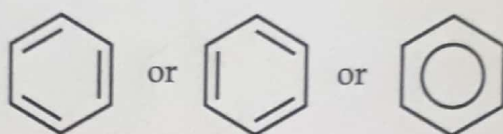


INTRODUCTION

Benzene and all those compounds which resemble benzene in their chemical behaviour are termed as aromatic. Benzene is an aromatic compound having molecular formulae C_6H_6 . It contains six carbon atoms, 6-hydrogen atoms and three conjugated double bonds. Aromatic compounds having one or more benzene rings in their molecules are called benzenoid compounds or benzenoids. For example, benzene, toluene, xylene, chlorobenzene, phenol etc. Basic structure of benzene is

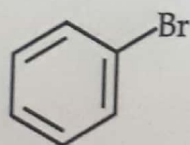


NOMENCLATURE OF DERIVATIVES OF BENZENE

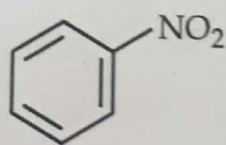
In IUPAC nomenclature there are various rules for naming benzene derivatives. These are as follows :-

(1) For Monosubstituted benzene derivatives

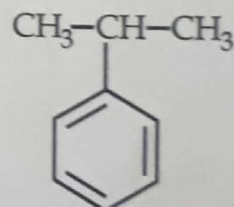
- a) Name of monosubstituted benzene derivative is obtained by placing prefix (name of substituent) to the word benzene. For example-



Bromobenzene

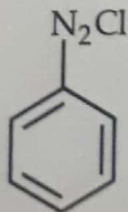
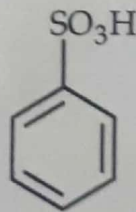


Nitrobenzene

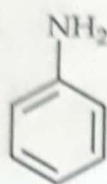


Isopropylbenzene

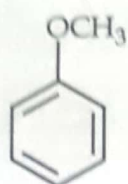
In some cases, name of the substituent is written after benzene.

Benzenediazonium
ChlorideBenzenesulphonic
acid

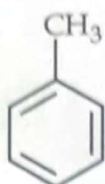
b) Some derivatives have special names like :-



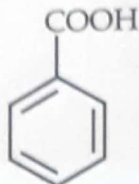
Aniline



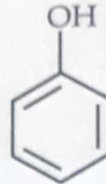
Anisole



Toluene



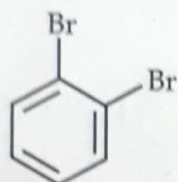
Benzoic acid



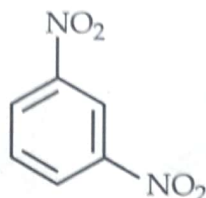
Phenol

2) For disubstituted benzene derivatives

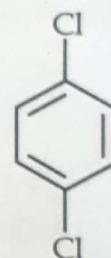
a) Derivatives having two similar groups, the prefix "di" is added before the name of the group and the relative positions of the two groups are indicated by the symbol 'O' (ortho) for 1,2; m (meta) for 1,3 and p (para) for 1,4 positions respectively. For example



o-dibromobenzene

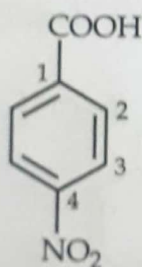


m-dinitrobenzene

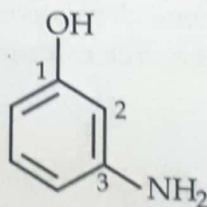


p-dichlorobenzene

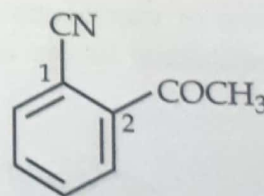
b) Derivatives having different groups are named as a derivatives of the compound with the main functional group at position 1. For example



4-nitrobenzoic acid

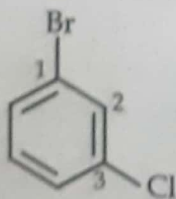


3-Aminophenol

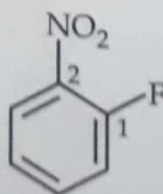


2-Acetylbenzonitrile

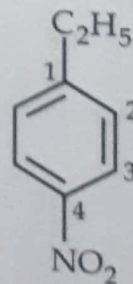
c) If both the functional groups present are substituent functional groups then they are arranged in alphabetical order. For example,



