

MODULE2. AROMATIC SYSTEM AND THEIR MOLECULAR STRUCTURE

Aromaticity is a characteristic in which any planar system in which there is complete delocalisation of pi electrons in the ring, and the system contains $4n+2$ pi electrons in the ring is called aromatic. Example: Benzene, naphthalene, anthracene etc. Due to the presence of pi bonds in resonance it gives increased stability compared to other geometric or connective arrangements with the same set of atoms. Aromatic rings are very stable and do not break apart easily.

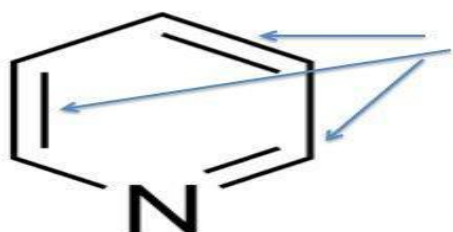
Characteristic properties of Aromatic compounds-

- Must be **Cyclic**.
- Must have **($4n + 2$) pi Electrons** ($n = 0, 1, 2, 3, 4, \dots$)
- Resist Addition reaction but **prefer Substitution reaction**.
- Must Possess **Resonance Energy**.
- Must have at least one **conjugated ring** of alternate single and double bonds, and exhibit extreme **stability**.
- Undergo substitution **reactions**, in which the **aromatic** hydrogen is replaced with an electrophile, hence their **reactions** proceed via electrophilic substitution.
- Coplanar structure, with all the contributing atoms in the same plane.

HUCKEL'S RULE- In 1931, German chemist and physicist Erich Huckel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar molecule has **$4n+2$ π electrons**, where **$n = 0$ or any positive integer**, it is considered aromatic. Thus for a molecule to be aromatic, the number of Pi electrons on the ring should be either 2, 6, 10 or 14 etc.

ANTIAROMATIC compound is **cyclic, planar, and has the conjugation of p orbitals**, but the difference is the number of electrons in the conjugated p orbitals. It has **higher energy** and **unstability** due to the presence of **$4n$ delocalised (π or lone pair) electrons** in it. Such compounds have 4, 8 or 12 electrons. For eg. Cyclobutadiene (4π - electrons) and Cyclo-octatetraene (8π - electrons).

NON-AROMATIC molecules are every other molecule that **fails one of these conditions** i.e non-aromatic compound is either **not cyclic or not planar**.



Pyridine has 6 pi electrons
(There are 3 double bonds: each double bond is counted as 2 pi electrons)

$$4n + 2 = 6$$

Find n:

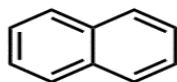
$$4n + 2 = 6$$
$$4n = 6 - 2$$
$$4n = 4$$
$$n = 1$$

An aromatic compound follows Huckel's rule if n is equal to zero or a positive whole number.

Pyridine is aromatic

Pyridine is cyclic, conjugated, and has three pi bonds. ... Therefore we can ignore the lone pair for the purposes of aromaticity and there is a total of six pi electrons, which is a Huckel number and the molecule is aromatic.

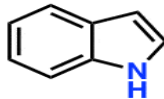
Some examples of aromatic compounds



Naphthalene



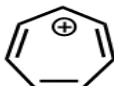
Furan



Indole



Pyridine

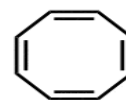


Tropylium ion



Cyclopentadienyl anion

Counter-example

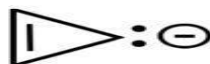


Cyclooctatetraene
(not aromatic)

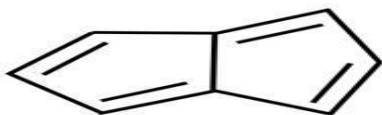
Huckel's Rule for Antiaromatic Compounds (Number of Pi Electrons = $4n$)



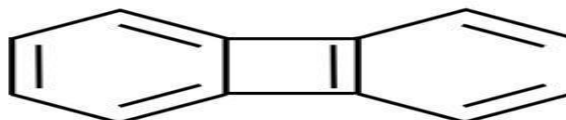
Cyclobutadiene
Pi electrons = 4
 $n = 1$



Cyclopropenyl anion
Pi electrons = 4
 $n = 1$



Pentalene
Pi electrons = 8
 $n = 2$



Biphenylene
Pi electrons = 12
 $n = 3$

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Summary: Anti-Aromaticity

Aromatic

*unusually
stable*

- Cyclic
- Conjugated
- $(4n+2)$ Pi electrons
- Flat

e.g.



benzene

(resonance energy of 36 kcal/mol)

Anti-Aromatic

*unusually
unstable*

- Cyclic
- Conjugated
- $(4n)$ Pi electrons
- Flat

e.g.



cyclobutadiene

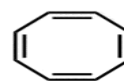
(only stable below $-100\text{ }^{\circ}\text{C}$)

Non-Aromatic

everything else

*Fails any one
of the 4 criteria
on the left*

e.g.



cyclooctatetraene

(adopts a tub-like shape to "escape" anti-aromaticity)

