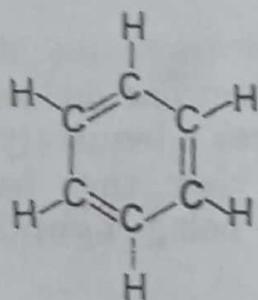
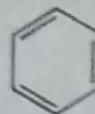


(4) **Kekule's Proposal.** In 1865, Kekule suggested that benzene consisted of a cyclic planar structure of six carbons with alternate double and single bonds. To each carbon was attached one hydrogen. Benzene according to this proposal, was simple 1,3,5-cyclohexatriene.

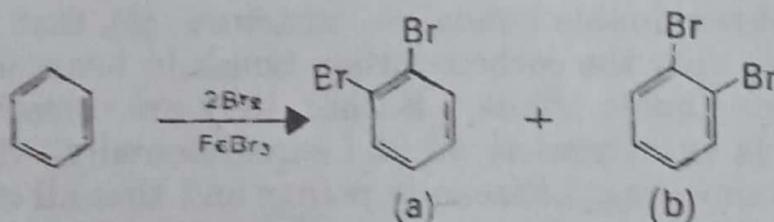


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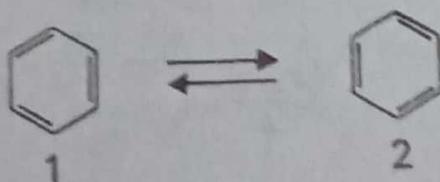


There were two objections :

*Objection 1.* If the Kekule's structure was correct, there should exist two *ortho* isomers of dibromobenzene. In one isomer, the two bromine atoms should be on carbons that are connected by a double bond, as shown in structure (a). In the other isomer, the two bromines should be on carbons connected by a single bond, as shown in structure (b). In fact, only one *ortho*-dibromobenzene could be prepared.

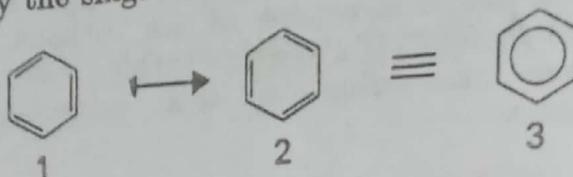


To overcome this objection, Kekule further suggested that benzene was a mixture of two forms (1 and 2) in rapid equilibrium.



*Objection 2.* Kekule's structures failed to explain why benzene with three double bonds did not give addition reactions like other alkenes. For example, benzene did not react with HBr or Br<sub>2</sub> in CCl<sub>4</sub>.

(5) **Structure Based on Resonance Theory.** The phenomenon in which two or more structures can be written for a substance which involve identical positions of atoms is called **resonance**. The actual structure of the molecule is said to be **resonance hybrid** of various possible alternative structures. The alternative structures are referred to as the **resonance structures** or **contributing forms**. A double headed arrow ( $\leftrightarrow$ ) between the resonance structures is used to represent the resonance hybrid. Thus in the case of benzene, Kekule's structures (1) and (2) represent the resonance structures. Actual structure of the molecule may be represented as hybrid of these two resonance structures, or by the single structural formula (3).



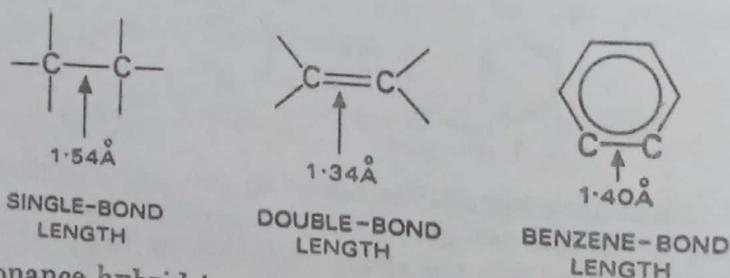
It should be clearly understood that the resonance structures (1) and (2) are not the actual structures of the benzene molecule. They exist only in theory. None of these structures adequately represents the molecule. In resonance theory, we view the benzene molecule (which of course is a real entity) as being hybrid of these two hypothetical resonance structures.

#### Points to Remember

You must know the difference between Kekule's proposal for the structure of benzene and the resonance description.

- According to Kekule each structure was real, but changed rapidly from one form to another.
- According to the resonance theory, both Kekule's structures are imaginary. The true structure of benzene is a hybrid, not a mixture, of the two Kekule forms.

Look at the structures (1 and 2) carefully. All single bonds in structure (1) are double bonds in structure (2), that is consider a hybrid of them, then the carbon-carbon bonds in benzene are neither single bonds nor double bonds. Rather, they are something halfway between. This is exactly what we find experimentally. Spectroscopic measurements show that benzene is planar and that all of its carbon-carbon bonds are of equal length,  $1.40 \text{ \AA}$ . This value lies in between the carbon-carbon single bond length ( $1.54 \text{ \AA}$ ) and the carbon-carbon double bond length ( $1.34 \text{ \AA}$ ).



Resonance hybrid is more stable than any of its contributing structures. For benzene, the stability due to resonance is so great that

$\pi$ -bonds of the molecule will normally resist breaking. This explains lack of reactivity of benzene toward addition.