1-Bromo-3-Chlorobenzene



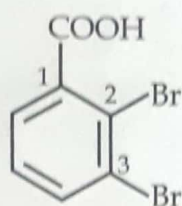
1-Fluoro-2-Nitrobenzene



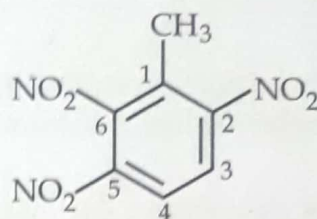
1-Ethyl-4-nitrobenzene

3) For Polysubstituted benzene derivatives

- a) If any substituent gives special name to the ring then the numbering of the ring begins with that substituent and the compound is named as its derivative. For example,

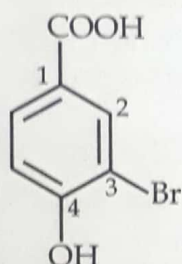


2,3-dibromobenzoic acid

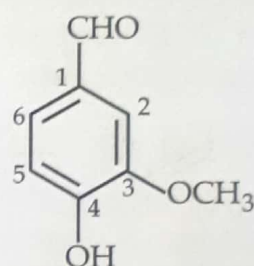


2,5,6-trinitrotoluene

- b) If three different functional groups are present, name is done as the derivative of the compound with the principal functional group at position 1. For example,

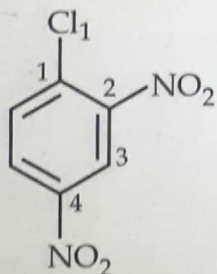


3-Bromo-4-hydroxy benzoic acid

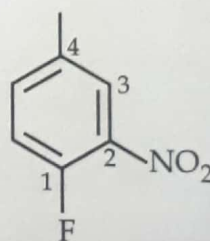


4-hydroxy-3-methoxy benzaldehyde

- c) Various groups are arranged in alphabetical order with the group named first in the alphabetical order getting the lowest locant. For example



1-chloro,2,4, dinitrobenzene

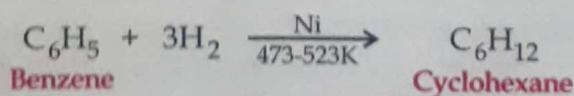


4-Ethyl-1-Fluoro-2-nitrobenzene

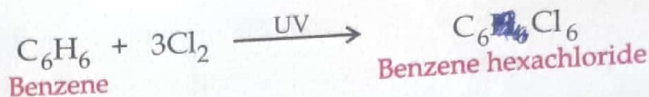
STRUCTURE OF BENZENE

The molecular formulae of benzene was found to be C_6H_6 . It means benzene has eight hydrogen atoms less than its corresponding saturated hexane whose molecular formulae is C_6H_{14} . So, benzene is a highly unsaturated compound. Various observations also supported this fact :

1. Benzene can take three molecules of hydrogen in presence of a catalyst like Nickel or Platinum to form cyclohexane



2. In presence of sunlight benzene readily adds three molecules of chlorine to form benzene hexachloride.

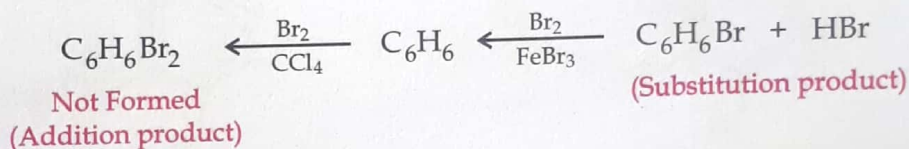


3. Benzene forms triozonide on reaction with ozone.

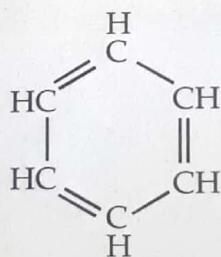


All the above three points proves that benzene has three double bonds. In spite of all these benzene behaves like a saturated compound. This was supported by following facts :

4. **Benzene resists oxidation** : All unsaturated compounds undergoes oxidation easily but benzene resists oxidation like all saturated compounds. Even powerful oxidising agents like chromic acid, potassium permanganate cannot oxidise benzene.
5. **Benzene shows substitution rather than addition reactions** : Being unsaturated in nature benzene is expected to undergo addition reactions but it does not decolourize bromine in CCl_4 solution and undergoes substitution reactions like nitration, sulphonation etc. All these reactions are typical of saturated compounds.



