Diel's Alder reaction

Diene + Dienophyl → adduct.



Classification :-

Depending upon the mechanism the pericyclic reactions are classified as follows.

Pericyclic Reactions.

- cyclo addition reactions
- electrocyclic reactions
- Sigmatropic reactions
- Group Transfer reactions

Characterstics :-

1) The pericyclic reactions proceeds in a concerted manner.

2) In these reactions no distinict intermediate is formed.

3) These reactions are takes place by the formation of cyclic Transition state.

4) The pericyclic reactions may takes place by the heat / light energy.

5) The pericyclic reactions depends on the symmetry properties of the reacting systems.

6) The entropy change of these is negative

i.e $\Delta S =$

7) all these reactions are first order reactions.

8) These reactions are uneffected by the catalyst and the solvent.

9) All these reactions are "highly stereospecific

10) The thermal pericyclic reactions takes place from the ground state of the reacting system.

1) The Photochemical pericyclic reactions takes place from the first excited state of the reacting system.

π - Molecular orbitals :-

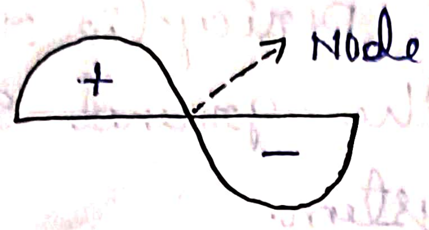
Most of the π - systems will be presented with a normal p-orbital.

The orbitals is defined as the probability of finding the electrons is maximum.

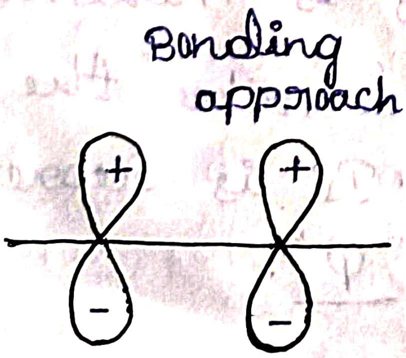
The atomic orbitals describes the wave nature of the electrons. It is represented by the wave function "ψ".

Phases :-

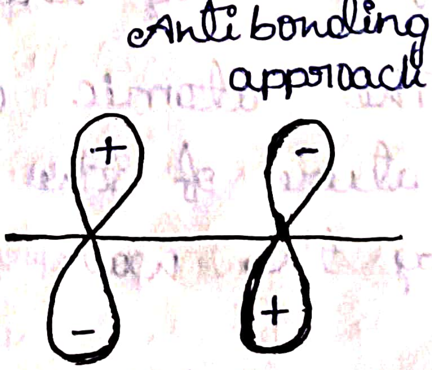
- In a wave the upward displacement shows the positive phase and downward displacement with the negative sign.
- At crossing the wave function is zero.



- The number of orbitals is eaual to the no. of carbon atoms in a π-system.
- If the orbital lobes have the same sign then it is called constructive wave function.
- If the orbital lobes are the an opposit sign then they are called distructive wave function.



(In phase)
constructive wave function



(Out of Phase)
distructive wave function

- For "ψ_n" - wave function if n is odd the terminal lobes are in same sign (in phase).

- If n is even the terminal lobes are in opposite sign (out of phase)

Node (or) Nodel plane :-

- The probability of finding electron is zero is called Node (or) Nodel plane.

- For ψ_n - wave function the number of nodes can be calculated by (n-1) formula.

Ex :- For ψ_1 no. of nodes = 0
ψ_2 no. of nodes = 1
ψ_3 no. of nodes = 2
⋮
ψ_n = n-1

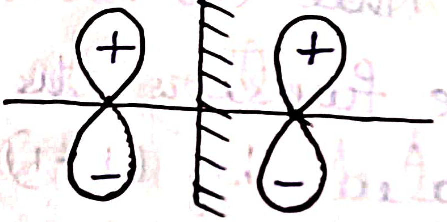
Symmetry properties :-

- For π - molecular orbitals there are 2 symmetry elements are possible.

1) Mirror plane of symmetry. (σ (or) m)
2) Two fold axis of symmetry. (C_2)

1) Mirror plane of symmetry (σ (or) m)

If an imaginary plane is passing through the molecular orbital system it by sets the molecular orbital system two equal half and they have mirror image relationship then the molecular orbital have mirror plane symmetry.



σ - Symmetric

C_2 - Asymmetric

Note :

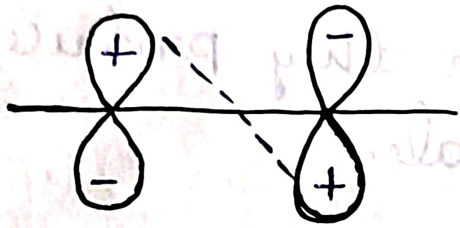
For odd wave function ψ_n (n is odd) the mirror plane symmetry (σ) is always symmetric.

2) Two fold axis of symmetry (C_2)

If we draw an imaginary line and extend through the centre of two lobes connecting the same sign. then it is have C_2 axis of symmetry.

(or)

If we rotate the orbital lobes by an angle 180° ($\frac{360^\circ}{2}$) and gets the same identical lobes then it is also called C_2 axis of symmetry.



C_2 - Symmetric
σ - Asymmetric

For even wave function ψ_n (n = even) the C_2 axis of symmetry is always symmetric.

wave function	σ	C_2
ψ_n (odd)	S	A
ψ_n (even)	A	S

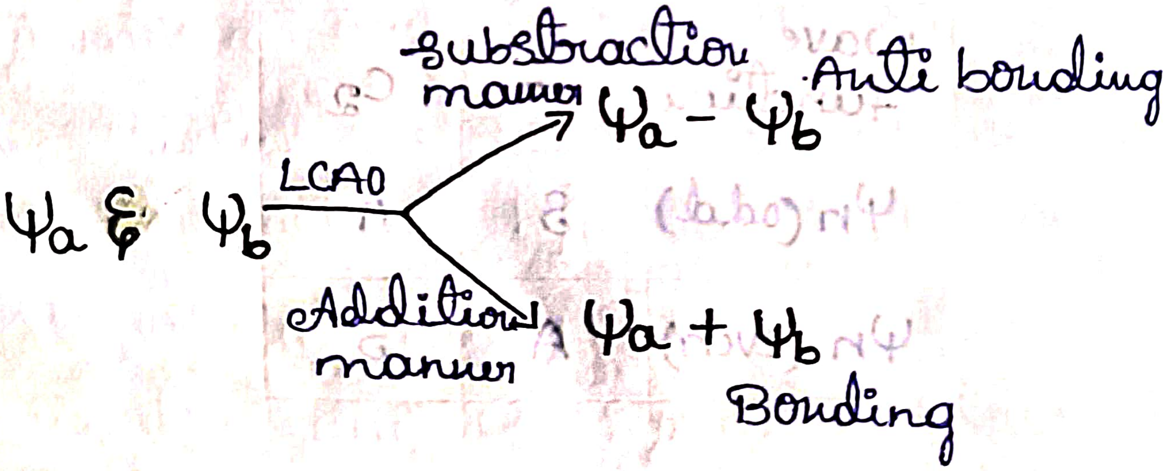
Construction of π - molecular orbitals

→ The molecular orbitals are formed by the linear combination of atomic orbitals. (LCAO).

→ If "n" no. of p atomic orbitals are involved in the LCAO then they produces n no. of molecular orbitals.

→ The molecular orbitals which are formed by the constructive approach (addition manner) those are called Bonding molecular orbital.

→ The molecular orbitals which are formed by the distructive approach (Substraction manner) those are called Anti bonding molecular orbital.



→ If even no. of atomic orbitals (n) are linearly combined then they produces n/2 no. of bonding molecular orbitals and n/2 no. of antibonding molecular orbitals.

→ If odd no. of atomic orbitals are linearly combined then they produces $(\frac{n-1}{2})$ no. of bonding molecular orbitals & $(\frac{n-1}{2})$ no. of anti bonding molecular orbitals and 1 non bonding molecular orbital.

→ The molecular orbitals are designated as $\psi_1, \psi_2, \psi_3, \psi_4 ---- \psi_n$.

→ The energy order the π-molecular orbitals increases ~~the~~ with the increase in n-values.

i.e. $\psi_1 < \psi_2 < \psi_3 < \psi_4 ---- \psi_n$.

→ The possible no. of nodes of a π-molecular system is equal to (n-1).

→ If the π-molecular orbitals has zero (or) even no. of nodes that is odd wave function then it has mirror plane symmetry.

→ If the π-molecular orbital has odd no. of nodes that is even wave function then it has C_2 axis of symmetry.

→ The molecular orbital with electrons having highest energy is called "HOMO" orbital.

→ The molecular orbital without electrons having least energy is called "LUMO" orbital.

Molecular orbital construction in Ethylene
($CH_2=CH_2$)

→ Ethylene system has two carbon atoms.

→ Each orbital of two carbon atoms linearly combined with each other & produces two molecular orbitals.

→ out of these two molecular orbitals ~~are~~ 1 orbital is bonding and the other orbital is antibonding.

→ These two molecular orbitals are designated as ψ_1 and ψ_2.

→ The ψ_1 orbital is formed by the bonding interactions b/w the two p-orbitals.

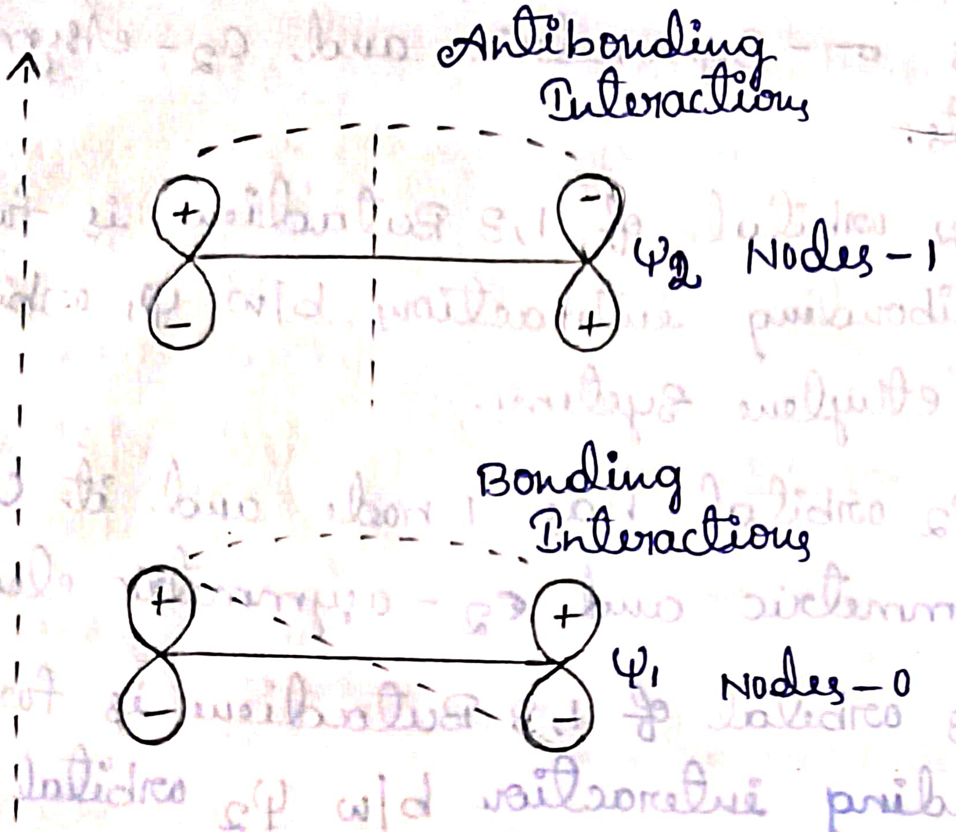
→ ψ_1 orbital has zero nodes and it has σ- symmetric and C_2 - asymmetric elements.

