

3(I)-1

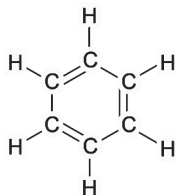
Introduction to Structure of Benzene

(Analytical, Synthetic and Other Evidences in the Derivation of Structure of Benzene, Orbital Structure, Resonance in Benzene, Aromatic Characters, Huckel's Rule)

Michael Faraday first isolated benzene in 1825 from the oily residue derived from the production of illuminating gas, giving it the **name**, bicarburet of hydrogen. He also determined C:H ratio to be 1:1. In 1834, **Eilhard Mitscherlich** produced it by distilling benzoic acid (from gum benzoïn) and lime. He gave the compound name, **benzin**, later known as benzene. He also determined its molecular formula, C_6H_6 . It contains eight hydrogen atoms less than the corresponding parent hydrocarbon, i.e. hexane (C_6H_{14}). It took several years to assign a structural formula to benzene because of its unusual stability and peculiar properties.

KEKULE STRUCTURE OF BENZENE

Benzene is most commonly encountered aromatic compound. In 1865, Kekule proposed the first acceptable hexagonal ring structure for benzene. In this structure, there is a hexagonal ring of carbon atoms distributed in a symmetrical manner, with each carbon atom carrying one hydrogen atom. The fourth valence of carbon atoms is fulfilled by the presence of alternate system of single and double bonds, means it can be recognized by the arrangement involving conjugated double bond system. Kekule structure is shown as:



Kekule structure for benzene

The above formula had many drawbacks as described below:

1. The presence of three double bonds should make the benzene molecule highly reactive towards addition reactions like alkene. But, contrary to this, benzene behaves like saturated hydrocarbons.
2. Moreover, two isomers should result in 1,2-disubstituted benzene as shown in Fig. 3.1.1. In one of the isomers, the bond between the substituted carbon atoms is single bond while in the other it is a double bond. Actually, only one 1,2-disubstituted (or *ortho*) isomer is formed.

Although Kekule formula could not explain the difference in properties between benzene and alkenes based on his structure, but he explained the lack of isomerism as in Fig. 3.1.2 by postulating a rapid interchange in the position of the double bonds as follows:

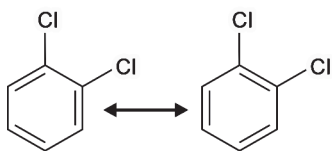


Fig. 3.1.1: Kekule isomers for 1,2-dichlorobenzene

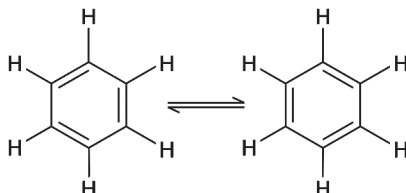


Fig. 3.1.2: Interchange of double bonds in Kekule structure of benzene

This structure is known as Kekule's dynamic formula.

RESONANCE STRUCTURE OF BENZENE

X-ray studies indicate that all the carbon-carbon bonds in benzene are equivalent and have bond length 1.39 Å which is intermediate between C-C single bond (1.54 Å) and C=C bond (1.34 Å). This shows that double bonds in benzene differ from those of alkenes.

Structure of benzene can be explained on the basis of resonance. Benzene (C_6H_6) may be assigned following two structures A and B. Structures A and B have same arrangement of atoms and differ only in electronic arrangement, means electrons are not localized in pi (π) bonds between two specific carbons, but distributed throughout the ring. Any of these structures alone cannot explain all the properties of benzene.

Structures A and B are known as resonating or canonical structures of benzene. The actual structure of benzene is different from both A and B, and cannot be represented by conventional formulae. The actual structure of benzene lies somewhere in between A and B and may be represented as C, referred to as resonance hybrid. To indicate two structures which are resonance forms of the same compound, a double headed arrow is used as shown in Fig. 3.1.3.

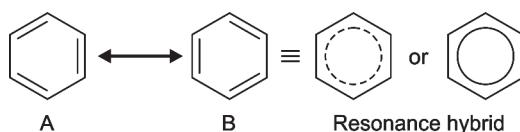


Fig. 3.1.3: Resonance structure of benzene

The resonance hybrid is more stable than any of the contributing (or canonical) A and B structures. The difference between the energy of the most stable contributing structure and the energy of the resonance hybrid is known as resonance energy.

