## The Resonance Theory

Generally, the Lewis structure of a compound provides information about its behaviour. For example, a compound with the structure CH_3—$\overset{b}{CH}$=$\overset{a}{CH}$—CH_2OH will add a molecule of bromine (due to carbon-carbon double bond) and will react with acetic anhydride to yield an ester (due to alcoholic group). The bond length of the bond a will be 1.54 Å and that of the bond b will be 1.33 Å. Similarly, if the properties of a compound are known, a Lewis structure can be drawn for it. But this is not true for a compound having a delocalised system of bonding, and the behaviour of such a compound sometimes differs so widely from what we expect from the Lewis structure ordinarily written for it that this structure becomes of little value and, in fact, does not seem to be the real structure of that compound. For example, the structure I ordinarily written for benzene is expected to add three molecules of bromine, but in actual practice it does not do so. Neither the bond length of the bond a is 1.54 Å and that of the bond b is 1.33 Å, rather both bond lengths are equal and are in between 1.54 Å and 1.33 Å.
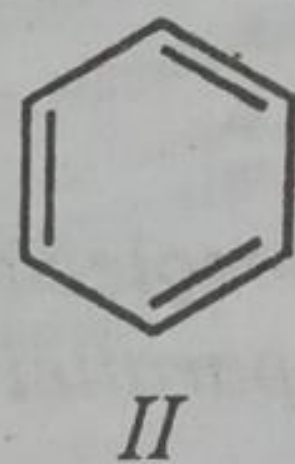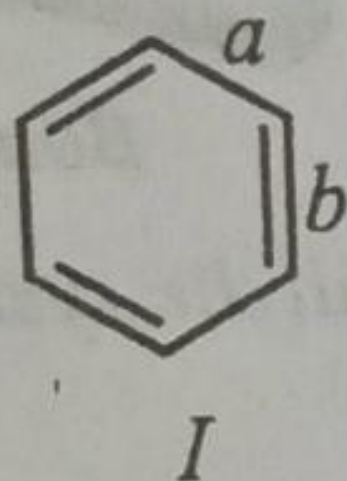
In such cases we have to include some more structures so that all the structures together are in a better position to explain the behaviour of the compound, but none of them is the real structure of the compound. For example, the structure II and some others (III–V) are also considered along with the structure I to better explain the characteristics of benzene. All these structures may not be of equal importance and may differ in the extent of their contribution toward explaining the properties of the compound. The real structure of the compound is considered to be a *weighted average* of all the contributing structures. *The representation of a real structure as a weighted average of two or more contributing structures* is called **resonance**. The contributing structures are called **canonical forms** and the real structure is called **resonance hybrid.**

Sometimes, the actual structure of a molecule can only be expressed by making reference to certain Lewis structures (canonical forms) and assuming that the actual structure is a resonance hybrid of them all. The canonical forms have no real physical existence. On the other hand, the structure of the molecule which does exist physically is not really known to us. For example, there is no substance any where in the world having structure I, and the actual structure of benzene is not known.

Previously, we have used only the *molecular-orbital method of approximation* to solve the Schrodinger wave equation (*Chapter 1*). There is another general method known as the *valence-bond method of approximation* for solving the wave equation, which is particularly useful when more than one structure are written to express the actual structure of a compound. In this method, various Lewis structures (canonical forms) that a molecule may possibly have, are drawn and a wave equation (ψ) is written for each of

them. The wave equation for the real structure (Ψ) is obtained by taking the sum of the wave equations of all the canonical forms with their corresponding weighting factors (C).

$$\Psi = C_A\psi_A + C_B\psi_B + C_C\psi_C + \text{----}$$

In this equation, each C represents the extent to which the corresponding canonical form contributes to the actual structure. Values for C are obtained by solving the equation for various values of each C and choosing the solution that gives lowest energy, as in the case of molecular-orbital method. In fact, both methods give similar solutions for molecules that contain only localized bonds. For compounds containing delocalized bonds, the valence-bond method becomes much more difficult to apply as the structures become more and more complicated, and in that case the molecular-orbital method is used much more often for the quantitative solution of wave equation. However, for the qualitative description of the structure of molecules, the valence-bond method is often used. The structure of benzene is best represented when canonical forms I–V with double headed arrows in between them, are put together. This is the resonance method of writing the structure of a molecule.


