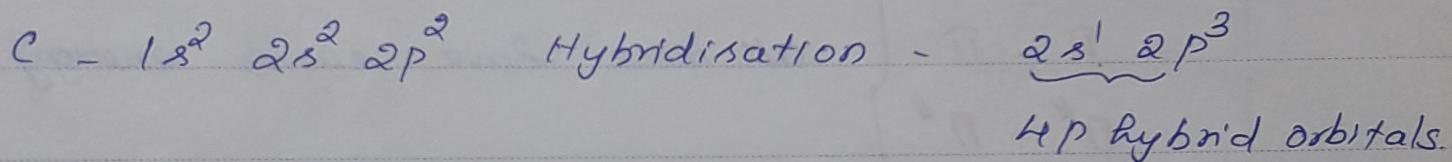


## Structure and Orbital Picture of Butadiene

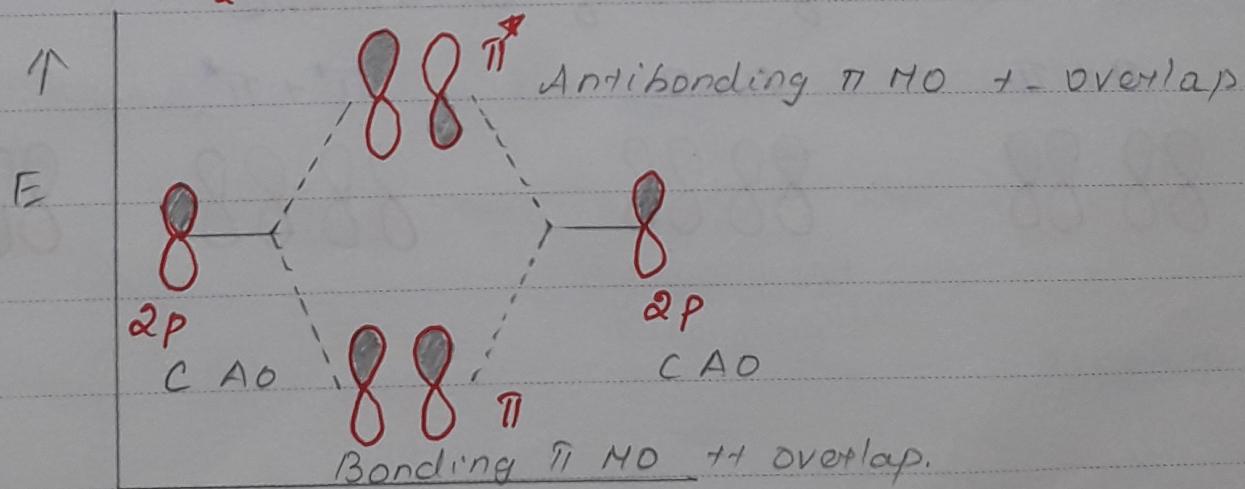
Conjugation can be visualised by constructing the  $\pi$  molecular orbitals of 1,3-butadiene.

Since 1,3-butadiene consists of 4  $2p$  orbitals of carbon, (i.e. 4  $sp^2$  hybridised C atoms each contributing a p atomic orbital containing 1 e<sup>-</sup>)

Butadiene is composed of 4 carbon atoms with two adjacent  $\pi$  bonds. These two  $\pi$  bonds are conjugated. Since butadiene consists of 4 individual p orbitals, the  $\pi$ -system of butadiene will contain 4  $\pi$  molecular orbitals.



$\pi$  molecular orbitals of butadiene can be constructed by combining the molecular orbitals of two ethylene molecules.



In ethylene  $H_2C=CH_2$  each  $2p$  orbital of two carbon atoms approach one another, their atomic orbitals produce two molecular orbitals. One is bonding & another one is anti bonding).