Here it should be noticed that the contributing structures (A) and (B) are of exactly same energy and they make equal contribution to the resonance hybrid and also stabilization due to resonance should be large.

Resonance energy of benzene has been found to be 152 kJ/mole. The value of resonance energy has been determined by studying the enthalpy of hydrogenation and enthalpy of combustion of benzene.

UNUSUAL STABILITY OF BENZENE

Reluctance of benzene to undergo alkene type reactions indicates that it must be unusually stable. The evidence for stability of benzene is obtained by comparing experimental and calculated values of enthalpies of hydrogenation of benzene. Benzene, cyclohexadiene and cyclohexene yield cyclohexane on hydrogenation (Fig. 3.1.4).

- Enthalpy of hydrogenation of cyclohexene is -120 kJ mol^{-1} .
- Enthalpy of hydrogenation of 1,4-cyclohexadiene is -240 kJ mol^{-1} .

Thus, the calculated or expected value of enthalpy of hydrogenation of 1,3,5-cyclohexatriene is -360 kJ mol^{-1} .

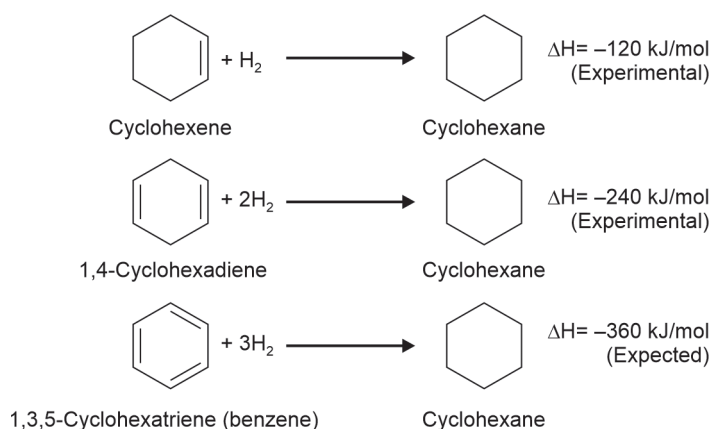


Fig. 3.1.4: Hydrogenation of cyclohexene, cyclohexadiene and cyclohexatriene

Thus, the expected enthalpy of hydrogenation for benzene if it were to be represented hypothetically as 1,3,5-cyclohexatriene is -360 kJ/mol . The experimental value of enthalpy of hydrogenation of benzene has been found to be -208 kJ/mol . Thus, 152 kJ/mol less energy is produced during hydrogenation of benzene than the expected for hypothetical 1,3,5-cyclohexatriene. In other words, benzene molecule is more stable by 152 kJ/mol than 1,3,5-cyclohexatriene (Kekule benzene). This is the resonance energy of benzene. The unusual stability of benzene makes it resistant to the usual addition reactions of alkenes. This unusual stabilization is due to resonance (delocalization of π (π) electrons) which is responsible for the aromatic character of benzene.

ORBITAL STRUCTURE OF BENZENE

According to orbital structure, all the carbon atoms in benzene are sp^2 -hybridized state. Each carbon has three sp^2 -hybrid orbitals lying in one plane and oriented at an angle of 120° . There is one unhybridized p-orbital having two lobes (one lying above and other below the plane of ring) lying perpendicular to the plane of hybrid orbitals. Each carbon atom uses two hybrid orbitals for axial overlap with similar orbitals of two adjacent carbon atoms on either side to form C–C sigma bonds. The remaining one sp^2 -hybrid orbital on each carbon atom overlaps axially with 1s orbital of hydrogen atom to form C–H sigma bond. The axial overlapping of hybrid orbitals to form C–C and C–H bonds has been shown in Fig. 3.1.5. As is clear, the framework of carbon and hydrogen atoms is coplanar with H–C–C or C–C–C bond angle as 120° .

