

# AROMATIC SYSTEMS

## AND THEIR MOLECULAR STRUCTURE.

### MODULE: 02

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**PREREQUISITE:** Students should know the difference between aliphatic compounds and cyclic compounds.

**COURSE OUTCOME:** Describe the concept of aromaticity and interpret it with relation to specific aromatic systems.

**INTRODUCTION:** In the earlier days of organic chemistry, the term 'aromatic' was used for compounds having characteristic aroma or certain fragrance. This term has been used for benzene and its derivatives because these compounds are associated with distinct and pleasing odour. However, there are some other organic compounds which have such odour but they are not classified as aromatic compounds.

The course provides an introduction to Aromaticity, Huckel's rule, Structure and bonding of benzene and pyrrole.

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#### **Q1. Explain Aromaticity.**

A. i. The property of unsaturated cyclic organic compounds, which give them unique stability and makes them chemically different from other open chain or cyclic compounds is known as 'Aromaticity'.

ii. Basically organic compounds show aromaticity only if they have cyclic structure and double bonds at alternate positions.

iii. Eg: Aromatic compounds: Pyrrole, Benzene, Pyridine.

Non-aromatic compounds: Cyclobutadiene, Cyclohexane.

#### **Q2. What are the conditions of aromaticity for cyclic aromatic compounds?**

A. To be an Aromatic Compound, the organic compound must have:

- cyclic structure
- double bonds in the ring [unsaturation] but less reactive than open chain compounds.
- planar flat structure
- should undergo electrophilic substitution reactions and should not undergo addition reactions easily.
- tendency to show resonance forms.
- $\pi$ -bonds present in the cyclic structure must have closed loop.
- all the atoms present in the ring, must be  $sp^2$  hybridised.
- all the  $\pi$ - orbitals [unhybridised  $p_z$  orbitals] must overlap sidewise.
- obey Huckel's rule .

#### **Q3. Explain Huckel's rule with examples.**

A. According to Huckel's rule, 'the cyclic unsaturated compounds containing  $(4n+2)$  delocalized  $\pi$ -electrons exhibit aromatic nature', where ' $n$ ' = 0, 1, 2, 3, 4, ....

For,  $n = 0$ ,  $\pi$ -electrons in aromatic compound =  $4n+2 = 4 \times 0 + 2 = 2$

For,  $n = 1$ ,  $\pi$ -electrons in aromatic compound  $= 4n + 2 = 4 \times 1 + 2 = 6$

For,  $n = 2$ ,  $\pi$ -electrons in aromatic compound  $= 4n + 2 = 4 \times 2 + 2 = 10$

For,  $n = 3$ ,  $\pi$ -electrons in aromatic compound  $= 4n + 2 = 4 \times 3 + 2 = 14$  and so on..

Examples:

1] Cyclopropenyl Cation:  $C_3H_3^+$  

i. Cyclopropenyl cation is a three membered cyclic and planar molecule.

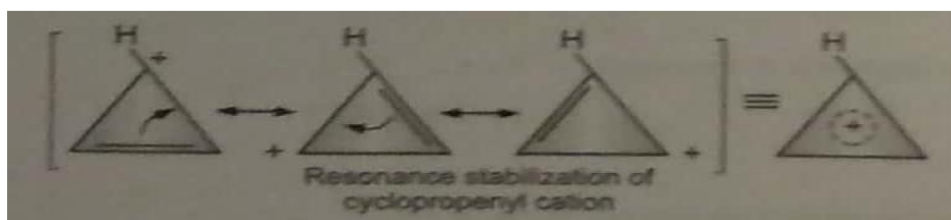
ii. All the three carbon atoms of the ring are  $sp^2$  hybridised. Thus  $p_z$  orbitals are available for the delocalization of  $\pi$ -electrons.


iii. from Huckel's rule, if  $n=0$ , then  $4n+2 = 4 \times 0 + 2 = 2$ .

iv. this shows that cyclopropenyl cation has  $2\pi$ -electrons and hence it obeys Huckel's rule of aromaticity.

v. therefore cyclopropenyl cation is an aromatic system.

vi. the following are resonance stabilization of cyclopropenyl cation:



2] Cyclobutadiene:  $C_4H_4$  

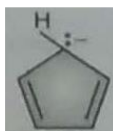
i. Cyclobutadiene is a four membered cyclic and planar structure.

ii. All the four carbon atoms of the ring are  $sp^2$  hybridised. Thus  $p_z$  orbitals are available for the delocalization of  $\pi$ -electrons.

iii. Cyclobutadiene has  $4\pi$ -electrons and hence it does not obey Huckel's rule of aromaticity.

v. Thus cyclobutadiene is not an aromatic compound as it does not satisfy all the necessary conditions of aromaticity.