KEKULE'S STRUCTURE OF BENZENE



Bond length
 $\text{C}-\text{C} = 1.543 \text{ \AA}$ (1.47 Å)
 $\text{C}=\text{C} = 1.337 \text{ \AA}$ (1.34 Å)
 $\text{C}\equiv\text{C} = 1.208 \text{ \AA}$
 Benzene: $\text{C}-\text{C}$ bond length
 1.39 Å

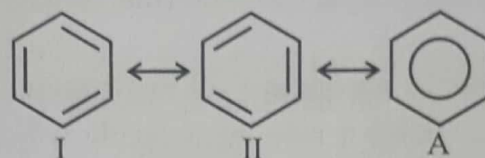
The structure of benzene was given by Friedrich August Kekule in 1865. According to him the six carbon atoms of benzene are joined together by alternate single & double bonds & forms a hexagonal ring. Each carbon is further connected to a hydrogen atom. But there are three main objections to Kekule's structure.

1. This structure could not explain the stability of benzene towards oxidising agents and cannot explain the substitution reactions after having three double bonds.
2. According to this structure only one monosubstituted and two disubstituted products exist but in actual only one monosubstituted product is known. The positions of single and double bonds are not fixed but they oscillate back and forth which is not explained by Kekule's structure.
3. Kekule's formulae for benzene contains two kinds of bonds i.e. single and double bonds but X-ray diffraction shows that benzene is a regular hexagon with an angle of 120° and all the C-C bond lengths are equal.

So, Kekule's structure failed to explain the unusual stability and equality of C-C bond lengths in benzene.

RESONANCE STRUCTURE OF BENZENE

To explain all the limitations of Kekule's structure, it has been proposed that benzene is a resonance hybrid of two Kekule's structure (I & II). These two structures are canonical forms of benzene. In actual, the benzene is a resonance hybrid of these two structures (A) it means that any two adjacent carbon atoms of the benzene molecule are neither joined by a pure single bond nor by a pure double bond. As a result, all the C-C bond lengths are equal i.e. 1.39\AA and lie in between C=C bond length of 1.34\AA and C-C bond length of 1.54\AA .



Resonance hybrid is always more stable than its canonical structures. This is the reason why benzene is more stable than either of the two Kekule's structures. Resonance structure of benzene explains all the facts like unusual stability and equality of C-C bond lengths in benzene.

MOLECULAR ORBITAL (MO) STRUCTURE OF BENZENE

Molecular orbital theory states that all the carbon atoms of benzene are assumed to be sp^2 hybridised. Each 'C' atom forms two C-C sigma bonds with the adjacent 'C' atoms and one C-H sigma bond with hydrogen atom. So, overall there are six C-C sigma bonds and six C-H sigma bonds, which lie in one plane and the angle between any two adjacent sigma bond is 120° .

Each carbon atom has an unhybridised p-orbital so, six unhybridised p-orbitals have one electron each which are parallel and perpendicular to the plane of sigma bonded carbon skeleton. So, p-orbitals on adjacent carbon atoms can overlap to form three pi-bonds.

Each 2p orbital overlaps well with adjacent 2p orbital on either side to form two doughnut shaped pi-electron clouds, one of which lies above and other below the plane of carbon and hydrogen atoms. When six 2p orbitals having electrons combines, six molecular orbitals results, out of which three are bonding while the remaining three are antibonding. Bonding orbitals are of lowest energy. So, all the six pi-electrons occupy three bonding molecular orbital and are delocalised over the entire conjugated system. Involvement of pi-electrons in the formation of more than one bond is called delocalisation of electrons & this delocalisation makes the molecule more stable. So, benzene can be represented as a hexagon with a circle in the centre. Circle represents the six completely delocalised pi-electrons.

AROMATICITY & HUCKEL RULE

Earlier, benzene and its derivatives having large resonance energies are called as aromatic compounds and their extra stability is referred to their special property called as aromatic character or aromaticity. But there are various limitations to this concept. Lower and higher (cyclobutadiene & cyclooctatetraene) derivatives also shows aromaticity. It means aromaticity is not related to cyclic conjugated polyenes but is related to number of π (pi) electrons in conjugated polyenes.