→ The ψ_2 orbital is formed by the anti bonding interactions b/w the two p-orbitals

→ The ψ_2 orbital has 1 node and it has σ - asymmetric and C_2- symmetric elements.

→ The energy order of these two orbitals is $\psi_1 < \psi_2$.

→ The π- molecular orbitals of ethylene system are picturized as below.



σ	C_2
A	S

σ	C_2
S	A

Molecular orbital construction in 1,3 Butadiene

→ 1,3 Butadiene has four carbon atoms.

→ Each p-orbital of four carbon atoms linearly combined with each other and produces four molecular orbitals.

→ out of these 2 are bonding and another two are antiboding.

→ The four molecular orbitals are designated as ψ1, ψ2, ψ3 & ψ4.

→ The ψ1 orbital of 1,3 Butadiene is formed by bonding interaction b/w ψ1 orbitals of two ethylene systems.

→ The ψ_1 orbital has zero nodes and it contains σ - Symmetric and C_2 - Asymmetric elements.

→ The ψ_2 orbital of 1,3 Butadiene is formed by antibonding interactions b/w ψ_1 orbitals of two ethylene systems.

→ The ψ_2 orbital has 1 node and it contains σ - asymmetric and C_2 - symmetric elements.

→ The ψ_3 orbital of 1,3 Butadiene is formed by bonding interaction b/w ψ_2 orbital of two ethylene systems

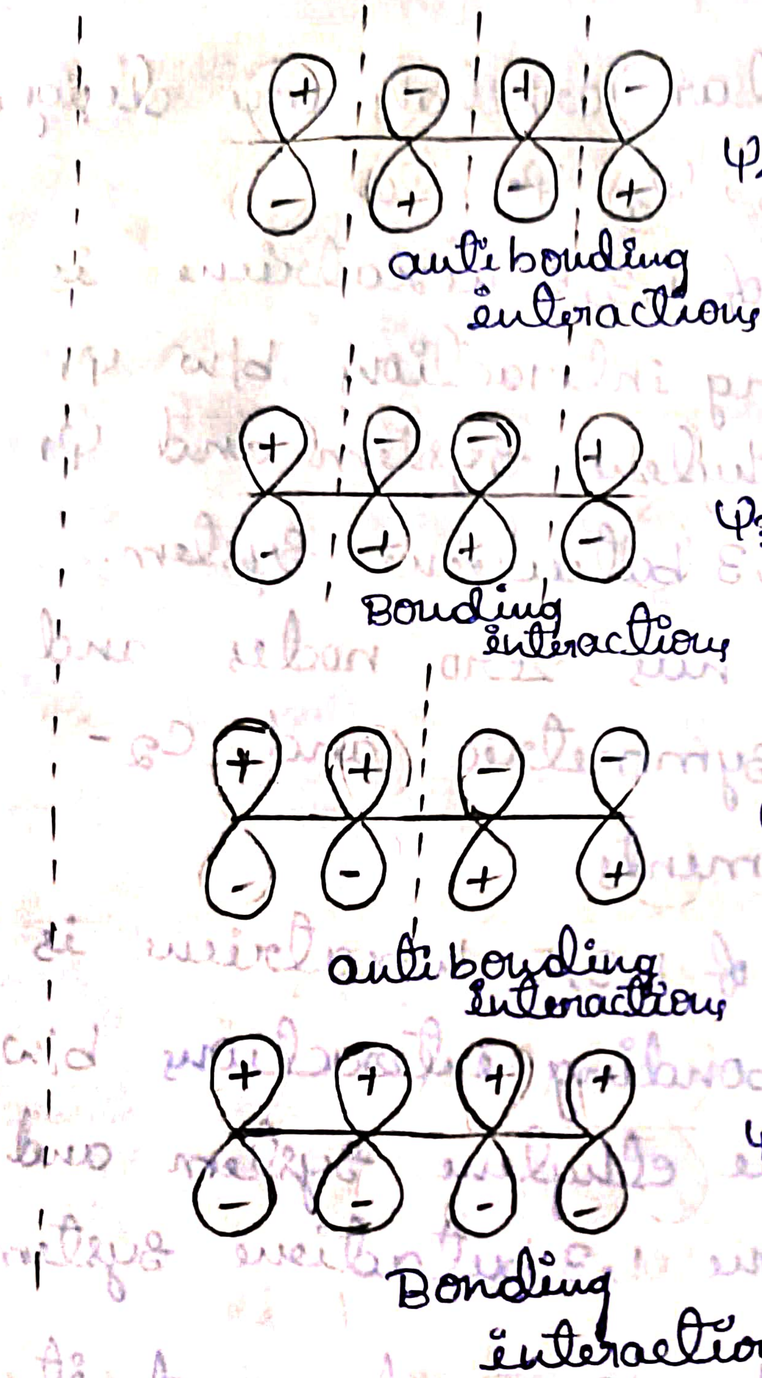
→ The ψ_3 orbital has 2 nodes and it contains σ - symmetric and C_2 - asymmetric elements.

→ The ψ_4 orbital of 1,3 Butadiene is formed by antibonding interaction b/w ψ_2 orbital of two ethylene systems.

→ The ψ_4 orbital has 3 nodes and it contains σ - asymmetric and C_2 - Symmetric elements.

→ The energy order of these four orbitals are $\psi_1 < \psi_2 < \psi_3 < \psi_4$.

→ The π - molecular orbitals of 1,3 Butadiene system are picturized as below.



ψ_4 Nodes = 3

σ	C_2
A	S

ψ_3 Nodes = 2

σ	C_2
S	A

ψ_2 Nodes = 1

σ	C_2
A	S

ψ_1 Nodes = 0

σ	C_2
S	A

Molecular orbital construction in 1, 3, 5 Hexatriene :

* 1, 3, 5 hexatriene has six carbons atoms.

* Each P-orbital of six carbon atoms linearly combined with each other and produces six molecular orbitals.

- * out of these 3 are bonding and another 3 are antibonding.

- * The six molecular orbitals are designated as $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5, \psi_6$.

- * The ψ_1 orbital of 1,3,5 hexatriene is formed by bonding interactions b/w ψ_1 orbital of one ethylene system and ψ_1 orbital of one 1,3 butadiene system.

- * The ψ_1 orbital has zero nodes and it contains σ-symmetric and C_2-Asymmetric elements.

- * The ψ_2 orbital of 1,3,5 hexatriene is formed by the bonding interactions b/w ψ_1 orbital of one ethylene system and ψ_2 orbital of one 1,3 butadiene system

- * The ψ_2 orbital has one node and it contains σ-asymmetric and C_2-symmetric elements.

- * The ψ_3 orbital of 1,3,5 hexatriene is formed by the antibonding interactions of one ethylene system b/w ψ_1 orbital of one ethylene system and one 1,3 butadiene system.

* The ψ_3 - orbital has 2 nodes and it contains σ - symmetric and C_2 - asymmetric elements.

* The ψ_4 orbital of 1,3,5 hexatriene is formed by bonding interactions b/w ψ_2 orbital of one ethylene system and ψ_3 orbital of one 1,3 butadiene system.

* The ψ_4 orbital has 3 nodes and it contains σ - asymmetric and C_2 - symmetric elements.

* The ψ_5 orbital of 1,3,5 hexatriene is formed by the antibonding interactions b/w ψ_2 orbital of one ethylene system and ψ_3 orbital of one 1,3 butadiene system.

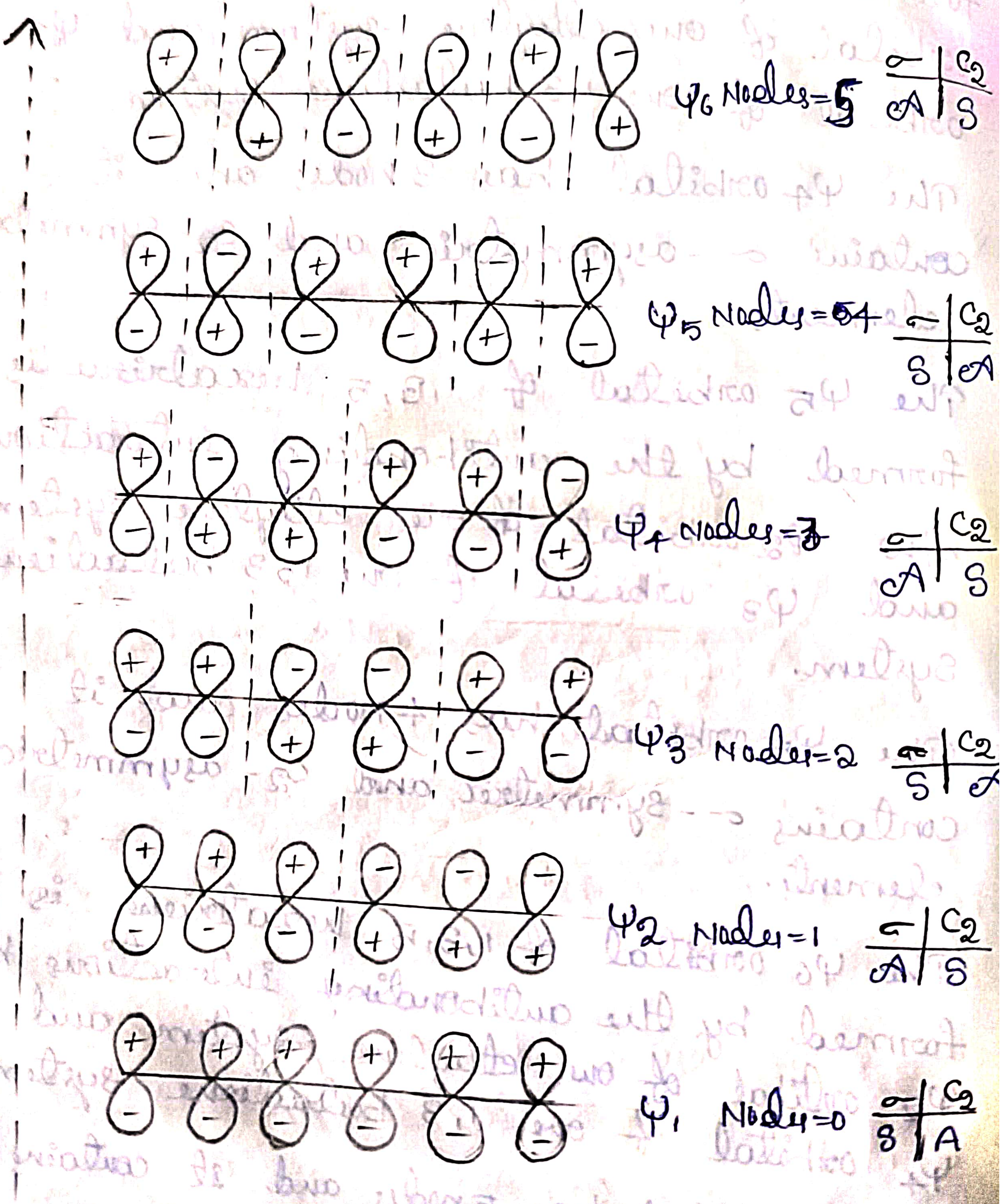
* The ψ_5 orbital has 4 nodes and it contains σ - symmetric and C_2 - asymmetric elements.