3] Cyclopentadienyl Anion:  $C_5H_5^-$



i. Cyclopentadienyl anion is a five membered ring with a planar structure.

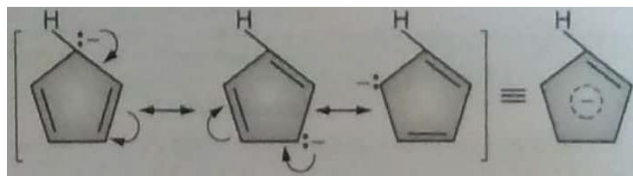
ii. All the five carbon atoms of the ring are  $sp^2$  hybridised. Thus  $p_z$  orbitals are available for the delocalization of  $\pi$ -electrons.

iii. it obeys Huckel's rule of aromaticity, as it has total six delocalized  $\pi$ -electrons.

If  $n=1$ , then  $4n + 2 = 4 \times 1 + 2 = 6$   $\pi$ -electrons

iv. the pair of electrons participates in delocalization along with  $\pi$ -electrons. Therefore the total number of delocalized electrons thus becomes six.

v. therefore Cyclopentadienyl anion is aromatic in nature because it satisfies all the necessary conditions of aromaticity.

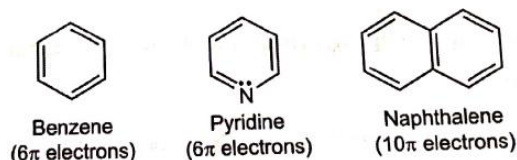


**Q4. What are the two types of aromatic compounds? Give examples.**

A. The two types of aromatic compounds are Benzonoids and Non-benzonoids aromatic compounds.

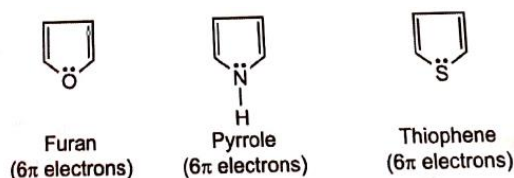
Benzonoids: The aromatic compounds which have one or more benzene rings in their structure are known as Benzonoid aromatic compounds.

Eg: Benzene, Pyridine, Naphthalene etc.



Non-benzonoids: The aromatic compounds which do not have benzene like rings in their structure are known as Non-benzonoid aromatic compounds.

Eg: Furan, Thiophene, Pyrrole etc.



**Q5. Explain aromatic sextet theory.**

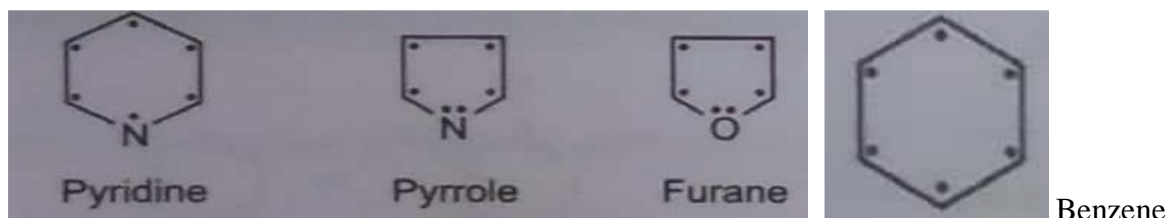
A. i. Sextet theory was proposed by Robinson in 1925 to describe the unusual stability and the aromatic nature of cyclic organic compounds like benzene.

ii. It says that, each of the carbon atoms in benzene molecule contributes one electron to the ring.

iii. This electron does not involve in hybridisation and is said to be delocalized.

iv. Thus six carbon atoms contribute six electrons which constitute a 'closed sextet'.

v. This sextet of electrons is responsible for the stability and aromaticity in benzene molecule.



**Q6. Explain in detail structure and bonding of benzene.**

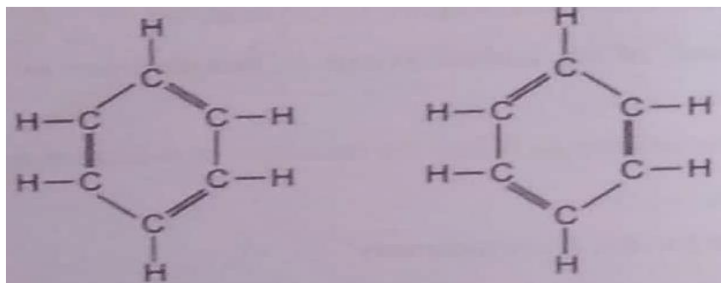
A. The structure and bonding of benzene is explained on the basis of the following:

I. Kekule's Structure II. Resonance structure III. Molecular Orbital Structure.

**I. Kekule's Structure:**

i. August Kekule suggested that benzene consisted of a cyclic planar structure of six carbon atoms with alternate double and single bonds.

