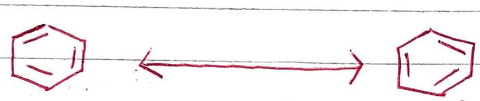
Resonance explanation of the structure of Benzene

According to the basic postulates of resonance theory, "whenever two or more Lewis structure can be written for a molecule that differs only in the position of their electron, none of the structure will be in complete accord with the compound's physical and chemical properties"

Therefore

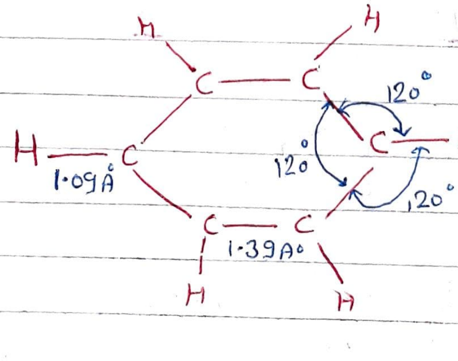
* Kekule structure I and II differs only in the position of electron and they do not represent two seprate molecules is equilibrium as proposed by Kekule.



(I) (not ⇌) (II)

* According to resonance theory, I and II are the resonance contributor to the real structure of benzene.

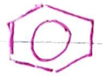
* A hybrid of Kekule structur I and II would have neither pure single bond nor pure double bond between the carbons. The bond order would be between that of a single and double bond.



bond length of C–C single bond between sp^2 hybridized atom $= 1.47 A^\circ$

Carbon - Carbon double bond $= 1.34 A^\circ$

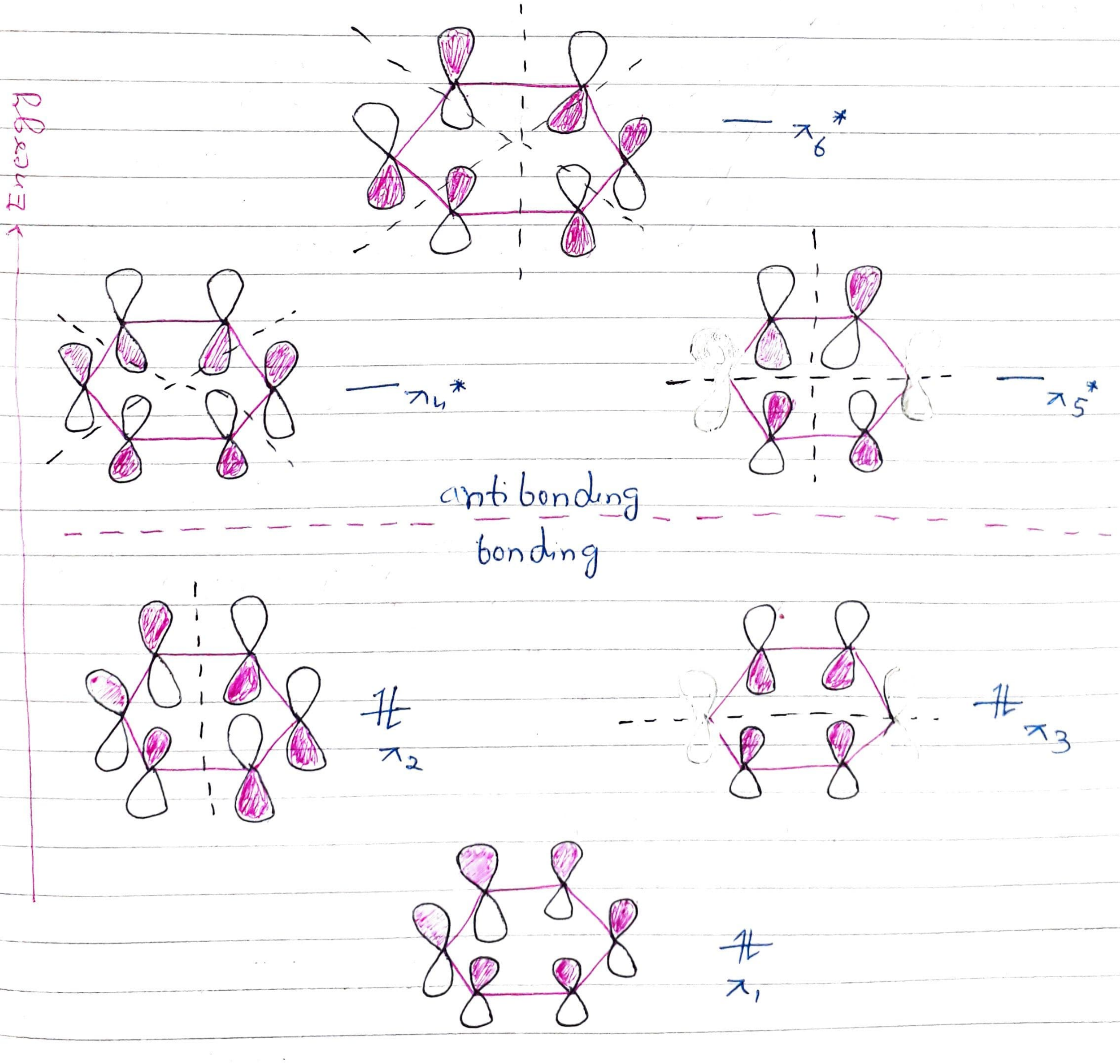
* The hybrid structure of benzene is represented by inscribing a circle inside the hexagon.