* The ψ_6 orbital of 1,3,5 hexatriene is formed by the antibonding interactions b/w ψ_2 ortibal of one ethylene system and ψ_4 orbital of one 1,3 butadiene system.

- The ψ_6 orbital has 5 nodes and it contains σ - asymmetric and C_2 - symmetric elements.

- The energy order of these six orbitals are $\psi_1 < \psi_2 < \psi_3 < \psi_4 < \psi_5 < \psi_6$.

- The π-molecular orbitals of 1,3,5 hexatriene system are picturised as below.



Theories of pericyclic Reactions :

- * Inorder to analyse the course of pericyclic reactions different scientists proposed some theories, those are called pericyclic reactio theories.
- * The important pericyclic reactions theories are gives below.

1) FMO theory.
2) Molecular orbitals symmetry conservatio theory.
3) eAromatic Transition Theory

FMO Theory :

Frontier - Molecular orbitals Theory :

- * This theory was proposed by fuckie in 1942.
- * It is a Key concept in understanding the pericyclic reactions.
- * FMO theory focuses on the interaction b/w HOMO & LUMO orbitals.
- * The molecular orbital with electrons having highest energy is called "HOMO" orbital.
- * The molecular orbital without electrons having least energy is called "LUMO" orbitals.

* The pericyclic reactions are governed by the orbital symmetry rules which are derived by FMO theory.

* For a pericyclic reaction ~~with~~ the symmetric properties of the reactants of HOMO & LUMO are in same Phase (Bonding interaction) then reaction is allowed.

* If the symmetry properties of HOMO and LUMO are in out of Phase (Anti bonding interaction) then the reaction is forbidden.

* HOMO is at Higher energy and it losses electrons easily and the LUMO is at lower energy and it can accept electrons easily.

* HOMO behaved as a nucleophile and LUMO behaves an electrophile.

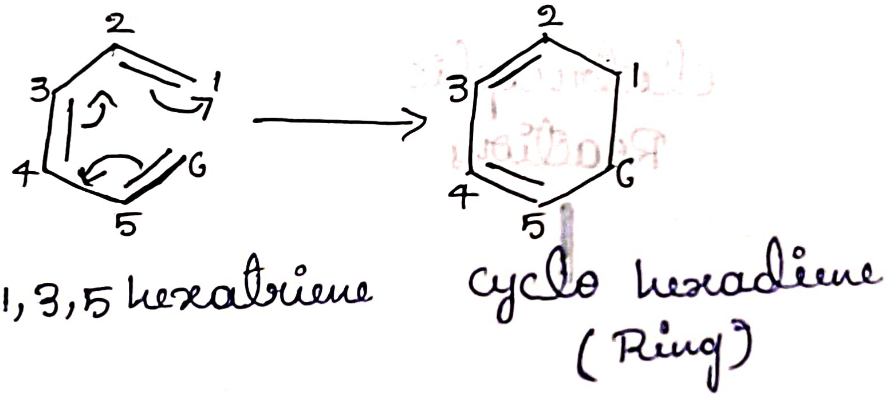
* The stereochemistry of the products depends on the stereochemistry of reaction.

Types of pericyclic Reactions :

Electrocyclic reactions

→ The pericyclic reactions in which the conjugated π-bonded electrons system are reorganised (or) cyclised to form a cyclic ring are known as electrocyclic reactions.

Ex :- cyclisation of 1,3,5 hexatriene



→ All these reactions are reversible reaction

→ During this reaction π-bond is lossed and σ-bond is formed.

→ These reactions are unimolecular reactions.

Conditions :

→ The molecules should contains conjugated double bonds.

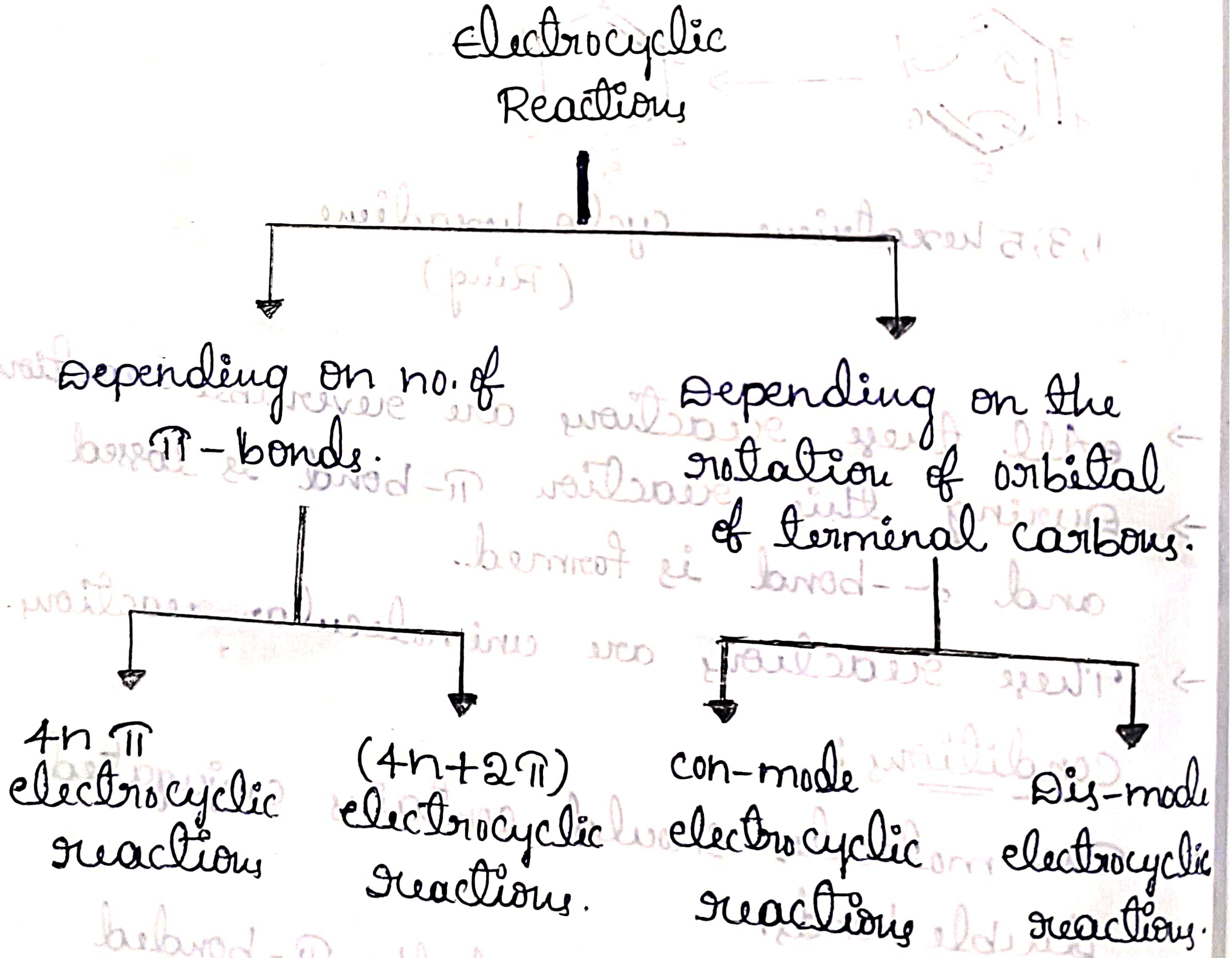
→ The terminal carbons of the π-bonded system are must be closer to eachother.

→ The terminal carbons of π-electron system should have less steric crowding.

- → The π-bonds may be cyclic (or) acyclic.
- → These reactions induced either by thermally (or) photochemically.

Classification :

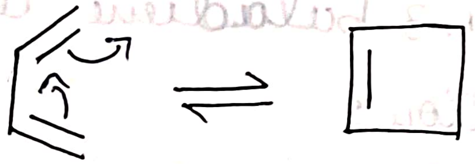
In general the electrocyclic reactions are classified based on no. of π-bonds and the rotation of orbital lobes at the terminal carbon atoms as follows.



4nπ- electrocyclic Reactions :

The electrocyclic reactions in which the conjugated π-electron system contains even no. of π-bonds. Those reactions are called "4nπ- electrocyclic reactions."

Ex :- cyclisation of 1,3 butadiene

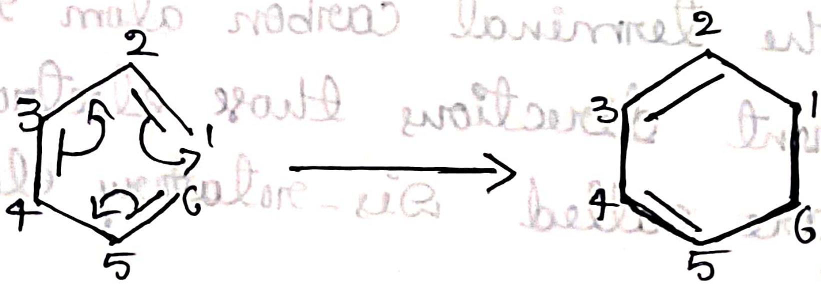


1,3 butadiene cyclobutene

(4n+2)π- Electrocyclic Reactions :

The electrocyclic reactions in which the conjugated π-electron system contains odd no. of π-bonds. Those reactions are called "(4n+2)π- electrocyclic reactions."

Ex :- cyclisation of 1,3,5 hexatriene

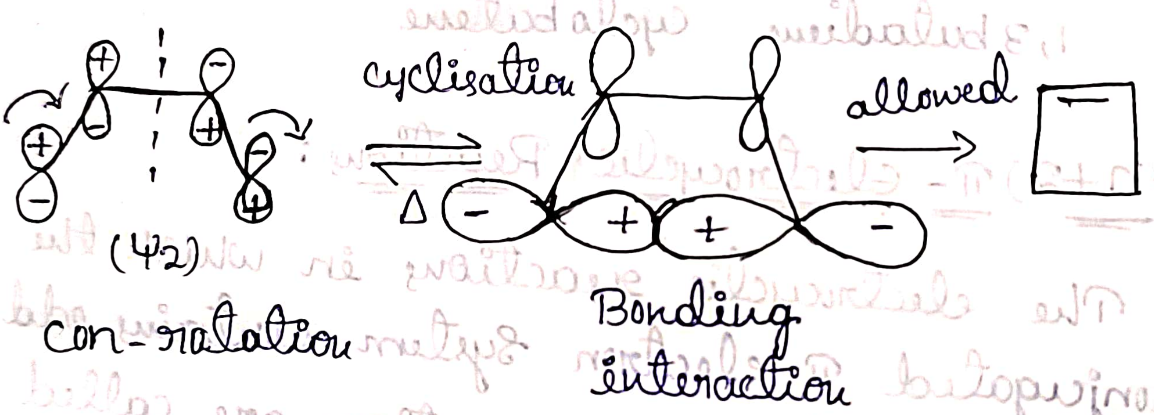


1,3,5 hexatriene

Con-mode electrocyclic reactions :

The electrocyclic reactions in which for the formation of new σ-bond if the orbital lobes at the terminal carbon atom rotate in same direction (either in clockwise or anti clockwise) those electrocyclic reactions are called "con-rotatory electrocyclic reaction"

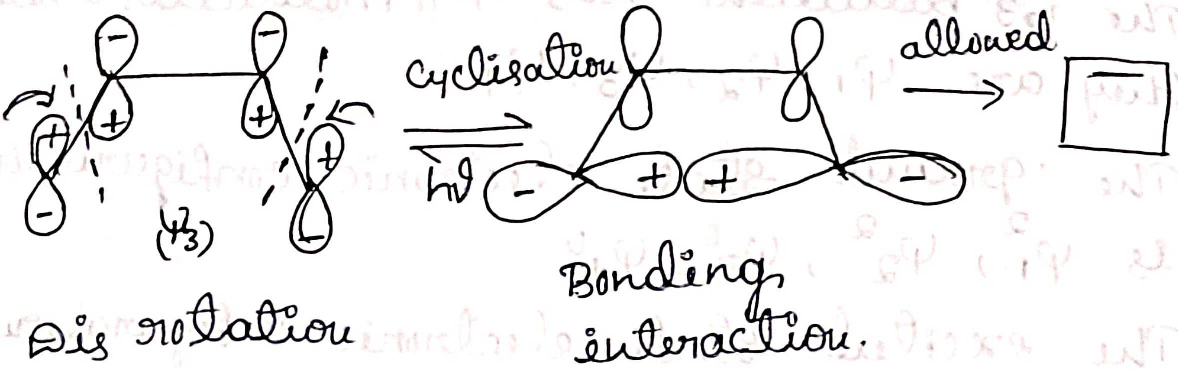
Ex :- cyclisation of 1,3 butadiene under thermal condition :



Dis-mode electrocyclic reactions :

The electrocyclic reactions in which for the formation of new σ-bond if the orbital lobes at the terminal carbon atom rotate in different directions those electrocyclic reactions are called "Dis-rotatory electrocyclic reactions."