- (6) **Molecular Orbital Structure of Benzene.** The structure of benzene is best described in terms of the modern molecular orbital theory. All six carbon atoms in benzene are  $sp^2$  hybridised. The  $sp^2$  hybrid orbitals overlap with each other and with  $s$  orbitals of the six hydrogen atoms forming C—C and C—H  $\sigma$ -bonds (Fig. 27-1).

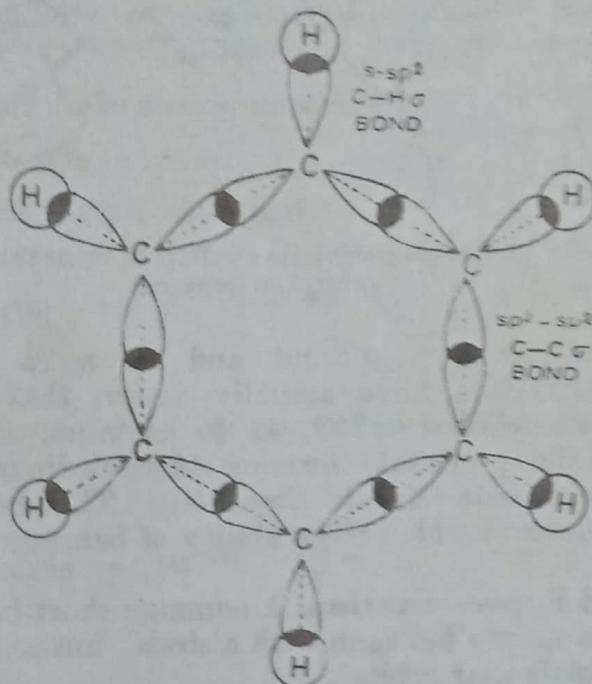


Fig. 27-1. Formation of  $\sigma$ -bonds in benzene.

Since the bonds result from the overlap of planar  $sp^2$  orbitals, all carbon and hydrogen atoms in benzene lie in the same plane. All  $\sigma$  bonds in benzene lie in one plane and all bond angles are  $120^\circ$  (Fig. 27-2).

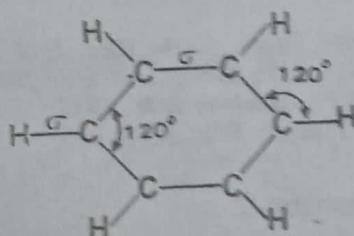


Fig. 27-2. All  $\sigma$  bonds (there are six C—C  $\sigma$  bonds + six C—H  $\sigma$  bonds) lie in one plane. All bond angles are  $120^\circ$ .

Also each carbon atom in benzene possesses an unhybridised  $p$  orbital containing one electron. These  $p$  orbitals are perpendicular to the plane of  $\sigma$  bonds. The lateral overlap of these  $p$  orbitals produces a  $\pi$  molecular orbital containing six electrons (Fig. 27-3). One half of this  $\pi$  molecular orbital lies above and the other half lies below the plane of the  $\sigma$  bonds.

The six electrons of the  $p$  orbitals cover all the six carbon atoms, and are said to be **delocalised**. As result of delocalisation

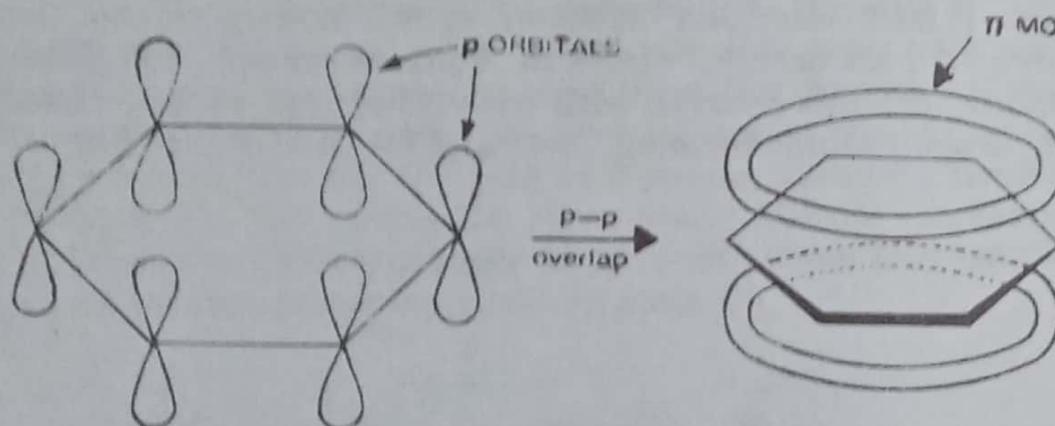


Fig. 27-3. Adjacent  $p$ -orbitals overlap to form the  $\pi$  molecular orbital in benzene

is formed a stronger  $\pi$ -bond and a more stable molecule. Thermochemical data have actually shown that the stabilisation energy of a delocalised  $\pi$  MO, as in benzene, is 36.0 Kcal/mole compared to the  $p$ -orbitals forming three ordinary  $\pi$ -bonds as in 1,3,5-cyclohexatriene (*Kekule Structure*). Thus benzene gives substitution reactions in which the stability of benzene ring is preserved.

**Short-Hand Representation.** A common short-hand representation of benzene is simply hexagon with a circle inside. The circle represents the  $\pi$  molecular orbital.



Short-hand representation of benzene