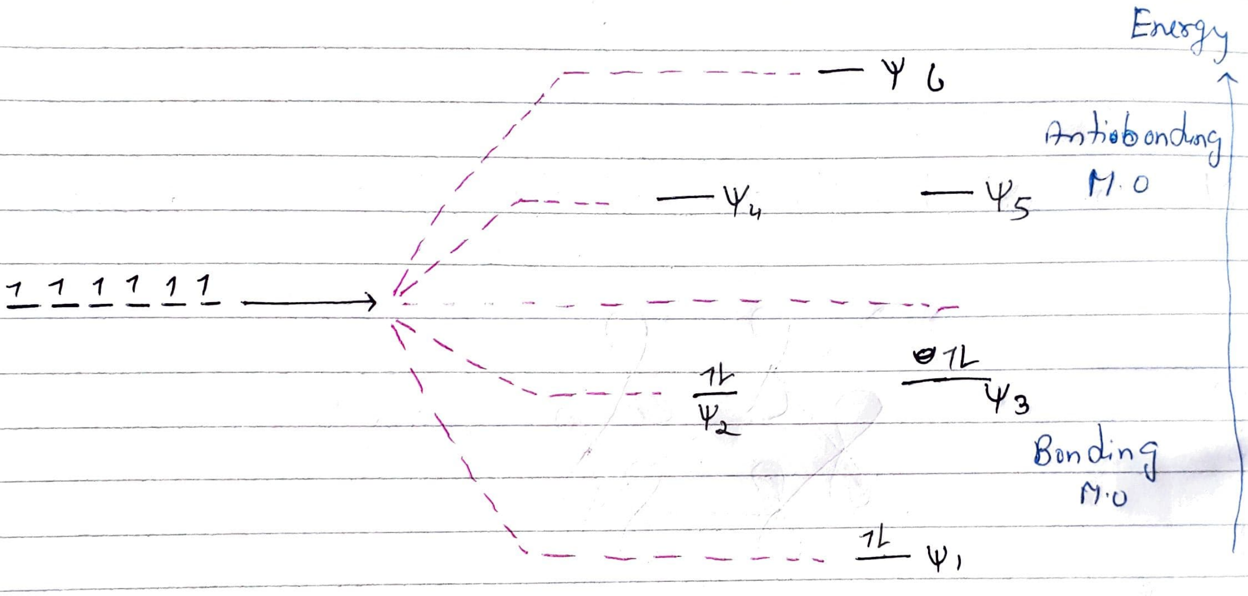
III

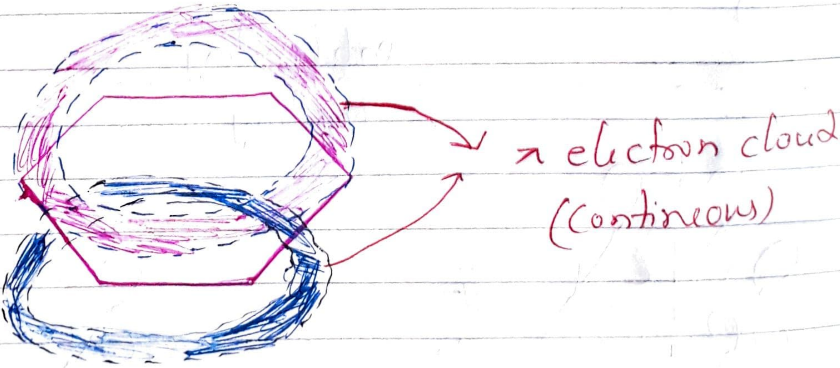
* An actual molecule of benzene (III) is more stable than either of the contributing resonance structure (I or II)

<u>Molecular Orbital explanation of the structure of Benzene:</u>



All the carbon atoms in benzene are sp^2 hybridised. The three sp^2 hybrid orbitals are lying in one plane and oriented at an 120°. The fourth unhybridized p-orbital having two lobes lying perpendicular to the plane of the hybrid orbital.
If we consider only the p-orbital contributed by the carbon atoms of benzene, there should by six π molecular orbitals.





structure of Benzene

Aromatic compounds: A compound is said to be aromatic, if it meets the following criteria -

i) It must have an uninterrupted cyclic cloud of π electrons above and below the plane of the molecule. In other words we can say that -

a) For the π cloud to be cyclic, the molecule must be cyclic

b) For the π cloud to be uninterrupted, every atom in the ring must have a p-orbital.

ii) The π cloud must contain an odd number of pairs of π electron.

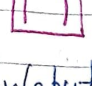
Huckel's rule: This rule states that for a planer cyclic compound to be aromatic, its uninterrupted π cloud must contain $(4n+2)\pi$ electrons. Where n is a whole number.

