

UNIT - III

3.1. AROMATIC COMPOUNDS

The concept of Resonance :

Definition : For certain organic compounds, a single structural formula cannot satisfactorily explain all the properties. Such compounds exist in a state which is some combination of two or more electronic structures. All these structures seem to describe most of the properties of the compound but none of them describing all the properties. This phenomenon (concept) is called **resonance**. This concept is based on the valence bond theory (VBT) of covalent bonds.

The various structures which describe all the properties of the compound are called **canonical structures** or contributing structures. The actual structure is a **resonance hybrid** of all the canonical structures.

Resonance energy :

The energy of a resonance hybrid is always less than any one of the contributing structure. The difference between the energy of the most stable contributing structure and that of the resonance hybrid is known as the **resonance energy** or delocalisation energy.

Resonance hybrid, i.e., the actual molecule is always more stable than any one of the contributing structures. Because of this fact we say that the compound is stabilised by resonance. Since the actual molecule has less energy than the energy of any of the resonating structures it is some times called energy deficit in a molecule.

Example : The enthalpy of formation of benzene calculated from bond energy values is $-5384.1 \text{ K.J. mole}^{-1}$. The experimental value of enthalpy of formation of benzene is $-5535.1 \text{ K.J mole}^{-1}$. The difference between the two values is $151 \text{ K.J.mole}^{-1}$. This is called resonance energy of benzene. We say benzene is stabilised by resonance to an extent of $151 \text{ K.J mole}^{-1}$.

Conditions for Resonance :

1. The contributing structures must have various atoms in the relative positions. i.e., the arrangement of atoms must be identical.
2. The number of electrons in the contributing structures must be the same.
3. The energy content of all the forms must be nearly the same.
4. When the contributing structures differ in energy contents i.e., relative stabilities, the more stable structures makes greater contribution towards the resonance hybrid.

Effects of Resonance :

1. Stability :

The compounds which exhibit resonance are more stable than their contributing structures E.g., Though there are three double bonds in the contributing structures of benzene I and II given below, it behaves as a saturated compound. It does not undergo addition reactions; instead undergoes only substitution reactions. The resonance energy is a measure of the stability caused by resonance.

2. Bond lengths:

The bond lengths in a resonance hybrid are different from those of the contributing structures. E.g., The contributing structures of benzene suggest that there are three C=C and three C-C bonds. Actually in benzene all the six carbon-carbon bond lengths are the same. The lengths are in between those of C-C and C=C bonds.

3. Dipole moments:

The observed dipole moments are different from the values expected from the contributing structures.

4. Colour :

The colour of organic compounds is a consequence of resonance. E.g., Dyes. When the number of contributing structures increase the intensity of the colour also increases.

Aromaticity:

According to this theory aromatic compounds have extensive delocalisation of π -electrons embracing the entire molecule. The molecules which obey $(4n + 2)$ π -electron rule of Huckle will be aromatic. The molecules should be confirm resonably flat. E.g., Benzene.

Huckel's $(4n + 2)$ Rule and its simple applications




Rule :

If a system contains $(4n + 2)$ π - electrons, then it wil be aromatic (Here $n = 0, 1, 2 \dots$).

Explanation :

Huckel, through M.O. calculations connected aromatic character (stability due to high delocalisation energy or high resonance energy) with the presence of $(4n + 2)$ π - electrons in a closed shell. Here 'n' is an integer.

Application / Examples of aromatic compounds which obey Huckel's Rule

Name		No. of π -electrons	n
Benzene		6	1
Napthalene		10	2
Anthracene		14	3

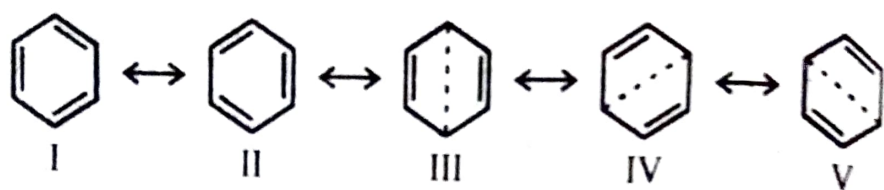
Characteristics of aromaticity.

1. They will have cyclic planar structure.
2. They will contain $(4n+2)\pi$ -electrons.
3. They will have unusual stability due to π -electron delocalisation.
4. They will have unexpected chemical properties (particularly substitution rather than addition)

Structure of Benzene (Resonance in benzene):

We get a true picture of benzene by the application of the theory of resonance.

Benzene is a resonance hybrid of two Kekule structure (I and II) and three Dewar structures (III to V).



Kekule structures contribute about 80% and the Dewar structures 20% to the benzene resonance hybrid. For most purpose we use only two equivalent Kekule structures (I and II) as the canonical forms of benzene.