In the same way, the MO's of butadiene can be constructed by combining two MO's of ethylene molecules. The possible combinations of MO's of butadiene are

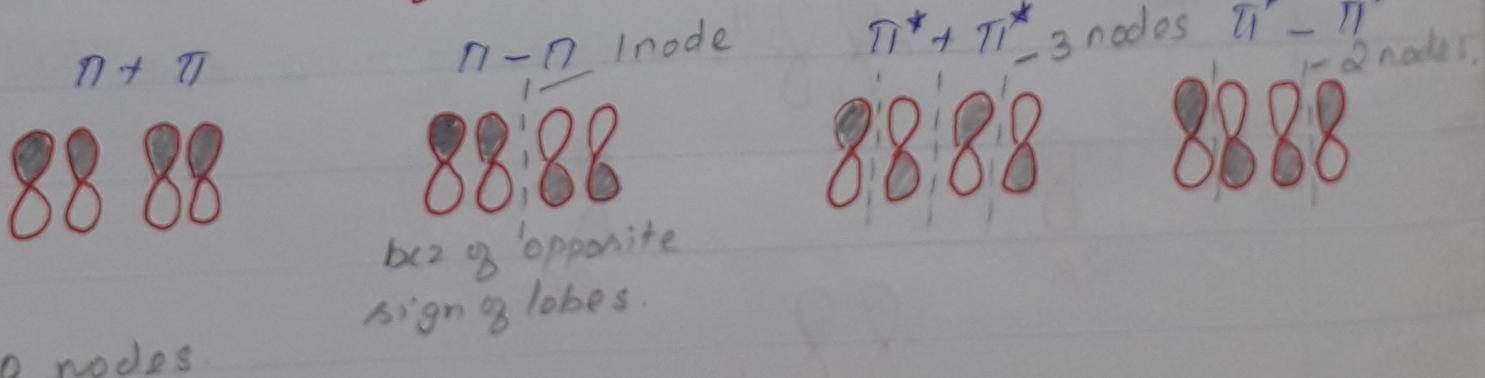
$\pi + \pi$   
 $\pi - \pi$   
 $\pi^* + \pi^*$   
 $\pi^* - \pi^*$

} possible combinations because all these have same energy.