$n = 0, 1, 2, 3 \ldots$ etc.

~~Huckel rule is a~~

Annulenes: Monocyclic hydrocarbons with alternating single and double bonds are called Annulenes.

A prefix in brackets denotes the number of carbons in the ring.

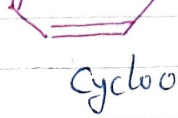


Cyclobutadiene

[4]-annulene

benzene

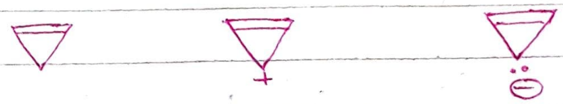
[6]-annulene



Cyclooctatetraene

[8]-annulene

Q→ Check the aromaticity

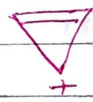


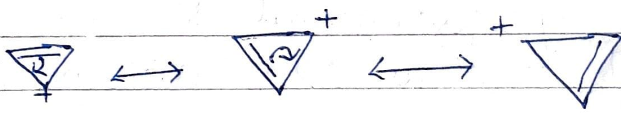
Cyclopropene   Cyclopropenyl cation   cyclopropenyl anion

Answer:

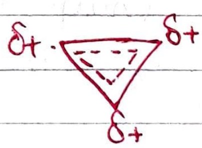
sp^3

Cyclopropene is not aromatic because it does not have an uninterrupted ring of p-orbitals bearing atom. One of its ring atom is sp^3 hybridized, and only sp^2 and sp^3 hybridised carbon have p-orbitals.



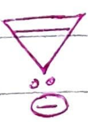


resonance contributor of cyclopropenyl cation

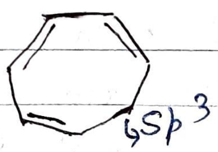


resonance hybrid.

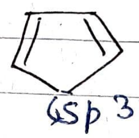
Cyclopropenyl cation is aromatic because it has an uninterrupted ring of p-orbital bearing atom and π cloud contains one (odd number) pair of delocalized π electron.



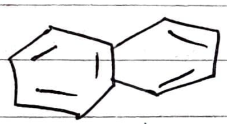
Cyclopropenyl anion is not aromatic because although it has an uninterrupted ring of p-orbital bearing atom, its π cloud has two (an even number) pair of π-electrons.



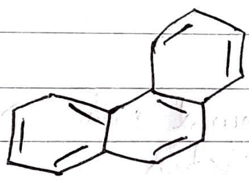
~~Cyclohetal~~
Cycloheptatriene
(not aromatic)



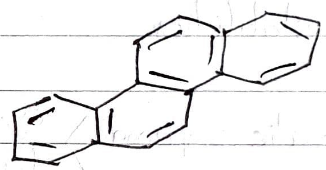
Cyclopentadiene
(not aromatic



naphthalene
(aromatic)



phenanthrene
(aromatic)

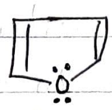


chrysene
(aromatic)

Aromatic Heterocyclic compounds.

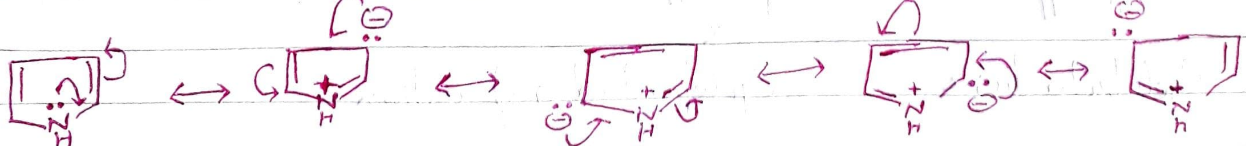
Pyridine

Pyrrole

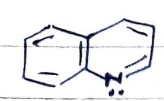


Furan

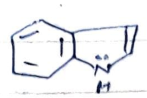
Thiophene



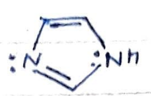
Resonance contributor of pyrrole



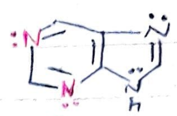
Quinoline



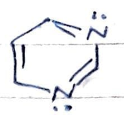
Indole



Imidazole



Purine



Pyrimidine

Antiaromaticity: An aromatic compound is more stable than the analogous cyclic compound with localized electron. in contrast, an antiaromatic compound is less stable than the analogous cyclic compound with localized electrons.

Aromaticity is characterised by stability whereas antiaromaticity is characterised by instability.

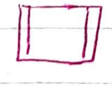
relative stabilities

Aromatic compound > Cyclic compound with localized electron > Antiaromatic compound.

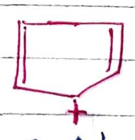
Rule for antiaromaticity: A compound is said to be antiaromatic if

i) It must be planer cyclic compound with uninterrupted ring of p-orbital bearing atoms

ii) π electron cloud must contain even number of pair of π electron ie. In other words it must contain 4nπ electrons. Where n is a whole number



Cyclobutadiene



Cyclopentadienyl cation