STRUCTURE AND BONDING OF BENZENE

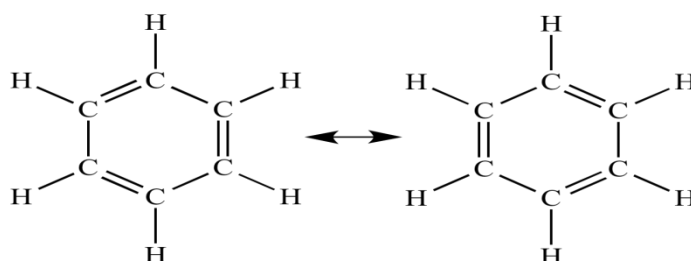


Fig: Kekule structure of Benzene

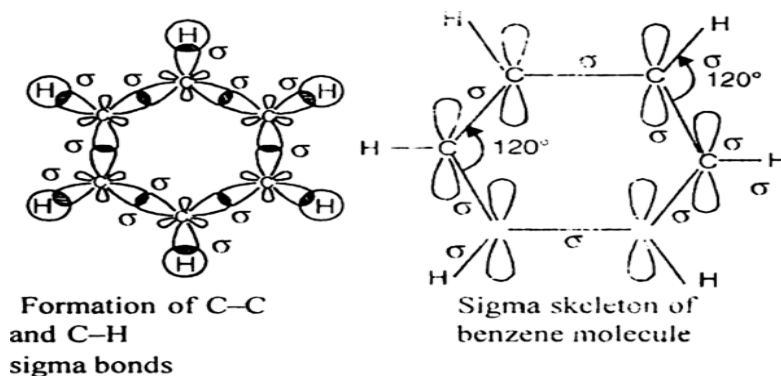
Kekule was the first to suggest a **structure** for **benzene**. They have **6 carbons** arranged in a **hexagon** with **alternate double and single bonds** between them. Each carbon atom is attached with one hydrogen. This structure fails to explain some properties of benzene.

The structure proposed by Kekule was unable to explain the following facts.

- The Kekule structure predicts that there should be two different 1,2-dibromobenzene. But in practice, only one 1,2-dibromobenzene has ever been found.
- According to Kekule, benzene contains three double bonds; the chemical properties of benzene should resemble those of alkene. But actually it is not so. **Benzene is highly stable and forms substitution compounds easily.**
- The **resistance** of double bonds in benzene **for addition reactions**. Ease of **substitution reactions**.
- Kekule structure predicts two types of bond lengths that is for single bonds 1.54Å and for double bonds 1.34Å. Actually **all the bonds of benzene are of equal length**.

Molecular Orbital Structure of Benzene:

The orbital structure of benzene can be easily described by orbital concept. According to this structure, all the carbon atoms in benzene are **sp² hybridised**. The three sp² hybrid orbitals are **lying in one plane** and oriented at an **angle of 120°**. The **fourth unhybridized p-orbital** having two lobes is **lying perpendicular** to the plane of the hybrid orbital. Two out of the three sp² hybrid orbitals of each carbon atom overlap axially with sp² hybrid orbitals of the neighbouring carbon atoms on either side to form carbon-carbon sigma bonds. The third hybrid orbital of each carbon atom overlaps axially with the half-filled 1s-orbital of the hydrogen atom to form carbon-hydrogen sigma bonds. Thus there are six sigma C-C bonds and six sigma C-H bonds. There is still one unhybridized 2p_z orbital on each carbon atom. This orbital consists of two lobes, one lying above and the other below the plane of the ring.



The unhybridized 2p_z orbital on each carbon atom can overlap sidewise with the 2p_z orbital of the two adjacent carbon atoms in two different ways . It results in the formation of three pi bonds. The six pi-electrons are enough to fill all the bonding Pi- molecular orbitals. Since a 2p_z orbital on any carbon atom can overlap sideways with the 2p_z orbital on adjacent carbon atoms on either side equally well. The net result is that there are two continuous rings like electron clouds, one above and the other below the plane of atoms as shown below. This delocalisation of pi electrons imparts unique stability to the benzene molecule.

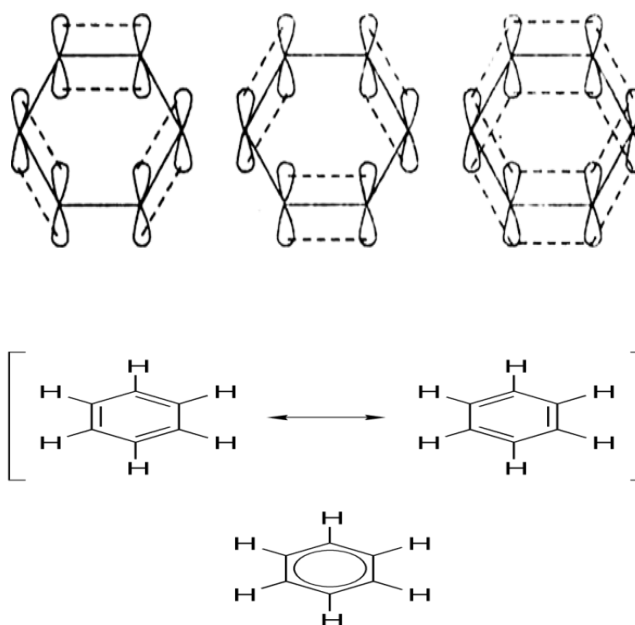
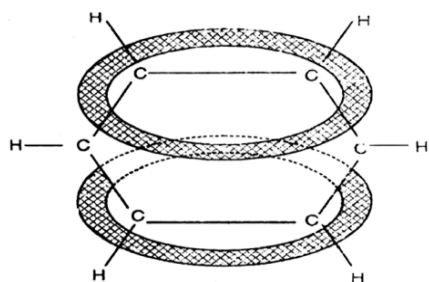