Huckel Rule

In 1931, a German physicist, Huckel gave certain rules for defining the aromaticity of organic compounds. In order to be aromatic, a compound must fulfill the following criteria:

1. The molecule or ion must be flat or planar.
2. It should have cyclic delocalised electron clouds above and below the plane of the molecule.
3. The total number of π -electrons in the molecule should be $(4n+2)$ where $n = 0, 1, 2, \dots$ etc.
4. The π -electron clouds should encompass all the carbon atoms of the cyclic system.

This rule is also known as $(4n+2)$ π rule. A molecule which does not possess or satisfy one or more of the above conditions are said to be non-aromatic.

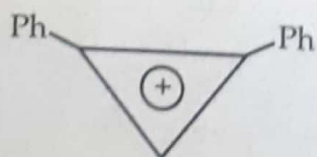
Huckel states that energies of the MO's of aromatic systems have a orbital of lowest energy followed by a degenerate pairs of orbitals (orbitals of same energy) in order of increasing energy and finally a orbital of highest energy. During filling of electrons, two electrons are filled in the lowest energy Mo then the electron goes to degenerate pairs of orbitals. So, if a conjugated planar monocyclic system has 2, 6, 10, 14 etc. pi electrons, the lowest energy MO and all the other degenerate pairs of MO's would be occupied by two electrons each. As a result of this closed shell filling of orbitals, these are quite stable and hence aromatic.

If a monocyclic planar conjugated system has 4, 8, 12 etc. π -electrons, there will be two singly occupied degenerate orbitals. As a result of this, such systems are highly unstable and are called as antiaromatic.

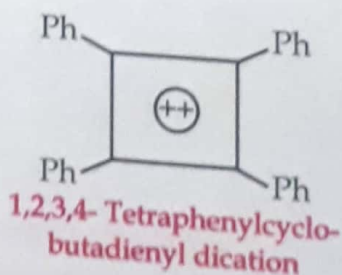
So, aromatic compounds need not contain benzene ring but they must be planar and should contain cyclic delocalised $(4n+2)$ π electrons above and below the plane of the ring. All the cyclic conjugated planar molecules containing $2(n=0), 6(n=1), 10(n=2), 14(n=3), \dots$ π electrons should be aromatic.

Various examples are :

1) Two π -electron system

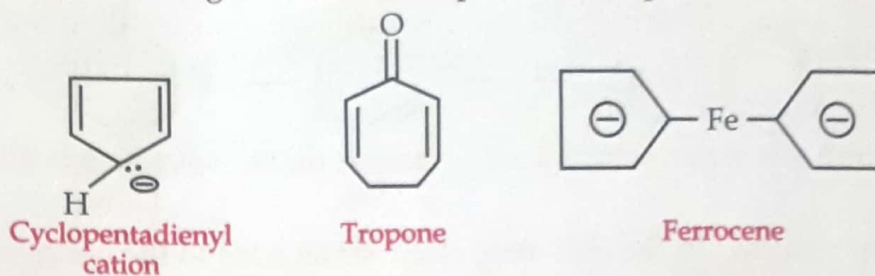


1,2-Diphenylcyclopropenyl cation

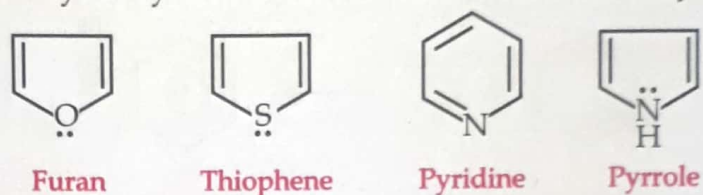


1,2,3,4-Tetraphenylcyclobutadienyl dication

2) **Six π -electron system** : e.g. Benzene is a perfect example



3) **Heterocyclic compounds** : e.g. pyridine, furan, thiophene, pyrrole, indole etc. are aromatic as they contain a cyclic system of 6π electrons which are fully delocalised.



4) **Polycyclic compounds** : Some polycyclic compounds are also aromatic. For example naphthalene contains 10π electrons ($n=2$), anthracene and phenanthrene has 14π electrons ($n=3$) and are aromatic.