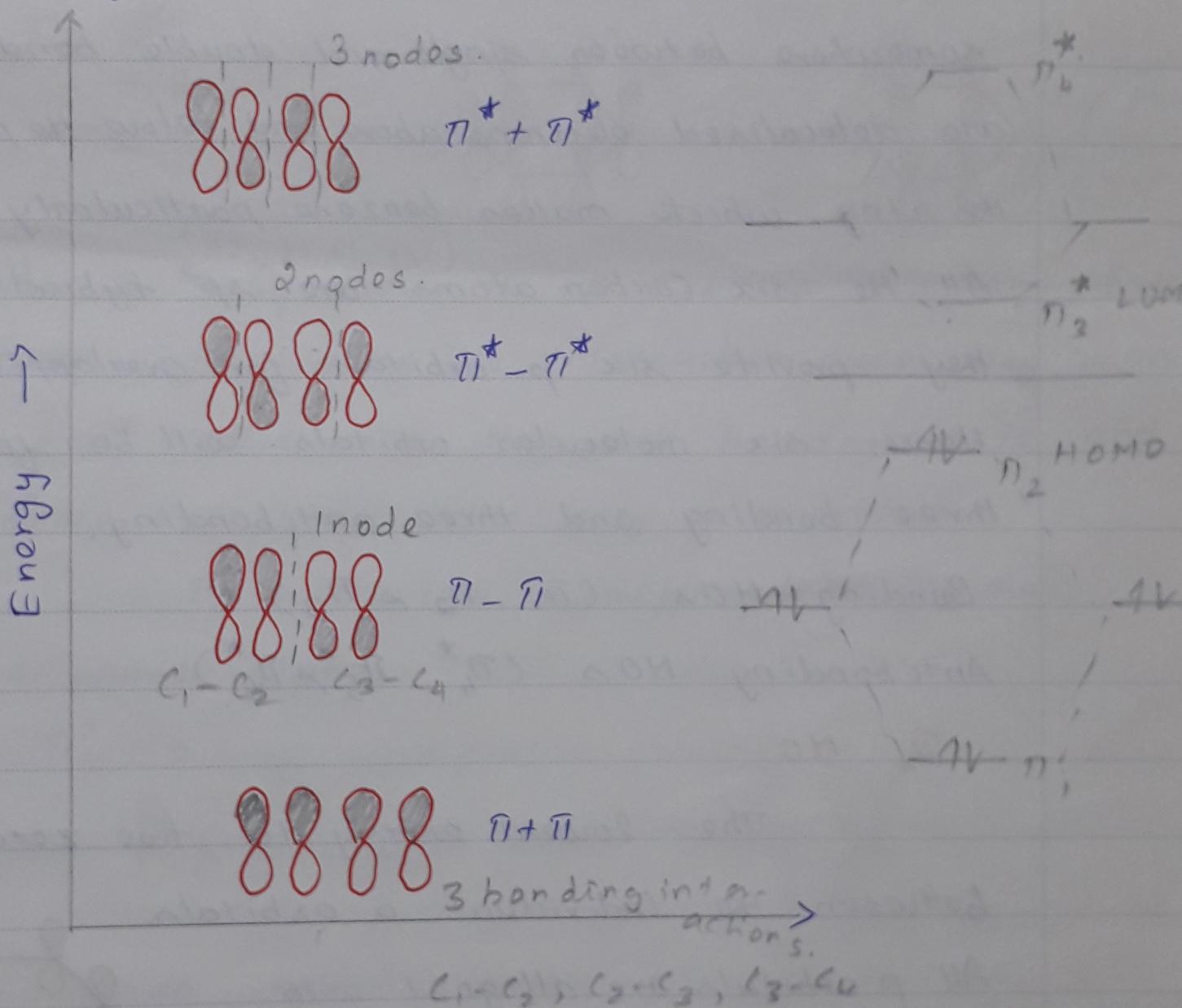
$\pi + \pi^*$   
 $\pi - \pi^*$

} overlapping is not possible in these cases because  $\pi \& \pi^*$  differ in energy.

Structures of MO's of butadiene



The smaller the no. of nodes, the better the overlap is and this will be lower in energy and highly stable. Hence, while constructing the orbital picture of butadiene, the MOs should be arranged in the order of increasing no. of nodes.



## $\pi$ molecular orbitals of benzene:

Benzene ( $C_6H_6$ ) is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached. The six carbon atoms form a perfectly regular hexagon. All of the C-C bonds have exactly the same lengths somewhere between single and double bonds. There are delocalised electrons above and below the plane of the ring, which makes benzene particularly stable. (bcz it is  $-CH_2-$ ) All the six carbon atoms are  $sp^2$  hybridized and they provide six p-orbitals for overlapping. Hence, six molecular orbitals will be formed, three bonding and three antibonding.

Bonding MOs ( $\pi_1, \pi_2 \text{ & } \pi_3$ )

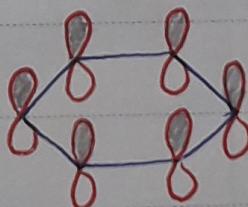
Antibonding MOs ( $\pi_4^*, \pi_5^* \text{ & } \pi_6^*$ )

$\pi, MO$ :

The lowest energy MO, has zero nodes between the individual p orbitals.

All p orbitals are aligned with phases positioning <sup>in</sup> the same direction.

In this orbital electrons are delocalized over the length

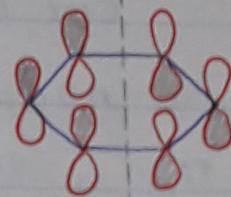


and on the lowest energy level.

1 nodal plane.