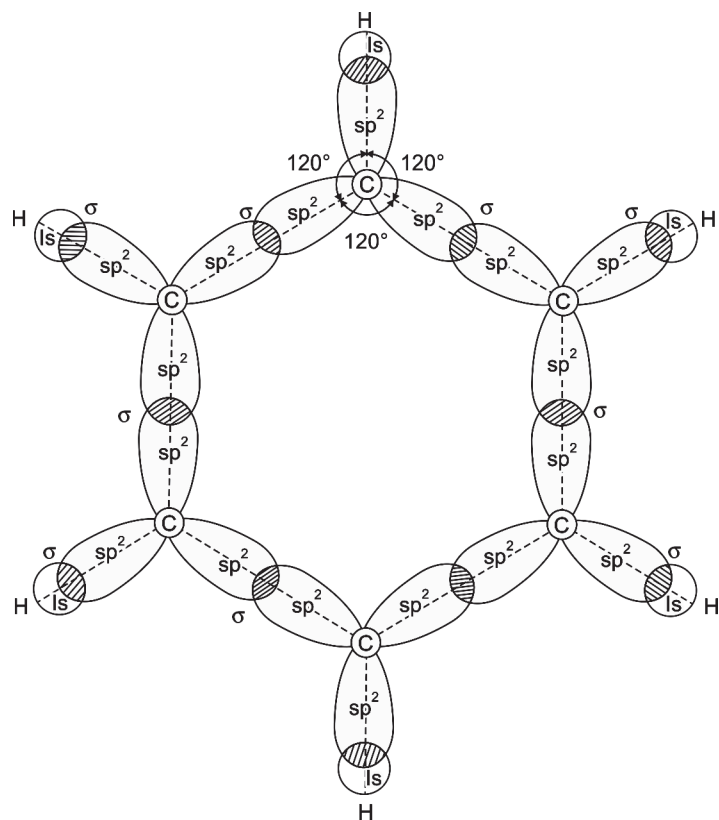


Fig. 3.1.5: Sigma (C–C and C–H) bonds formation in benzene

The unhybridized p-orbital on each carbon atom can overlap to a small but equal extent with the p-orbitals of the two adjacent carbon atoms on either side to constitute pi (π) bonds as shown in Figs 3.1.5 and 3.1.6.

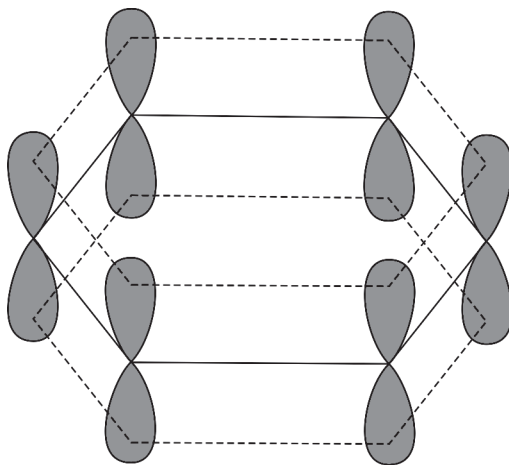


Fig. 3.1.6: Sidewise overlapping of orbitals (six π molecular orbitals)

The molecular orbital containing pi (π) electrons spread uniformly over the entire carbon skeleton and embraces all the six carbons as shown in Fig. 3.1.7.

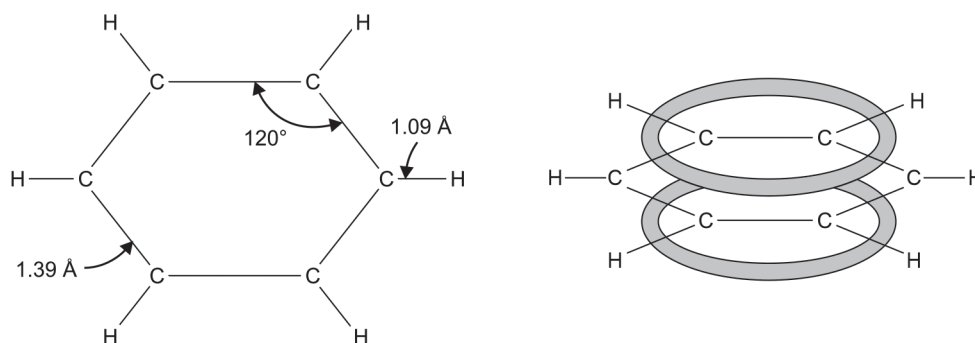


Fig. 3.1.7: Orbital picture of benzene

This spreading of pi (π) electrons in the form of ring of pi (π)-electrons above and below the plane of carbon atoms is called delocalization of pi (π)-electrons. This delocalization of pi (π)-electrons, results, in the decrease in energy, and hence, accounts for the stability of benzene molecule. The C–C bond length in benzene is 1.39 Å and C–H bond length is 1.09 Å.