Ex :- cyclisation of 1,3 butadiene under photochemical condition.



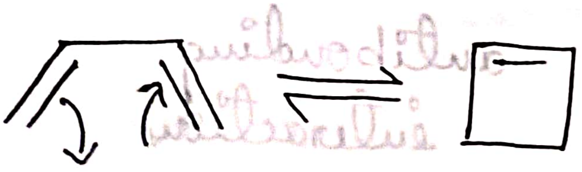
Electrocyclic reactions FMO approach

- * According to FMO theory the HOMO orbitals of the conjugated π- electron system participated in electrocyclic reactions.
- * Under thermal conditions, the HOMO orbital is selected from ground state.
- * Under photochemical conditions, the HOMO orbital is selected from excited state.
- * The bonding interactions b/w the orbital lobes will allows the reaction.
- * The antibonding reactions will forbidden the reaction.

Ex-1

Electrocyclic reactions in 4nπ system:

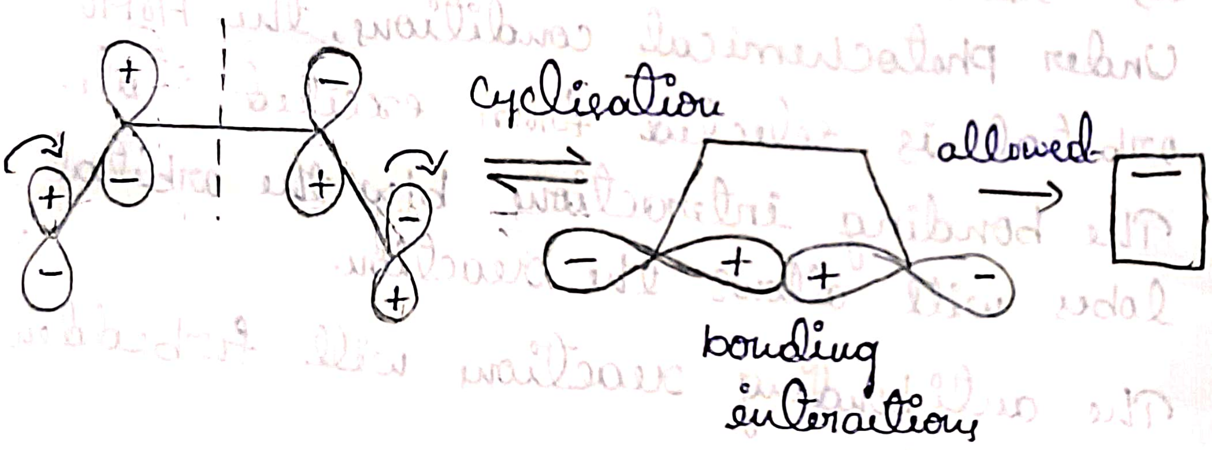
The cyclisation of 1,3 butadiene is a 4nπ- electrocyclic reaction.



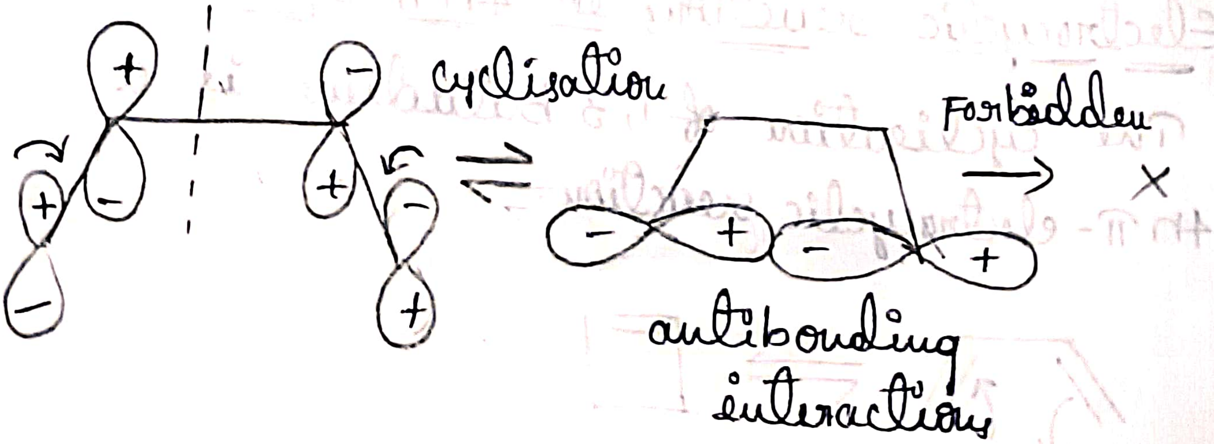
* The 1,3 butadiene has 4 π molecular orbitals, they are $\psi_1, \psi_2, \psi_3, \psi_4$.
* The ground state electronic configuration is $\psi_1^2, \psi_2^2, \psi_3^0, \psi_4^0$.
* The excited state electronic configuration is $\psi_1^2, \psi_2^1, \psi_3^1, \psi_4^0$.
* Under ~~Photo~~ thermal conditions the HOMO orbital is ψ_2.
* Under Photochemical conditions the HOMO orbital is ψ_3.

Under thermal conditions :- (HOMO $= \psi_2$)

Con-mode

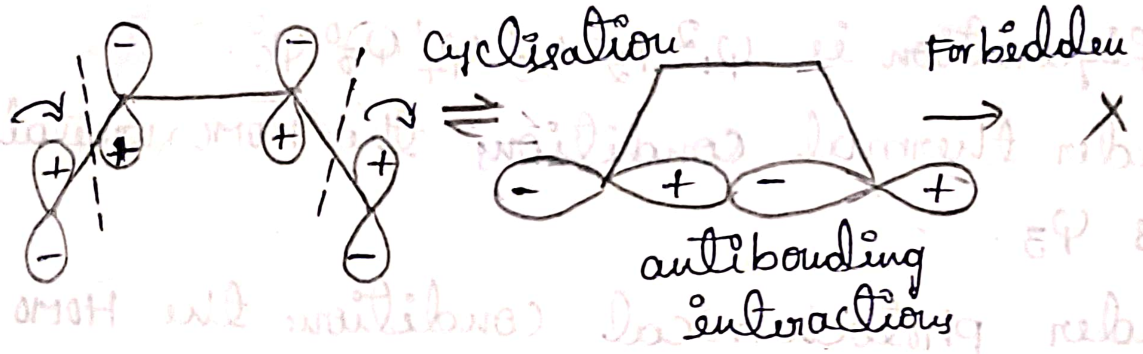


Dis-mode

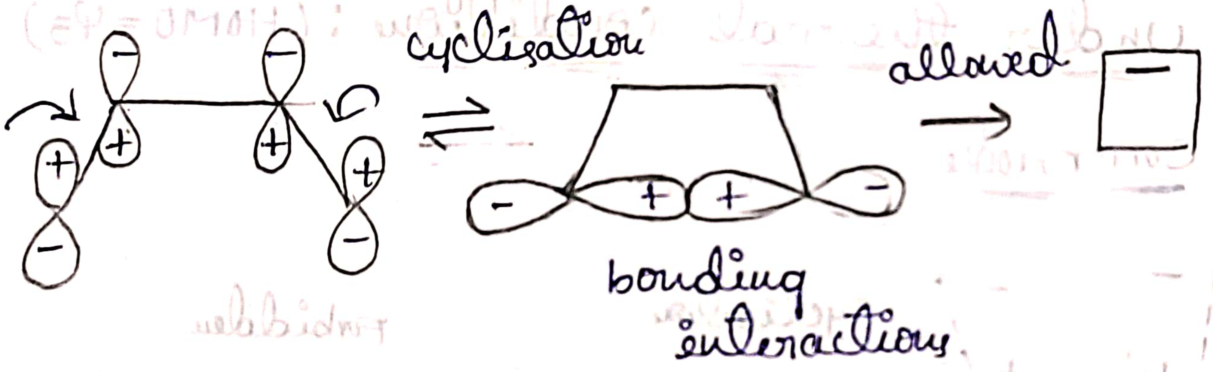


Under photochemical conditions : (HOMO = ψ_3)

Con-mode



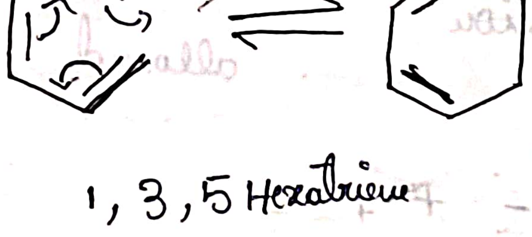
Dis-mode



Ex-2

Electrocyclic reactions in 4n+2π system :

The cyclisation of 1,3,5 hexatriene is a (4n+2π) electrocyclic reaction.



1, 3, 5 Hexatriene

* 1, 3, 5 hexatriene system has six π-molecular arbitals, they are ψ_1, ψ_2, ψ_3, ψ_4, ψ_5, ψ_6.

* The ground state electronic configuration is $\psi_1^2, \psi_2^2 \psi_3^2 \psi_4^0 \psi_5^0 \psi_6^0$.

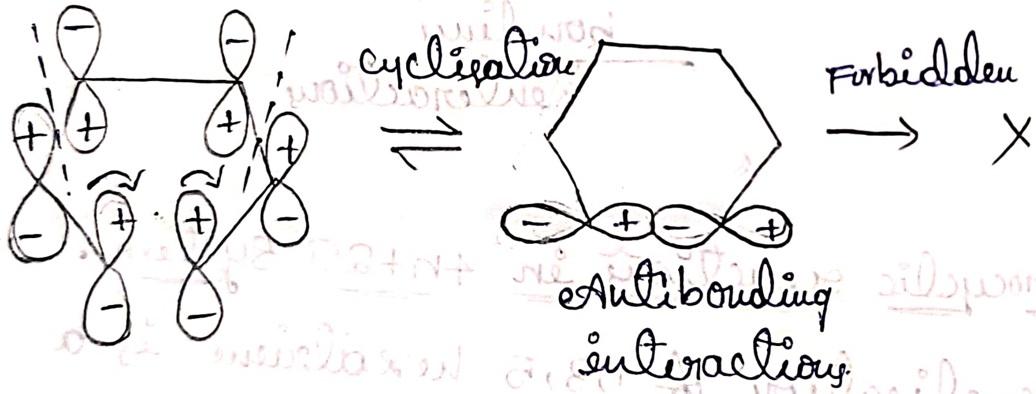
* In the excited state the electronic configuration is $\psi_1^2 \psi_2^2 \psi_3^1 \psi_4^1 \psi_5^0 \psi_6^0$.