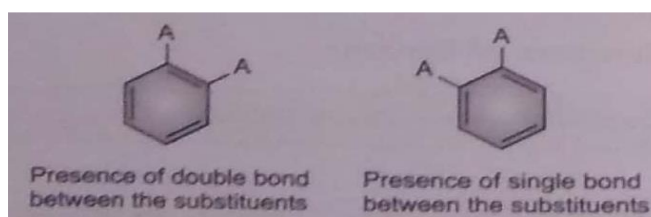
ii. Each carbon atom of benzene is attached to one hydrogen atom. Thus benzene was considered to have molecular formula  $C_6H_6$  with hexagonal ring structure.



iii. It was found that Benzene is highly stable but does not undergo addition reactions as that of alkenes; rather it undergoes electrophilic substitution reactions very easily.

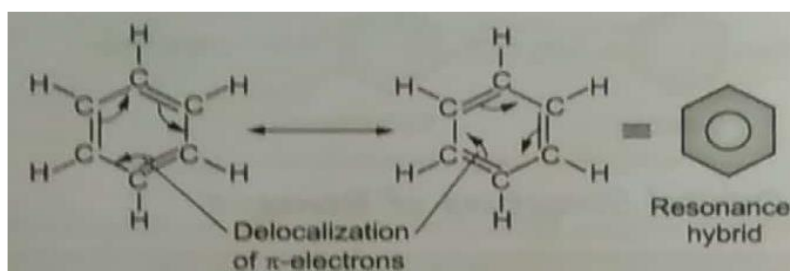
iv. According to Kekule's findings, the bond length for carbon-carbon single bond is  $1.54\text{\AA}$  and for carbon-carbon double bond is  $1.34\text{\AA}$  but then all the bonds of benzene exhibit equal bond lengths of  $1.39\text{\AA}$ .

v. According to Kekule's structure of benzene, two o-dimensional products of benzene are possible which are as follows:



where A is an electrophile. But only one o-dihalobenzene is known.

**II. Resonance structure:** [The phenomenon in which two or more structures can be written for a substance which involve identical positions of atoms, differing in the position of their electrons is called Resonance and the structures as resonance structures.]



i. According to the resonance theory, the position of double bonds in benzene molecule are not fixed i.e. the  $\pi$ -electrons associated with double bonds are delocalized in benzene ring.

ii. A single bond length (C-C) is  $1.54\text{\AA}$  and a double bond length (C=C) is  $1.34\text{\AA}$ .

X-ray diffraction and Electron diffraction analysis of benzene reveal that, all the carbon-carbon bonds of benzene have same bond length i.e.  $1.397\text{\AA}$ .

iii. This shows that all the C-C bonds of benzene have a partial double bond nature. It is possible when all six  $\pi$ -electrons of benzene are delocalized i.e. positions of double bonds are not found.

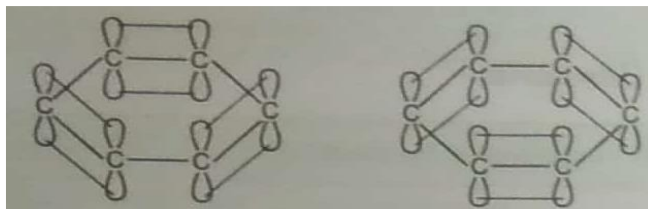
iv. There are six C-H bonds in benzene and all the six C-H bond length are also found to be of same length which is  $1.09\text{\AA}$ .

v. The theoretical enthalpy change of hydrogenation for benzene should be  $-360\text{ KJ/mol}$  but experimental data shows that the enthalpy change of hydrogenation for benzene should be  $-208\text{ KJ/mol}$ . Therefore benzene is more stable than the expected value from about  $152\text{ KJ/mol}$  [ $-360 - (-208) = 152\text{ KJ/mol}$ ].