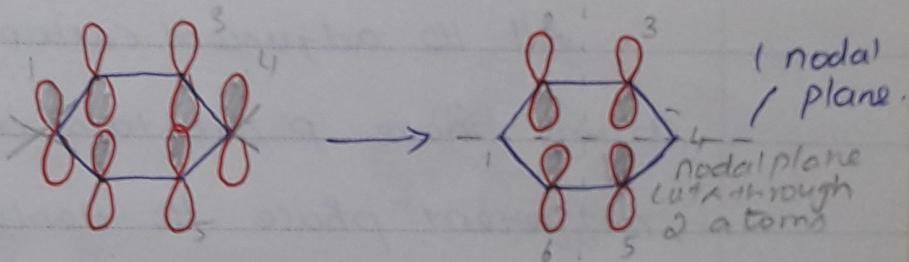
### $\pi_2$ MO :

Here 3 p orbitals of one half lie in one phase and other 3 p orbitals of the second half will lie in another phase giving rise to 1 nodal plane.



nodal plane cuts through 2 of the single bonds.

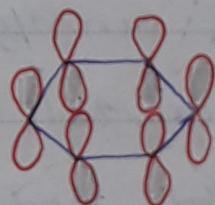
### $\pi_3$ MO :



As  $C_1$  &  $C_4$  have the p orbitals in same phase and lying along the internuclear axis, they cancel each other i.e. they will be degenerate and hence we will have only 4 p orbitals.

$\pi_2$  &  $\pi_3$  will be degenerate as they have 1 nodal plane.

### $\pi_4^*$ MO :



The line passing through the complete two nodal planes molecule is calculated for node have negative lobes.

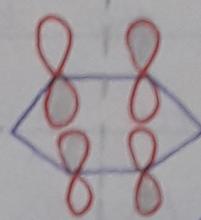
In  ~~$\pi_4$~~   $\pi_4^*$ , the two carbon atoms  $C_1$  &  $C_4$  contribute atomic lobes.

no p orbitals for  $\pi_3$  MO. That's why they are represented without any p orbital.

$\pi_5^*$  MO

Cut through atoms.

2 nodal planes.



2 nodal planes.

$\pi_4$  &  $\pi_5$  degenerate as they have same no. of planes.

These two orbitals are of equivalent energy.

$\pi_6^*$  MO

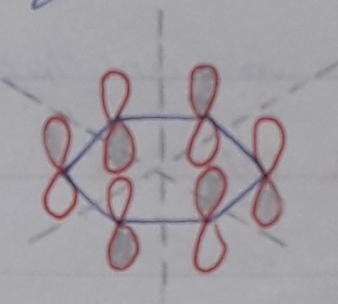
All the adjacent carbon atoms have p orbitals in different phase. Hence

the no. of nodes are  $(n-1)$

$n = \text{no. of atoms (or) p orbitals.} \therefore 6-1 = 5 \text{ nodes.}$

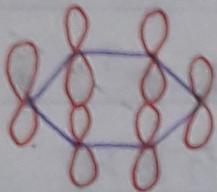
Highest in energy level. 5 nodes are possible in case of a cyclic molecule (hexatriene). But in benzene as it cuts the molecule into 2 it has 2 nodal plane and has the highest energy and it is unstable.

This orbital has zero overlap between adjacent p orbitals and therefore electrons in this orbital have minimum possible delocalisation & possess highest energy.

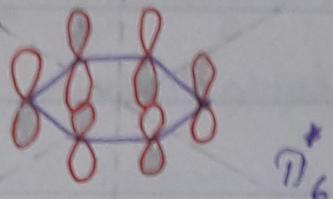


Energy Increasing.