Thus benzene is a resonance hybrid of the two Kekule's structure I and II. This means that benzene does not correspond to either I or II but to a structure intermediate between I and II. Structures I and II are said to make equal contributions to the hybrid. This does mean that benzene consists of molecules half of which correspond to I and half to II. Further it does not mean that a molecules changes back and fourth between I and II. All the molecules are the same. Each molecule has a structure in between I and II. The hybrid structures are represented by putting a double headed arrow between the two contributing structure (as shown).

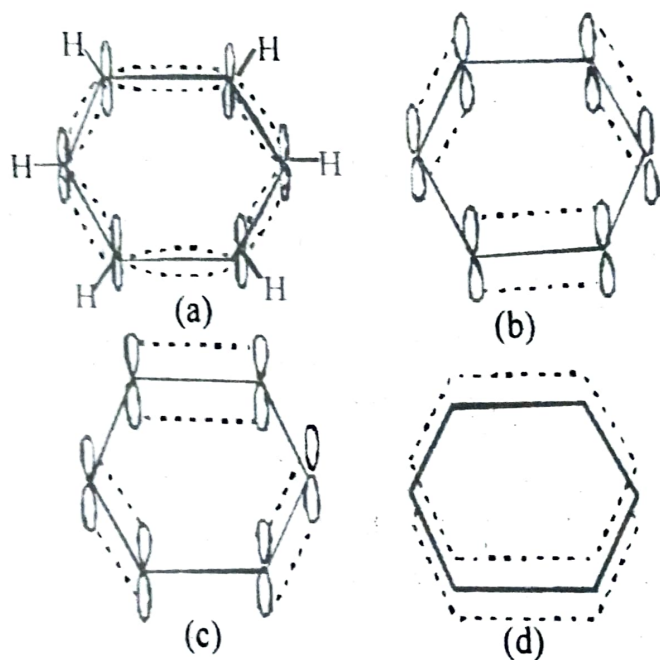
The enthalpy of formation calculated from bond energy values for the hypothetical Kekule structure is $-5384.1 \text{ KJ mole}^{-1}$. The experimental value of formation of benzene is $-5535.1 \text{ KJ mole}^{-1}$. The. The difference between the two values is 151 KJ. This is called resonance (stabilization) energy of benzene. Thus we see resonance makes benzene more stable. We say benzene is stabilised by resonance to an extent of 151 KJ mole^{-1} .

The fact that benzene is a resonance hybrid of the two Kekule' structures is confirmed by X-ray diffraction studies. The X-ray diffraction

studies show that (i) The carbon sextet is flat and (ii) All bond lengths are equal (1.40\AA). This bond length is intermediate between those of single bond length (1.54\AA) and a double bond length (1.33\AA). This confirms that the actual structure of benzene is in between I and II.

Delocalised π - cloud in Benzene

If the molecule of benzene viewed in terms of molecular orbitals, it may be noted that the carbon atoms are in a state of sp^2 hybridisation. The three hybridised orbitals of each carbon are involved in the formation of three σ bonds. (Two bonds are formed with adjacent carbon atoms and one with hydrogen). Thus all the six carbon and the six hydrogen atoms lie in the same plane.



The unhybridised p -orbitals are perpendicular to the plane of the carbon hexagon (fig. a). Side overlap of these orbitals takes place. They can give three localised π - bonds (fig. b or c). But there is no reason why the overlap should be limited in this way. Thus the mutual overlapping of all the unhybridised p -orbitals give a delocalised molecular orbital. The net result is that there are two continuous ring-like electron clouds, one lying above and the other below the plane of atoms as show in fig. d.

This enables us to imagine a picture of molecule which corresponds to the resonance hybrid of Kekule' structures. It also confirms the flatness of molecule.

In actual practice benzene is generally represented either by structure I or II. It is also represented either by structure VI or VII.



VI



VII

Stability of benzene (Resonance energy) :

In the ground state the total energy of the three pairs of delocalised π - electrons (Fig. d.) is less than that of three pairs of localised electrons (Fig. b or c). The difference is known as the delocalisation energy or resonance energy). We say that the benzene molecule is stabilised by delocalisation or resonance.

This concept of delocalisation is based on the Molecular orbital Theory (MOT) of covalent bonds.

Benzene, is an aromatic compound, because

1. Benzene has cyclic planar structure as shown by X - ray analysis and other experimental results.
2. It contains 6 π -electrons thus satisfying $(4n + 2)$ π -electron rule where $n = 1$.
3. It has exceptional stability (by about 150 KJ / mole)
4. Though its molecular formula suggests the presence of three double bonds it undergoes substitution reactions rather than addition reactions.