* Under thermal conditions the HOMO orbital is ψ_3.

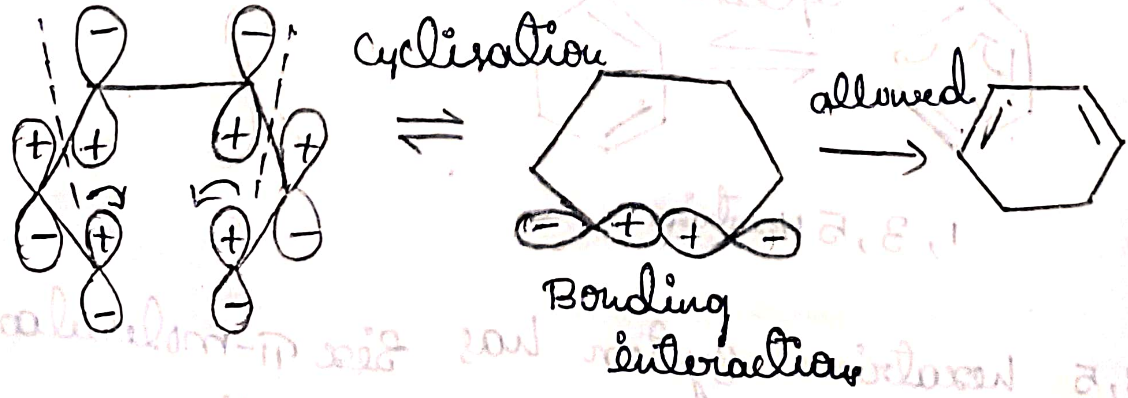
* Under photochemical conditions the HOMO orbital is ψ_4.

Under thermal conditions : (HOMO = ψ_3)

con-mode

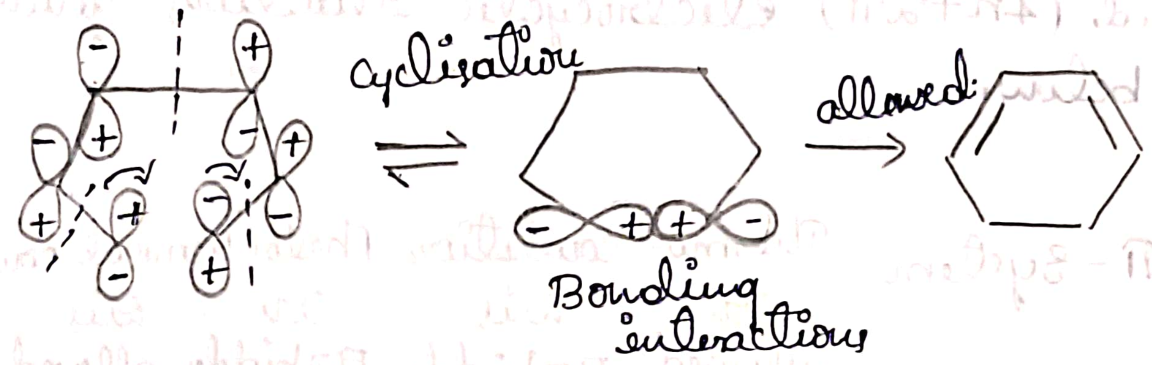


Dis-mode

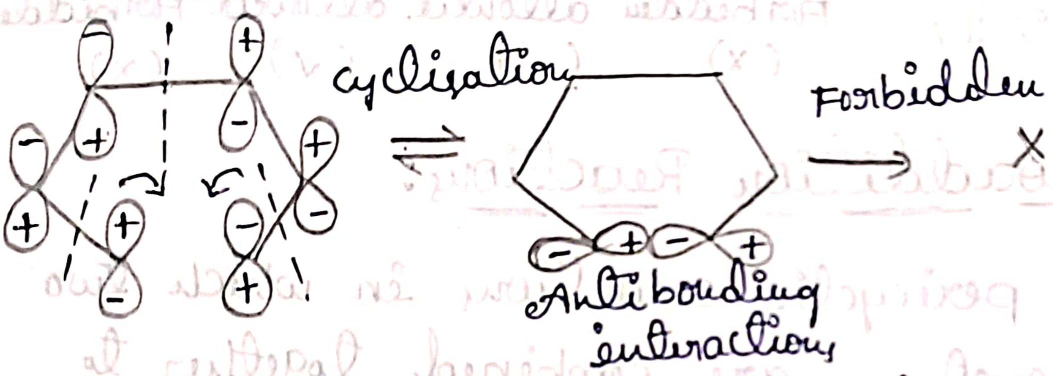


Under Photochemical conditions : (HOMO = ψ_4)

con - mode



Dis-mode



Woodward Hoffman selection rules for Electrocyclic reactions :

In order to predict the feasibility of an electrocyclic reaction, wood ward and Hoffman proposed some emperical rules based on FMO theory. Those rules are known as "wood ward Hoffman selection rules."

- For 4nπ systems under thermal conditions con rotation and under photochemical conditions dis rotation is allowed.
- For (4n+2π) system under thermal conditions dis rotation and photochemical conditions con rotation is allowed.

* The wood ward Hoffman selection rules of the electrocyclic reactions for 4nπ and (4n+2π) electrocyclic reactions given below.

π-System	Thermal condition		Photochemical con.	
	con	Dis	con	Dis
4nπ	allowed (✓)	Forbidden (x)	Forbidden (x)	allowed (✓)
(4n+2π)	Forbidden (x)	allowed (✓)	allowed (✓)	Forbidden (x)

Cycloaddition Reactions:

* The pericyclic reactions in which two $\pi e^{\ominus}$ systems are combined together to form a cyclic ring via the cyclic transitio state those reactions are called cycloadditio reactions.

* During the cycloaddition reactions two π-bonds are lossed and two new σ-bonds are formed.

* Depending on the no. of π-electrons present in the π-partners, the cycloaddition reactions are designated as $(m^{\pi}+n\pi)$ cyclo additions reactions, where m and n are the no. of electrons present in two π-partners respectively.

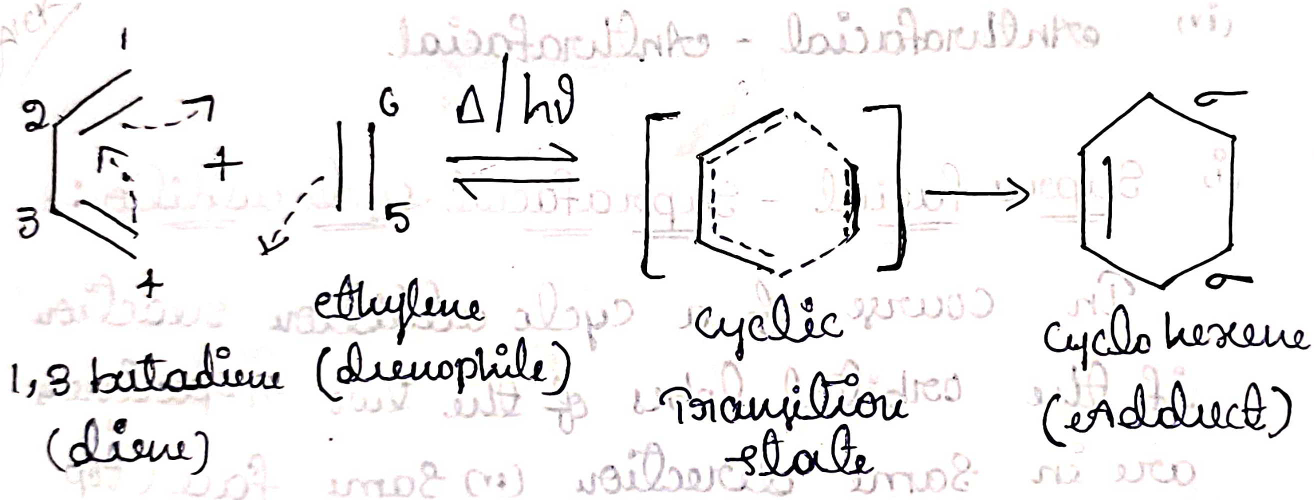
* All these reactions are reversible reactions.

* These are the bimolecular reactions.

Ex :- Diel's Alder reaction.

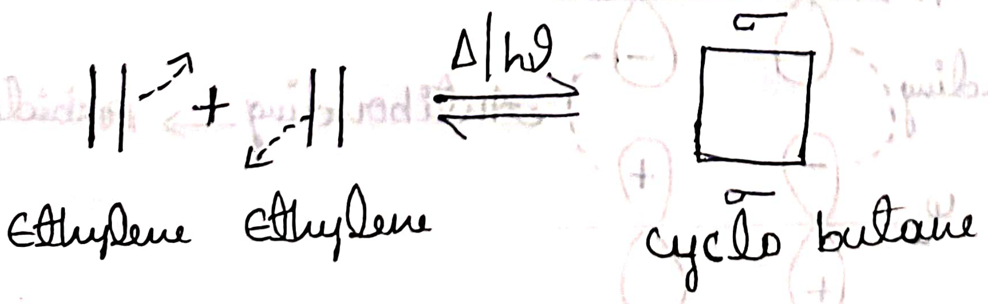
A diene and dienophile are added with eachother to give an adduct. It is called "Diel's Alder reaction."

The addition of 1,3 butadiene and ethylene is classic example of diel's alder reaction



* It is a 4π, 2π cycloaddition reaction.

$(2^{\pi} + 2^{\pi})$ cyclo addition :



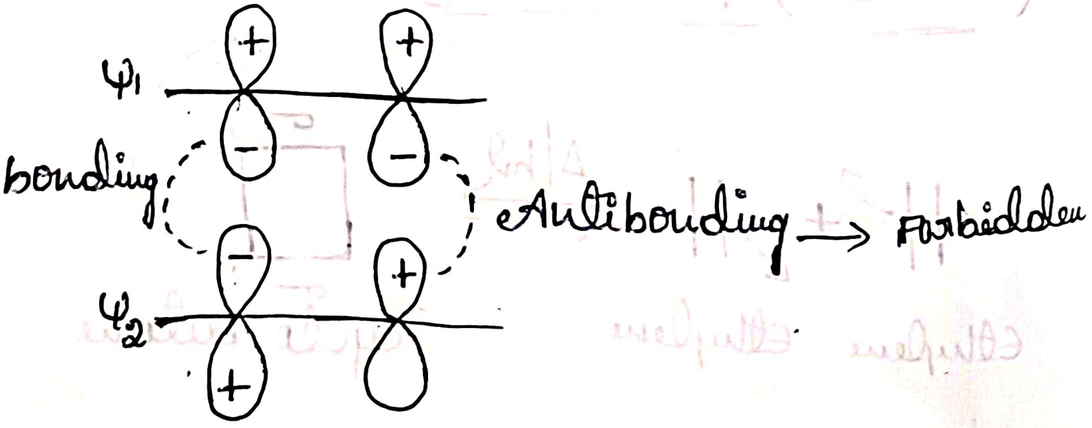
Classification

Depending on the direction of orbital lobes of the terminal carbon atoms of 2π partners the cyclo addition reactions are classified into 4 types.

(i) Suprafacial - Suprafacial
(ii) Suprafacial - Antarafacial
(iii) Antarafacial - Suprafacial
(iv) Antarafacial - Antarafacial.