Fig: Resonating structure of Benzene



In benzene molecules all C-C-C and H-C-C angles are 120° and each C-C bond length is 1.39 \AA .

Evidence in support of orbital structure of Benzene:-

1. **Unusual stability-** Benzene exhibits unusual stability and resist the formation of addition products. This can be explained by delocalisation of π - electrons in benzene molecule.
2. **Isomer number-** according to orbital concept, all the 6 carbons are completely equivalent. Similarly all the 6 hydrogen atoms also occupy identical positions. Thus benzene should form only one mono-substituted and three distributed products.
3. **Electrophilic substitution reactions-** there are two continuous rings like electron clouds, one above and the other below the plane of carbon atoms. The π - electrons are easily attacked by electrophiles. Hence, benzene undergoes electrophilic substitution reactions.

HALOGENATION OF BENZENE

a)Chlorination



b)Bromination

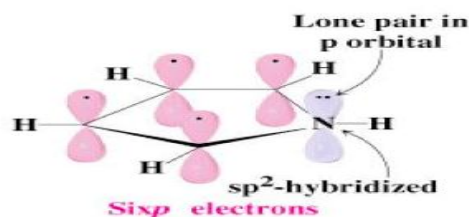
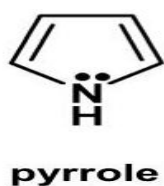


c) Iodination

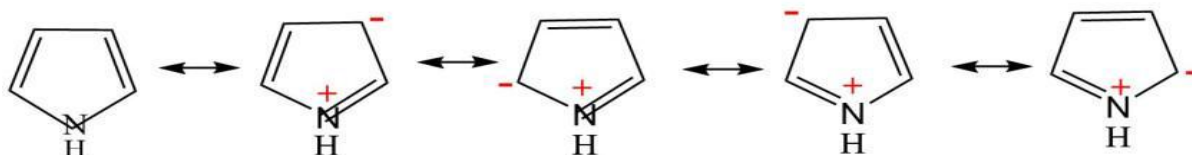


Molecular Orbital Structure and Bonding of Pyrrole:-

Pyrrole has a planar pentagonal structure in which each of the ring atoms (four carbons and one nitrogen) is linked to three other atoms (two adjacent ring atoms and hydrogen) by a σ bond, and is thus Sp^2 hybridized. This leaves one unhybridized p orbital on each ring atom, which is perpendicular to the plane of the ring and parallel to other p orbitals. After contributing one electron to each of the three σ bonds each carbon atom of the ring is left with one electron to occupy the p orbital. The five p orbitals of the ring atoms overlap sidewise to form a cyclic π molecular orbital containing six π electrons (one πe^- from each carbon and two from nitrogen) The delocalized six π electrons are often referred to as the aromatic sextet. The stabilization of the ring system due to the delocalization of the six electrons causes it to be aromatic. The pyrrole is an aromatic compound because six electrons fit Huckel's $4n + 2$ rule ($n=1$), which is extended to include heteroatoms.



Resonance structures of pyrrole



The resonance hybrid structure of pyrrole shows that the **pyrrole ring** is electron-rich.

The reason for the weak basic character of pyrrole is that the lone pair of electrons on nitrogen is involved in the formation of the delocalized π molecular orbital and is not available for the formation of a new bond with a proton. The Pyrrole cation behaves as a typically conjugated diene and undergoes polymerization readily. The nitrogen in pyrrole is more electronegative than carbon; therefore, the molecule has bipolar structure. Dipolar structures make important contributions to the resonance hybrid of the substance. The charge distribution in the pyrrole provides the carbon portion of the nucleus with a partial negative charge and nitrogen atom with a positive charge and accounts for the dipole moments of the pyrrole.

The stability of the pyrrole ring is due to the delocalization of the π electrons. The stability of the ring is reflected by its abnormally low heat of combustion and its capacity to undergo substitution reactions.

The resonance stabilization energy as calculated from heats of combustion for pyrrole is about 105 KJ/mol, which is less than that of benzene (150.5 KJ/mol). But both resonance and molecular orbital methods suggest that the structure of the pyrrole resembles to that of benzene. Thus pyrrole gives electrophilic aromatic substitution reactions such as nitration, sulphonation, Friedel-Crafts reactions etc. more readily than benzene.