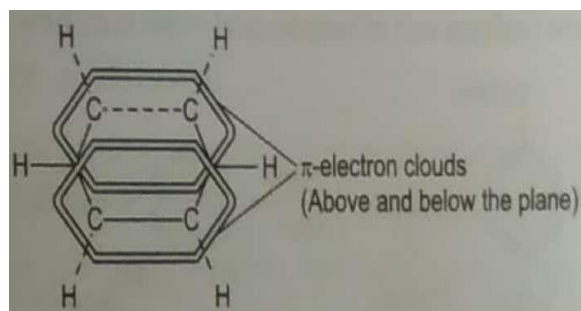
### III. Molecular Orbital Structure of Benzene:

i. According to molecular orbital concept, all six carbon atoms of benzene are  $sp^2$  hybridised and thus each one of them forms three sigma bonds and one  $\pi$ -bond.

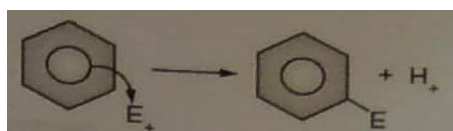
- ii. Each of the carbon atom of benzene forms two sigma bonds with two adjacent carbon atoms and one with hydrogen atom.
- iii. Thus all 6 carbon atoms and 6 hydrogen atoms of benzene lie in the same plane. The angle between two adjacent bonds is  $120^\circ$ .
- iv. Each carbon atom of benzene has an unhybridised  $\pi$ -orbital ( $p_z$ -orbital). It lies above and under the plane of benzene ring.
- v. These  $\pi$ -orbitals of six carbon atoms overlap sidewise to form two sets of  $\pi$ -electron clouds.



- vi.  $\pi$ -electrons of  $p_z$  orbitals are delocalized and they can move over all the six carbon atoms of benzene.
- vii. Such delocalization of  $\pi$ -electrons constitute continuous ring like electron clouds above and below the plane of ring.

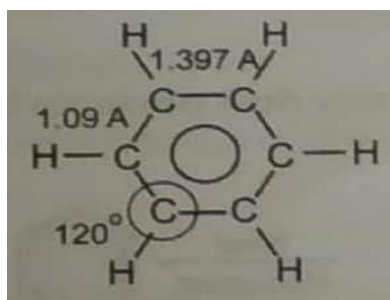


- viii. the  $\pi$ -electron clouds can be easily attacked by electrophile. Hence it readily undergoes electrophilic substitution reactions.



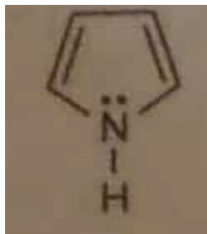
where 'E' is an electrophile. As the aromaticity of benzene is not disturbed in the electrophilic substitution reactions, therefore these reactions are highly spontaneous in nature.

- ix. the final molecular orbital structure with bond angle and bond length is as follows:



## Q7. Explain in detail structure and bonding of pyrrole.

A. i. Pyrrole is a cyclic five membered unsaturated heterocyclic compound. The molecular formula of pyrrole is  $C_4H_5N$ . It has four carbon atoms and one nitrogen atoms in the ring. There are two double bonds between four carbon atoms.



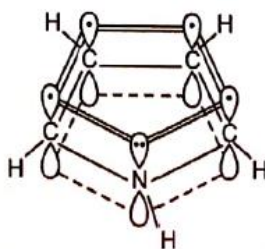
ii. Nitrogen atom of pyrrole carries a lone pair of electrons, it gets involved with the  $4\pi$  electrons of the pyrrole ring.

iii. Thus, total number of delocalized electrons in a pyrrole molecule is six and obeys Huckel's rule of aromaticity.

iv. All the four carbon atoms are  $sp^2$  hybridised.

v. The p-orbitals of four  $sp^2$  hybridised carbon atoms each with one electron and an orbital of nitrogen atom with lone pair of electron form a  $\pi$ -electron cloud.

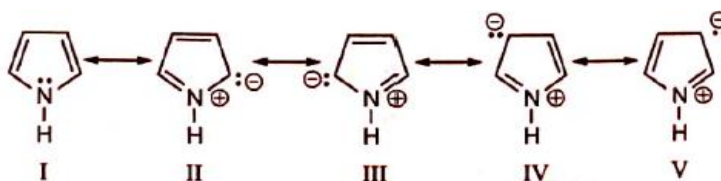
vi. The  $\pi$ -electron cloud lies above and below the plane of the ring.



vii. The pyrrole ring is planar pentagon in terms of its molecular orbitals. The six electrons taking part in the delocalization constitute Huckel system of  $(4n+2)$   $\pi$ -electron.

viii. Thus the heterocyclic pyrrole molecule is an aromatic molecule.

ix. According to the resonance theory, pyrrole is considered to be a hybrid of the following five resonance structures.



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