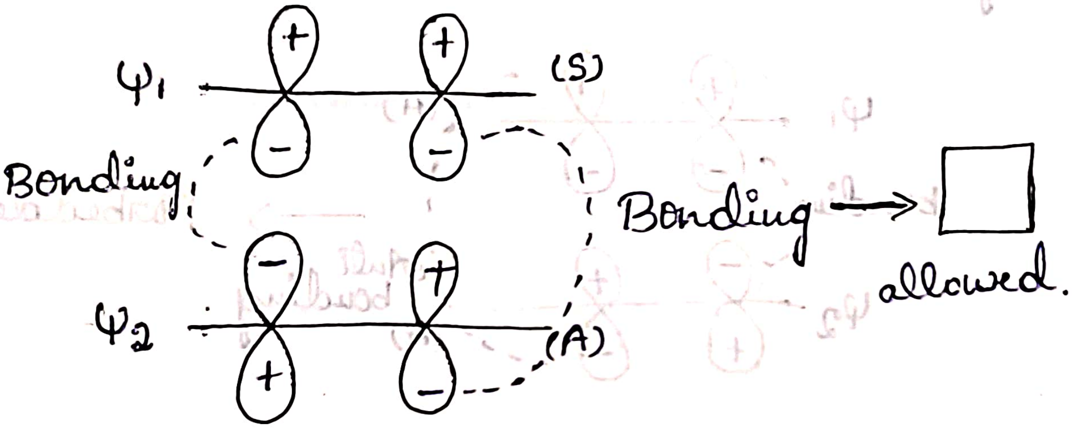
(i) Suprafacial - Suprafacial cyclo addition:

In course of a cyclo addition reaction if the orbital lobes of the two π-partners are in same direction (or same face (top or bottom) these reaction are called Suprafacial - Suprafacial cyclo addition.



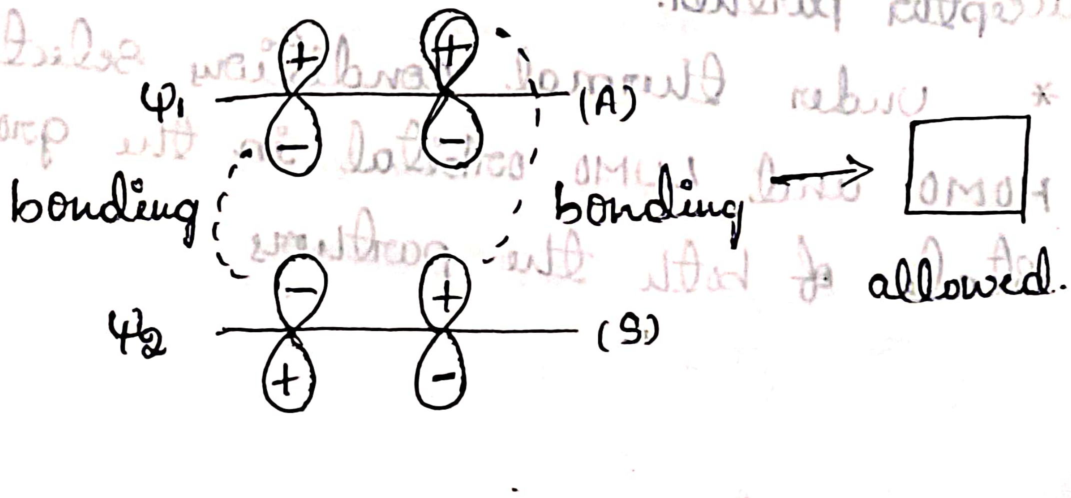
(ii) Suprafacial - Anthra facial cycloaddition:

In course of a cyclo addition reaction of the orbitals lobes of one π- partner are in same direction and the other π-partner in opposite direction are called Suprafacial - Anthra facial cyclo addition.



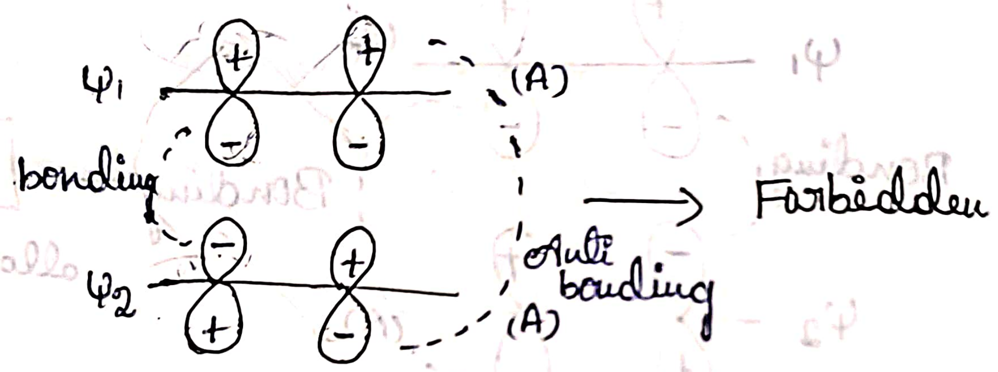
(iii) Anthrafacial - Suprafacial cyclo addition:

In course of a cyclo addition reaction if the orbital lobes of one π partner are in opposite direction and other π-partner in same direction those reactions are called Anthra facial - Supra facial cyclo addition.



(iv) Anthra facial - Anthra facial cyclo addition:

In course of a cyclo addition reaction if the orbital lobes of one π-partner direct are in opposite direction & other π partner in opposite, those reactions are called Antha facial - Anthra facial cyclo addition.



Cyclo addition reaction "FMO" approach

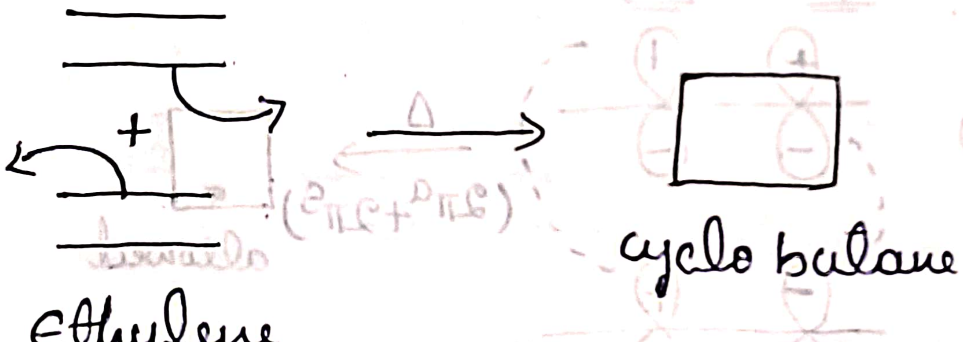
* According to FMO approach one π-partner is taken as donor and other π-partner is taken as "acceptor." Select the HOMO orbital from that donar partner and LUMO orbital from the acceptor partner.

* Under thermal condition select the HOMO and LUMO orbital in the ground state of both the partners

- * Under photochemical conditions select the HOMO orbital of donar from the excited state and LUMO orbital from the acceptor in the ground state.
- * The bonding interactions will allows the reactions and leads to the product.
- * The antibonding interactions Forbidden the reaction and does not give the product.

Ex-1

(2π+2π) cyclo addition on 4n π cycloaddition



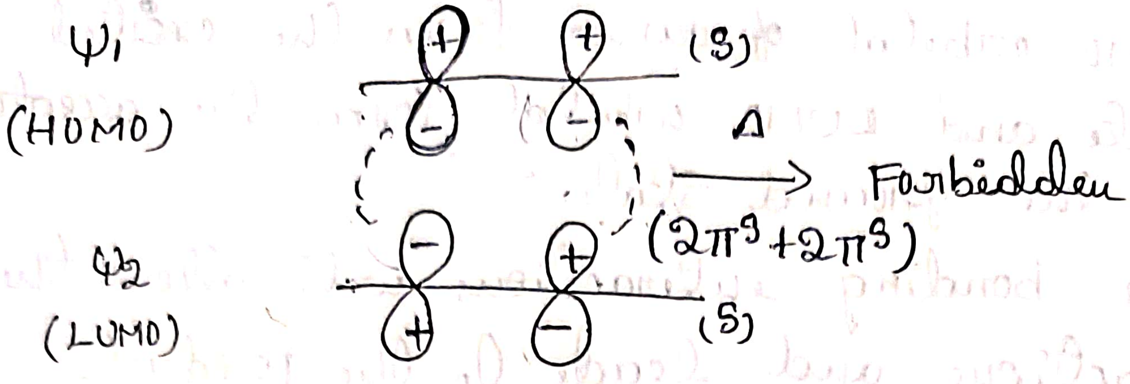
In ethylene the ground state electronic configuration is ψ_1^2, ψ_2^0

Under thermal conditions

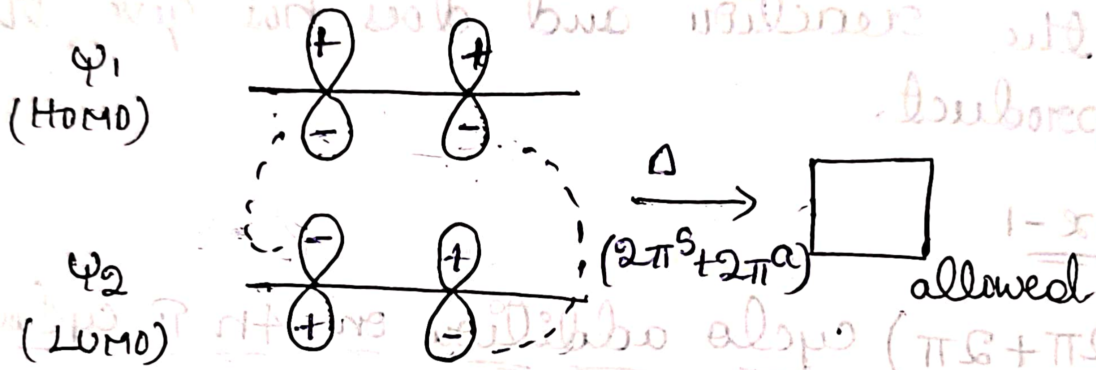
HOMO = ψ_1

LUMO = ψ_2

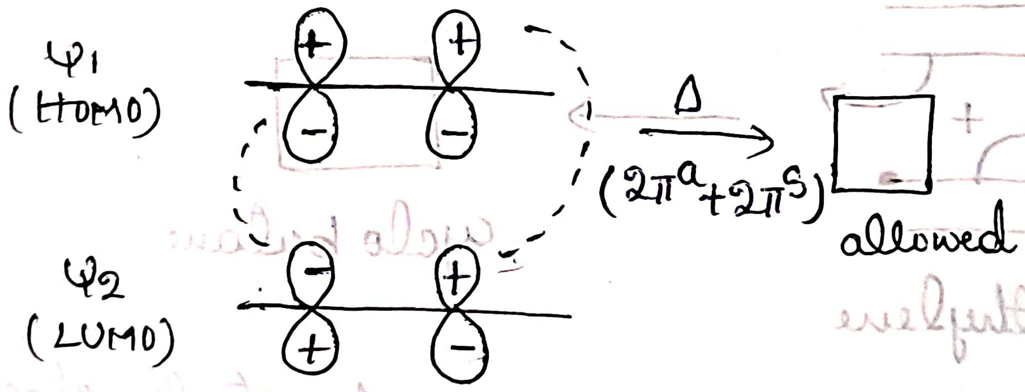
(i) Supra - Supra mode :



