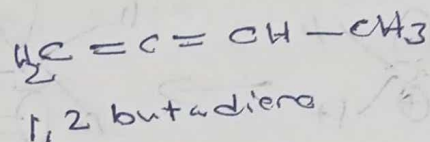
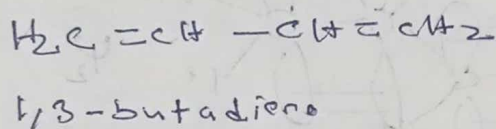
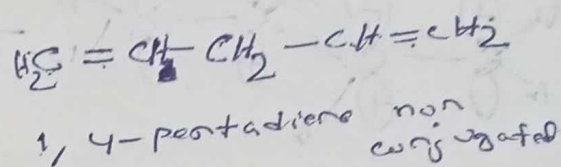
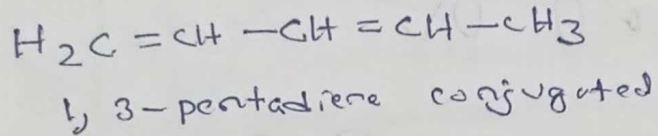


π -Molecular orbitals of butadiene

- * When atomic orbitals overlap laterally (side to side), resulting molecular orbital is called $\pi(\pi)$ orbital.
- * π -Molecular orbitals in the molecules affect their properties like stability, chemical activity etc.



- * The relative stability of dienes is in the following order
Conjugated diene > Isolated diene > cumulated diene
Most stable Least stable

- * The stability of conjugated dienes is due to delocalisation of π -electrons which is known as resonance.

Orbital picture of 1, 3 butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$)

- * Each of the four carbon atoms of 1, 3-butadiene uses three sp^2 hybrid orbitals for the formation of sigma bonds and an unhybridized p-orbital for the formation of π -bond.
- * The LCAO of these four p-orbitals give four molecular orbitals having the wave functions $\psi_1, \psi_2, \psi_3^* \& \psi_4^*$
- * ψ_1 & ψ_2 = bonding orbitals, containing two electrons in each MO while ψ_3^* & ψ_4^* = antibonding orbitals remain vacant in the ground state of the molecule.
- * ψ_1 = lowest energy, it has no node, ψ_2 = one node, ψ_3^* = 2 node, & ψ_4^* = 3 node.

- * Overlap between the p-orbitals of C_2 & C_3 atoms are lesser than C_1 & C_2 or C_3 & C_4 .
- * The partial overlap of C_2-C_3 gives partial double bond character and allows the four- π electrons to be delocalized over all four atoms.
- * The participation of π -electrons in more than one bond is called delocalisation of electrons.