The delocalized structure of benzene also accounts for the X-ray data (all C–C bond lengths equal) and the absence of the type of isomerism shown in Fig. 3.1.1.

AROMATICITY OR AROMATIC CHARACTER

Benzene undergoes substitution reactions in spite of the high degree of unsaturation. This behaviour of benzene is referred to as aromaticity or aromatic character. Aromatic character of benzene can be explained on the basis of resonance structure of benzene or on the basis of orbital structure of benzene.

In terms of resonance structure, benzene prefers to undergo substitution reactions because during addition reactions the resonance stabilized benzene ring could be destroyed. On the other hand, during substitution ring structure aromaticity remains preserved (Fig. 3.1.8).

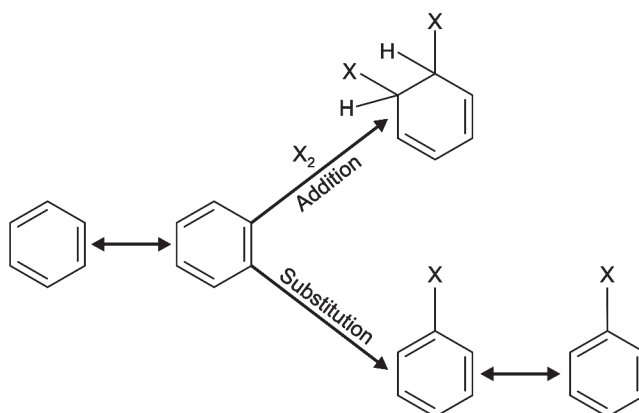


Fig. 3.1.8: Addition and substitution reactions in benzene

Huckel ($4n + 2$) rule for aromaticity

Aromatic compounds are cyclic and planar (e.g. sp^2 hybridization). They undergo substitution reaction rather than addition reactions. This property is common to every aromatic compounds and is referred as aromaticity or aromatic character.

Aromaticity is due to extensive delocalization of pi (π) electrons in a planar ring system. Erich Hückel, German physical chemist, formulated a simple expression of the relationship between the structure of a compound and aromaticity. It is known as Huckel rule. According to Huckel rule, all aromatic compounds must have $(4n + 2)$ pi electrons where n is an integer (e.g. $n = 0, 1, 2, 3$) and shows unusual stability due to complete delocalization of pi (π) electrons.

Huckel rule is not applicable to non-aromatic compounds, even then, they are cyclic and planar in nature. Some examples are given here to verify the rule:

Example 1**Benzene**

In benzene, there are three double bonds. All the six carbon atoms are sp^2 hybridized (with 6 π electrons).

$$\begin{aligned} 4n + 2 &= 6 \\ 4n &= 6 - 2 = 4 \\ n &= 1 \end{aligned}$$

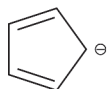
Benzene is an aromatic compound as $n = 1$.

Example 2**Cyclopentadiene**

In cyclopentadiene, there are two double bonds. All the five carbon atoms are not sp^2 hybridized (with 4 π electrons).

$$\begin{aligned} 4n + 2 &= 4 \\ 4n &= 4 - 2 = 2 \\ n &= 0.5 \text{ (not an integer)} \end{aligned}$$

Cyclopentadiene is a non-aromatic compound as ' n ' is not a integer.

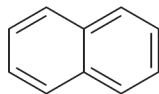
Example 3**Cyclopentadienide ion**

In cyclopentadienide ion, there are 6 π electrons used in delocalization (including one lone pair). As per Huckel rule, $n = 1$.

$$\begin{aligned} 4n + 2 &= 6 \\ 4n &= 6 - 2 \\ n &= 1 \end{aligned}$$

Example 4**Naphthalene**

Naphthalene



In naphthalene, there are 10 (π) electrons, used in delocalization. As per Huckel rule, $4n + 2 = 10$
 $n = 2$ (integer)

$$\begin{aligned} 4n + 2 &= 10 \\ 4n &= 10 - 2 \\ n &= 2 \end{aligned}$$

Example 5**Cyclooctatetraene**

In cyclooctatetraene, there are 8 (π) electrons, used in delocalization. As per Huckel rule, $4n + 2 = 8$
 $n = 1.5$ (not a integer), so non-aromatic