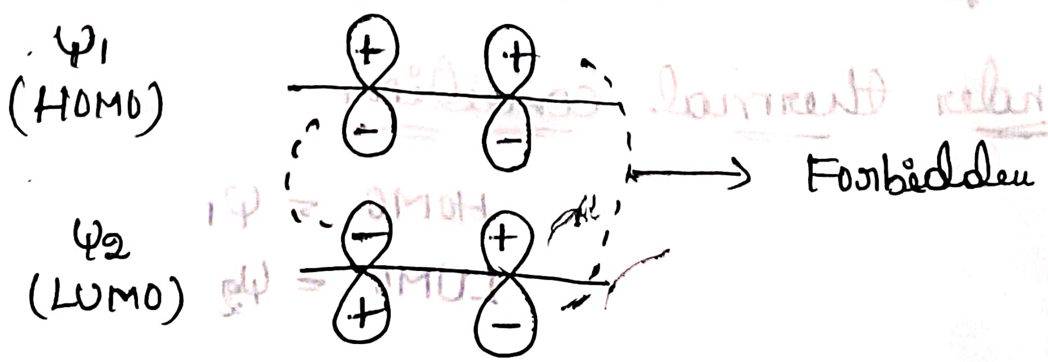
(ii) Supra - Anthra mode :-



(iii) Anthra - Supra mode :-



(iv) Anthra - Anthra mode :-



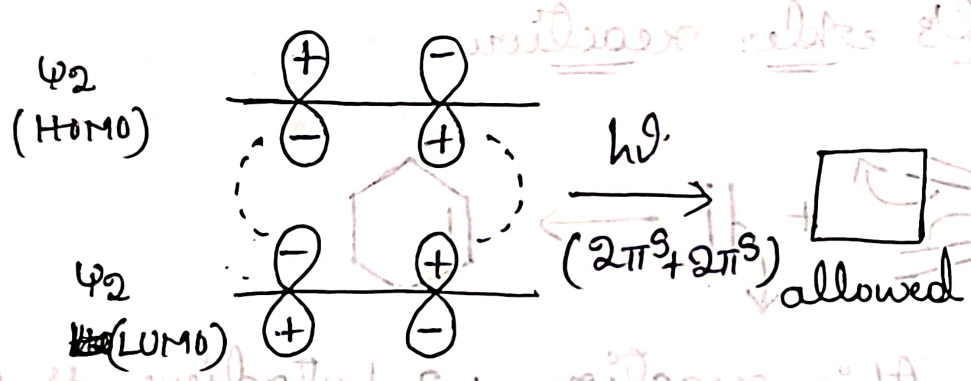
Under photochemical conditions

Under photochemical conditions HOMO of one ethylene molecule is taken from excited state.

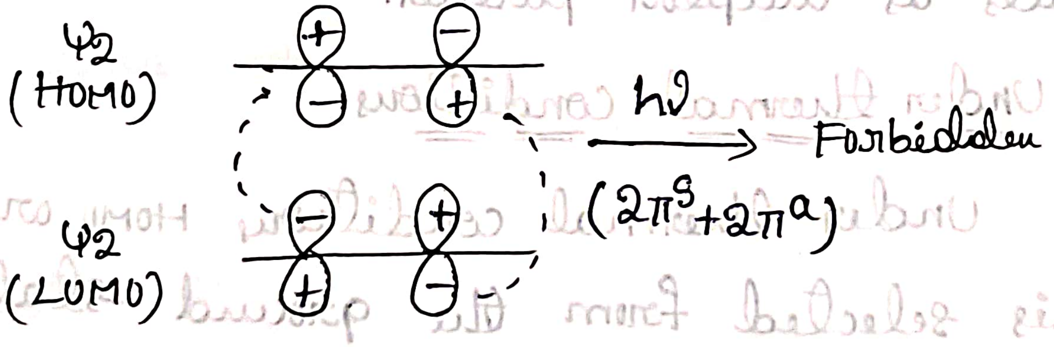
The LUMO of other ethylene is taken from the ground state.

HOMO = ψ_2 & LUMO = ψ_2

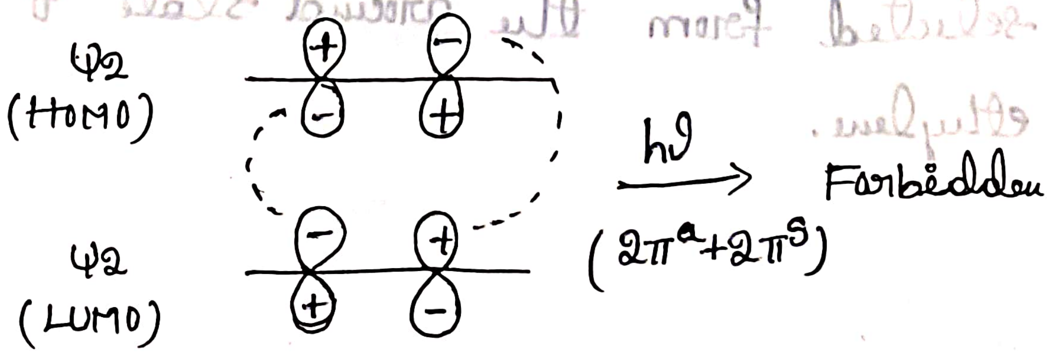
(i) Supra - Supra mode :



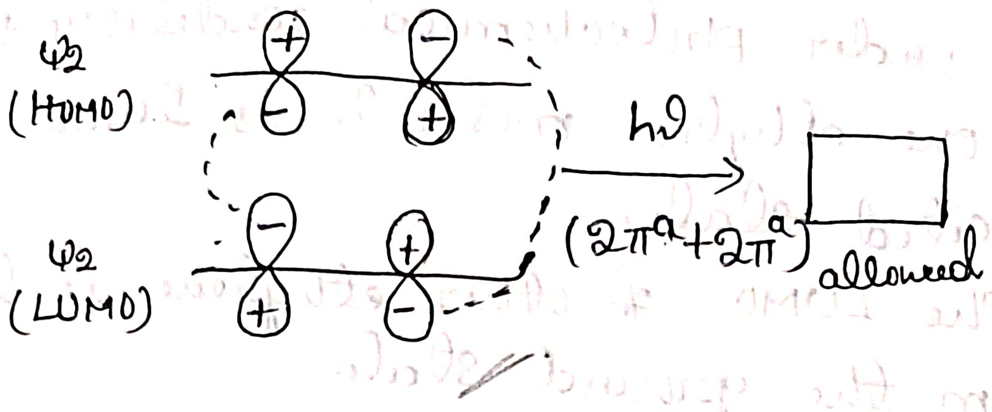
(ii) Supra - Antara mode :-



(iii) Antara - supra mode :-



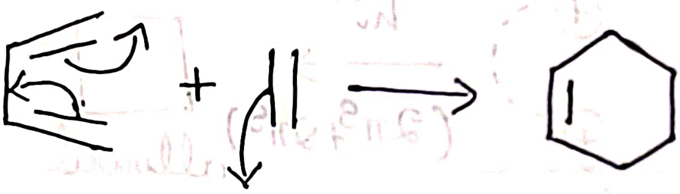
(iv) Anthra - Anthra mode



Ex-2

(4π+2π) cyclo addition

Diel's Ader reaction



In this reaction 1,3 butadiene is acts as a donar partner where as ethylene acts as acceptor partner.

Under thermal conditions

Under thermal conditions HOMO orbital is selected from the ground state of 1,3 butadiene the LUMO orbital is selected from the ground state of ethylene.

* 1,3 butadiene

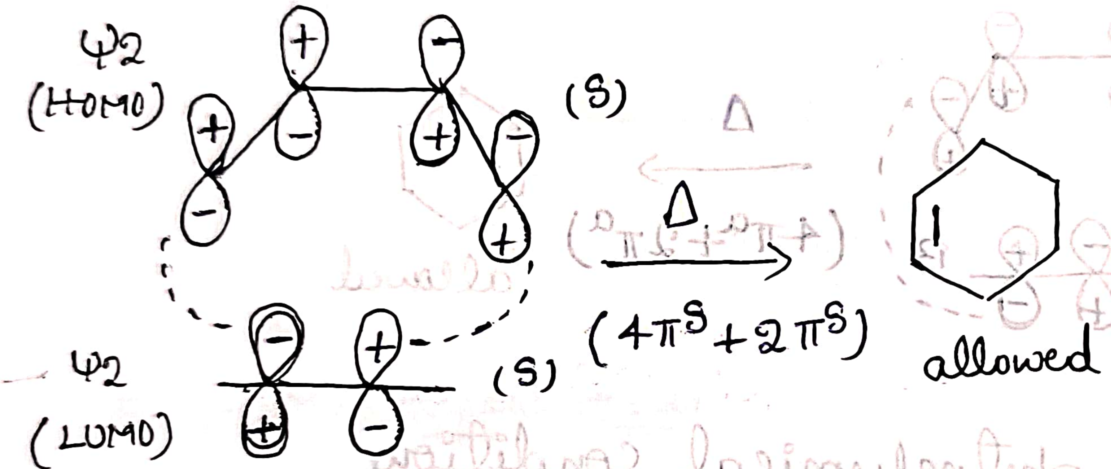
E.C :- $\psi_1^2, \boxed{\psi_2^2}, \psi_3^0, \psi_4^0$

G.S HOMO.

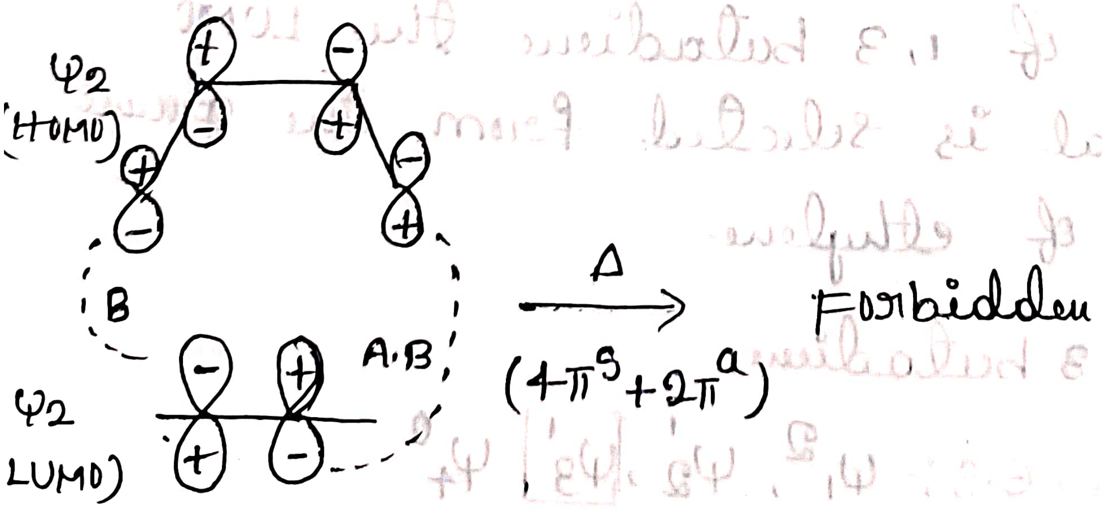
Ethylene E.C :- $\psi_1^2, \boxed{\psi_2^0}$