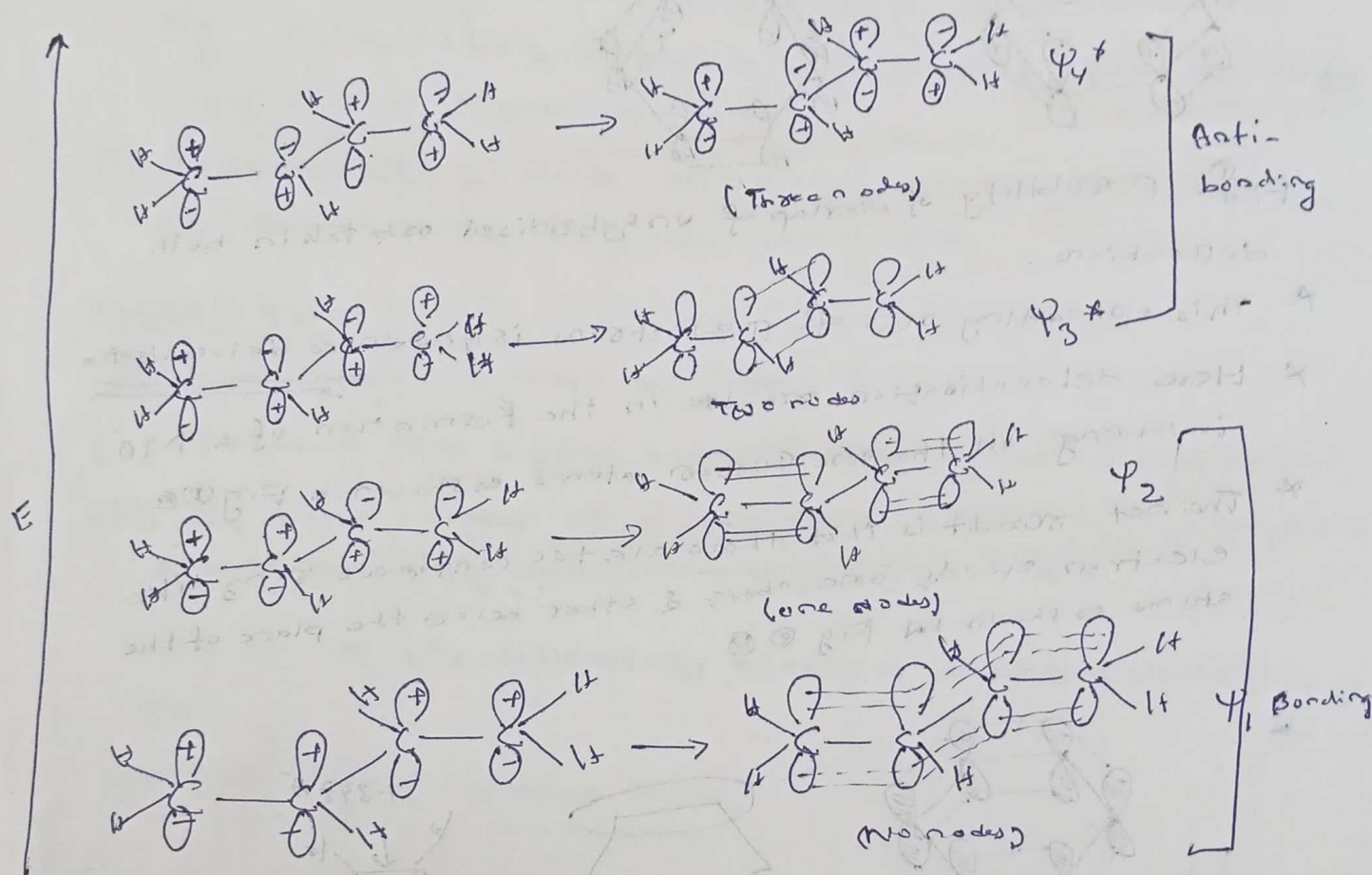


Fig: LCAO of four p-orbitals of 1,3-butadiene

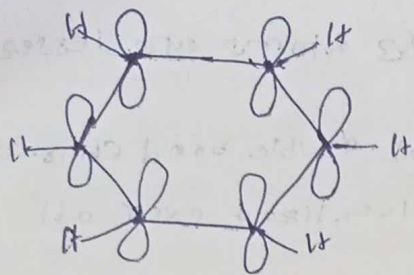
Orbital structure of Benzene & Delocalisation of electrons

- * According to orbital theory, each of the six carbon atoms in benzene is in a state of sp^2 hybridization.



- * The six carbon & six hydrogen atoms lie in the same plane and angle between any two σ -bonds are 120° . Therefore benzene molecule is a planar.

- * Unhybridised p-orbital of each of the carbon atoms overlap to a small extent but equally. The p-orbitals of both the carbon atoms linked by σ bonds



sp^2 hybridised carbons each forming 3 σ bonds.