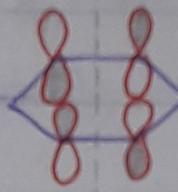
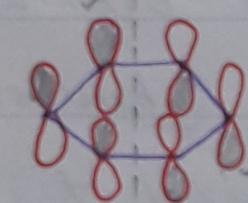
2 nodal planes

 $\pi_4^*$ 

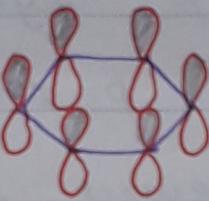
3 nodal planes

 $\pi_6^*$ 

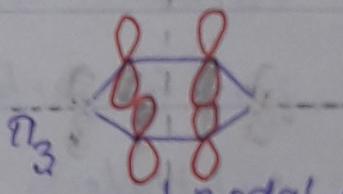
2 nodal planes

 $\pi_5^*$ Anti bonding.  
Bonding $\pi_2$ 

1 nodal plane

 $\pi_1$ 

0 nodal plane.

 $\pi_3^*$ 

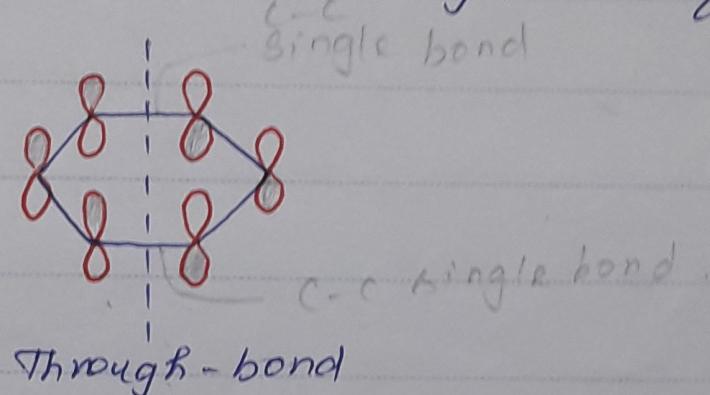
1 nodal plane

The line passing through the complete molecule is calculated for node. That's why in benzene it is called as a nodal plane instead of node.

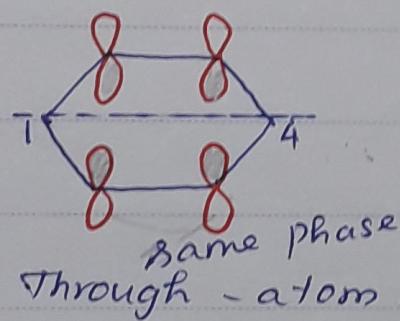
## Benzene continued.

$\pi_2$  &  $\pi_3$  are degenerate bonding orbitals as they have one nodal plane.

In  $\pi_2$  the nodal plane is drawn through bond C<sub>2</sub>. A nodal plane cuts through two of the single bonds.



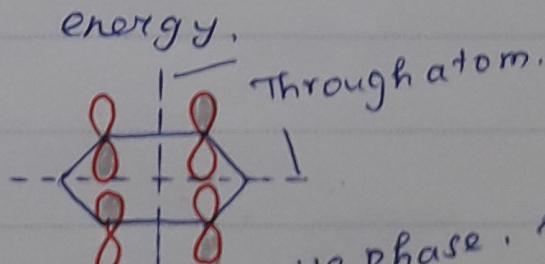
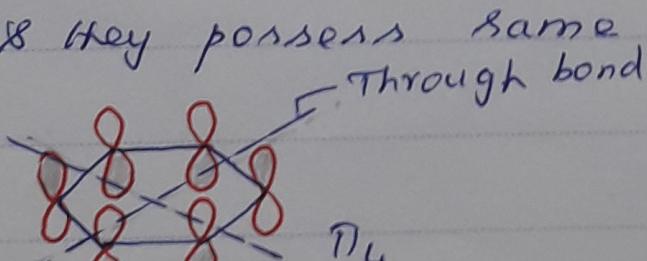
$\pi_3$  - If a nodal plane is drawn through the atoms, then we have



The atoms C<sub>1</sub> & C<sub>4</sub> are not connected. There is no bond between them.

$\pi_4$  &  $\pi_5$  are degenerate bonding orbitals as they have two nodal planes.

$\pi_4$  MO can be drawn by cut through the atoms and  $\pi_5$  MO can be drawn by cut through the atoms & they possess same energy.



in phase, so no bond.