G.S LUMO

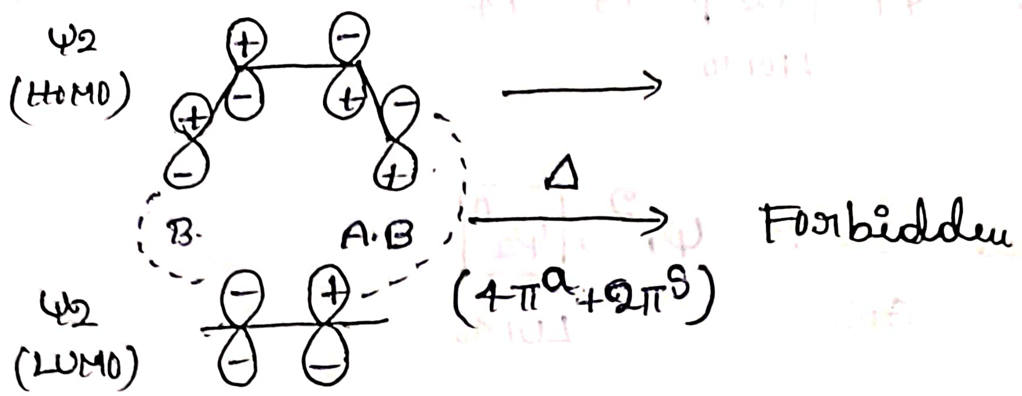
(i) Supra - Supra mode :-



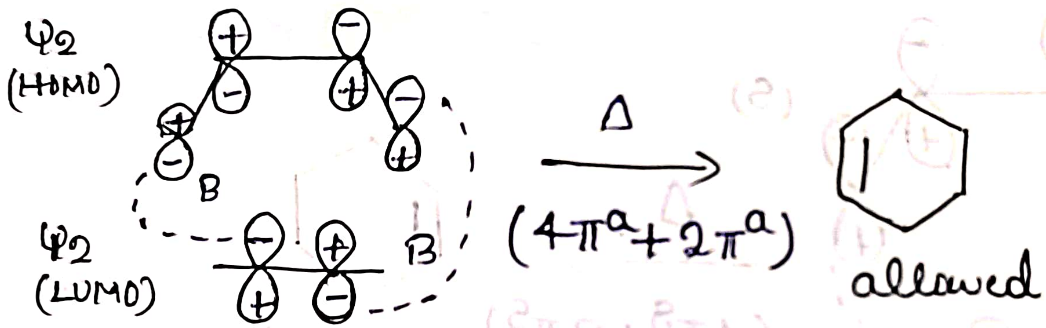
(ii) Supra - Anthra mode :-



(iii) Anthra - Supra mode :-



(iv) Anthra - Anthra mode :-



Under photochemical conditions

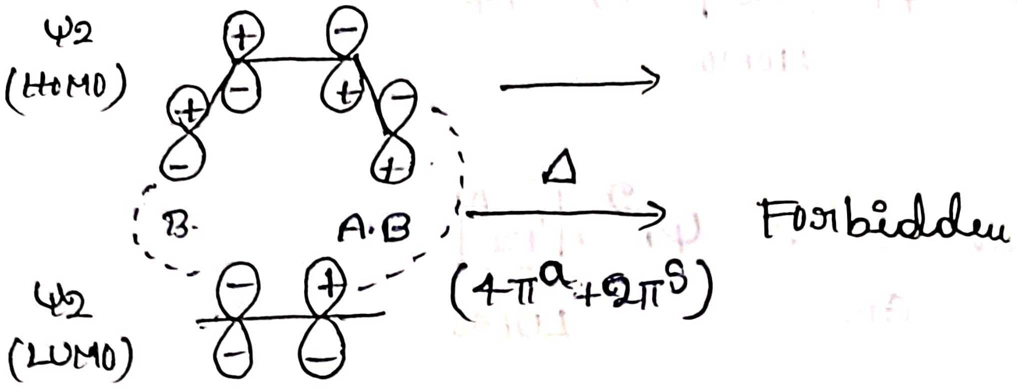
Under photochemical conditions HOMO orbital is selected from the excited state of 1,3 butadiene the LUMO orbital is selected from the ground state of ethylene.

1,3 butadiene

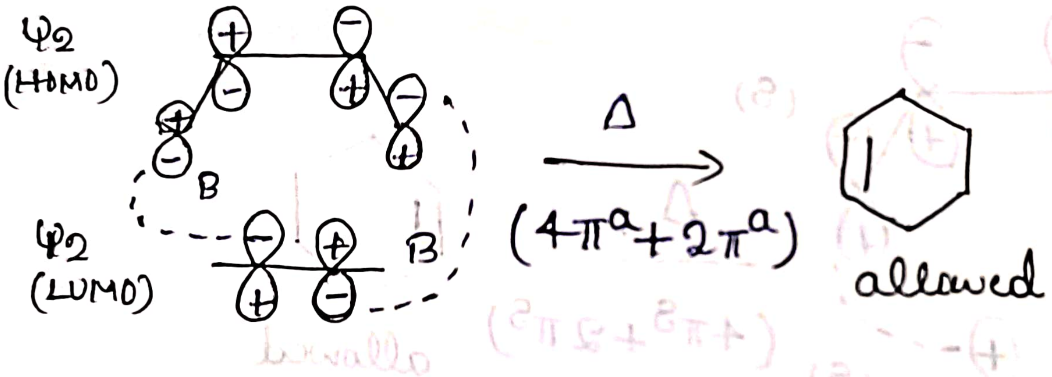
E.S :- $\psi_1^2, \psi_2^1, \boxed{\psi_3^1}\ \psi_4^0$

HOMO

(iii) Anthra - Supra mode :-



(iv) Anthra - Anthra mode :-



Under photochemical conditions

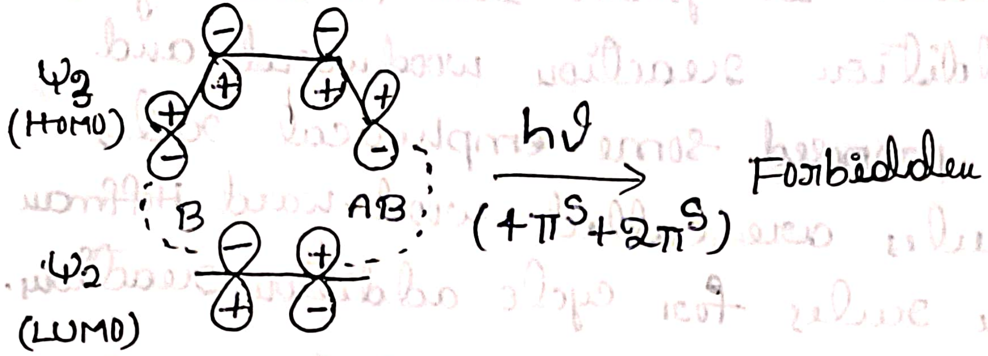
Under photochemical conditions HOMO orbital is selected from the excited state of 1,3 butadiene the LUMO orbital is selected from the ground state of ethylene.

1,3 butadiene

$E.S :- \psi_1^2, \psi_2^1, \boxed{\psi_3^1}\ \psi_4^0$

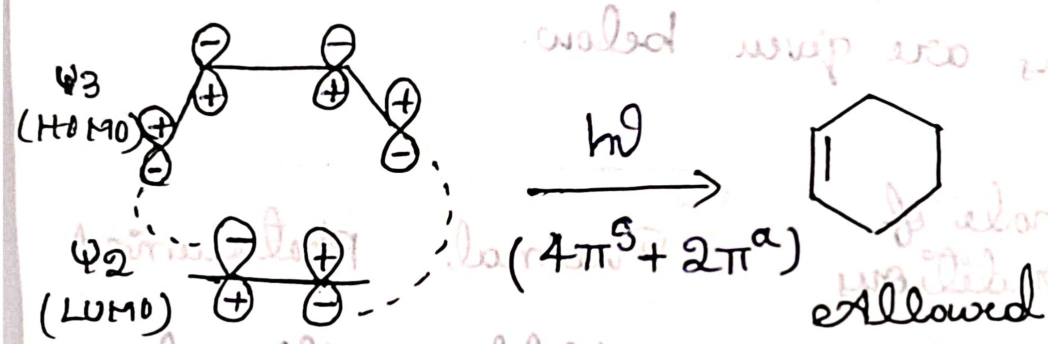
HOMO

(i) Supra - supra mode :-



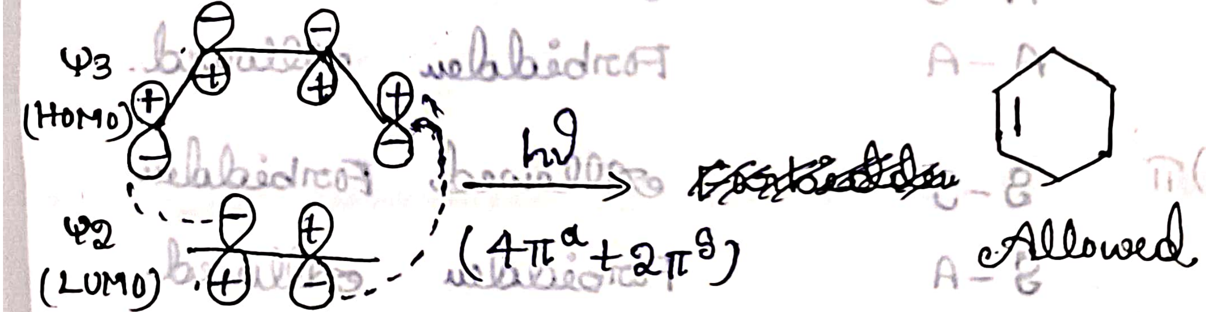
Forbidden

(ii) Supra - Anthra mode :-



Allowed

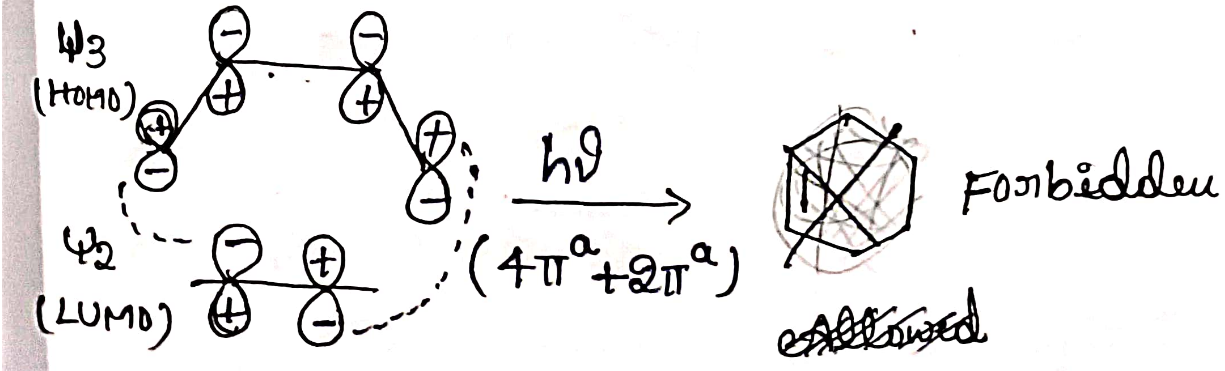
(iii) Anthra - supra mode :-



~~Forbidden~~

Allowed

(iv) Anthra - Anthra mode :-



Forbidden

~~Allowed~~

wood - ward Hoffman

* In order to govern the feasibility of cyclo addition reaction woodward and Hoffman proposed some emphirical rules these rules are called wood-ward Hoffman selection rules for cyclo addition reactions.

* The wood ward Hoffman selection rules for ~~4π~~ $4n\pi$ and $4n+2\pi$ cyclo addition reactions are given below.

system	mode of conditions	Thermal	Photochemical
$4n\pi$	S - S	Forbidden	Allowed
	S - A	Allowed	Forbidden
	A - S	Allowed	Forbidden
	A - A	Forbidden	Allowed.
$(4n+2)\pi$	S - S	Allowed	Forbidden
	S - A	Forbidden	Allowed.
	A - S	Forbidden	Allowed
	A - A	Allowed	Forbidden