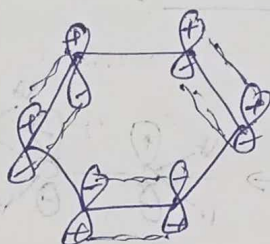
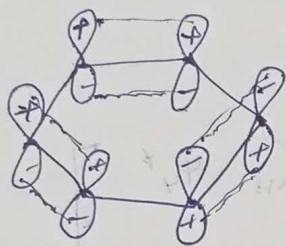
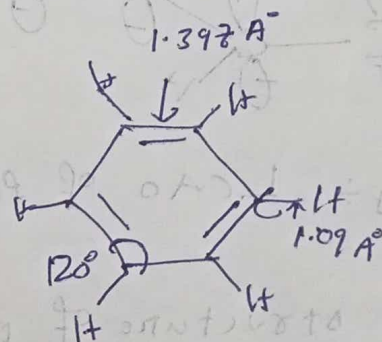
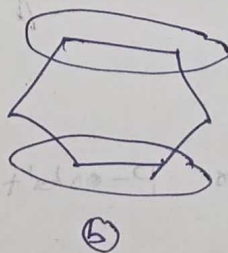
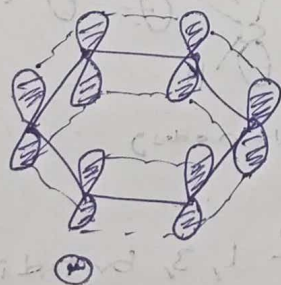


Fig 1: possibility of overlap of unhybridised orbitals in both directions.

* This spreading over of π electrons is known as delocalisation.

* Here delocalisation results in the formation of a MO involving all the six carbon atoms as shown in Fig 2(a).

* The net result is that there are two continuous ring like electron clouds, one above & other below the plane of the atoms as shown in Fig 2(b).



orbital structure of benzene,

* This process of delocalisation of π -electrons results in bonds which are stronger than normal π -bonds and accounts for the stability of the molecule.

Aromaticity

Some of the important properties of aromatic compounds are as follows.

- (1) They are usually cyclic compounds.
- (2) Their molecules have been shown to be planar by X-ray & electron diffraction methods.
- (3) These compounds undergo substitution reaction.
Eg: halogenation, nitration, sulphonation, Friedel-Crafts alkylation & acylation
- (4) Their molecules have resonance stabilization. The π -electrons in the ring are delocalised.

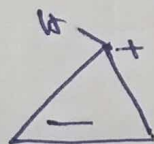
Huckel rule

- (i) Molecule or ion must be cyclic & must be planar
- (ii) It should have cyclic cloud of delocalized π -electrons.
- (iii) The total number of π -electrons in the molecular species should be $4n+2$, where $n = 0, 1, 2, 3, \dots$ etc.

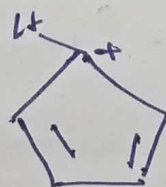
These points are collectively known as Huckel rule or $(4n+2)$ rule.

Applications of Huckel Rule

(i) Monocyclic systems.



Cyclopropenyl cation
(planar, 2π -electrons aromatic)

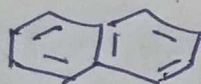


Cyclopentadienyl cation
(planar, 4π -electrons, not aromatic)



Cyclopentadienyl anion
(planar, 6π -electrons, not aromatic)

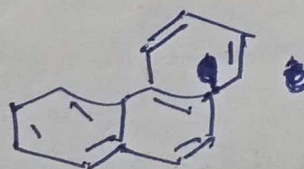
(ii) Poly cyclic compounds



Naphthalene (Aromatic)

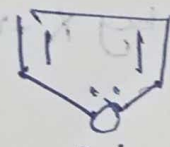
$$4n+2 = 10$$

$$4n = 8$$
$$n = 2$$

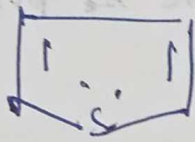


phenanthrene

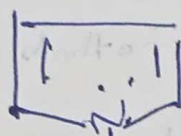
(iii) Heterocyclic compounds. Heterocyclic compounds such as pyridine, furan, thiophene & pyrrole are all aromatic since each one of them is planar and has a cyclic system of 6π electrons which is completely delocalized over the entire ring.



Furan



Thiophene

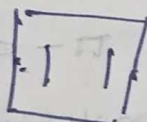


Pyrrole



Pyridine.

(iv) Annulenes completely conjugated monocyclic polyenes containing an even number of carbon atoms are called annulenes. Their general formula is $(CH=CH)_n$, $n = 2, 3, 4$ etc.



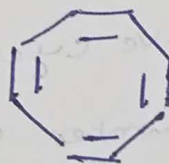
[4]-Annulene

Cyclobutadiene



[6]-Annulene

Benzene



[8]-Annulene.

Cyclooctatetraene

Applications of Huckel rule