| I | II | III | IV | V |
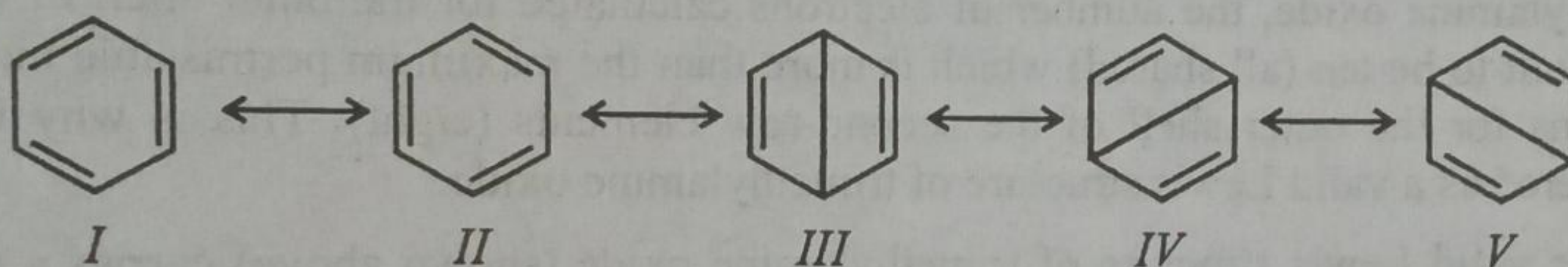
When the wave equation is solved by considering that all these canonical structures contribute to the resonance hybrid, the energy value obtained is lower than that of any of the canonical forms. *The difference in energy between the resonance hybrid and the canonical form of lowest energy* is called the **resonance energy**. The contribution of structures I and II to the actual structure has been calculated to be 39% each, whereas that of III, IV and V is 7.3% each. The carbon-carbon bond length is more than that of a double bond and less than that of a single bond, i.e., its character is in between a double bond and a single bond, but all the bonds have the same length.

The resonance method of describing the structure of a molecule, as shown above in the case of benzene, does not mean that the structure rapidly shifts between the canonical forms, neither it means that some molecules have one canonical form and some have another. In fact, all the molecules of a substance have the same structure and for all the times, in which the electrons are delocalized over the whole system involved in the resonance.

Canonical forms. For drawing the canonical forms to express the actual structure of a molecule we are guided by certain rules which are as follows:

1. *All the canonical forms must be bonafide Lewis structures.* Each canonical form should follow the rules of valence, i.e., it should not have more than two electrons in the outer shell (valence shell) of first-row elements (e.g., H), more than eight electrons in the outer shell of second-row elements (e.g., C, N, O) and more than twelve electrons in the outer shell of third-row elements (e.g., P, S). Thus, the structure VI, not being a valid Lewis structure, cannot be considered as a canonical form of trimethylamine oxide.
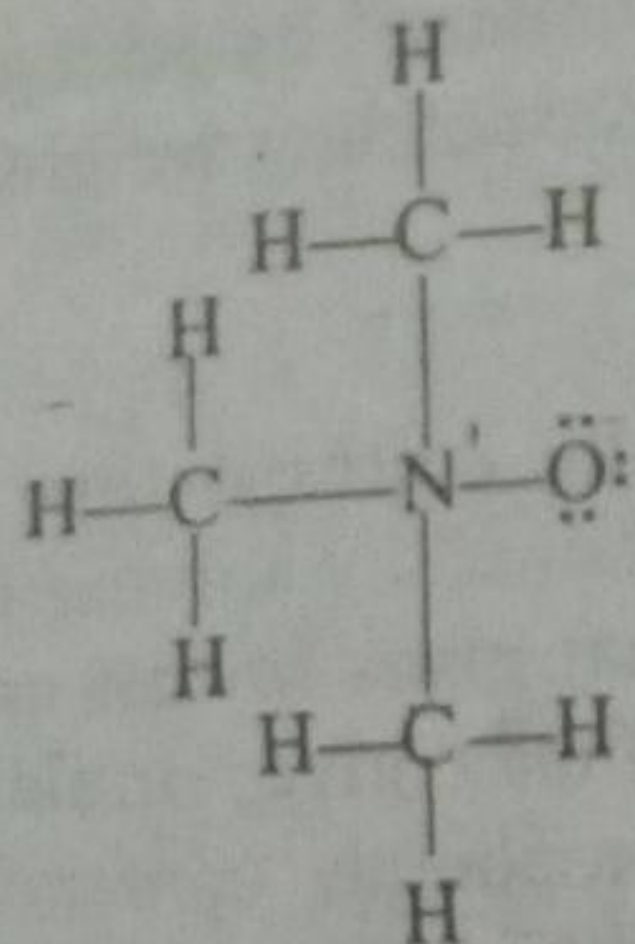
Trimethylamine oxide
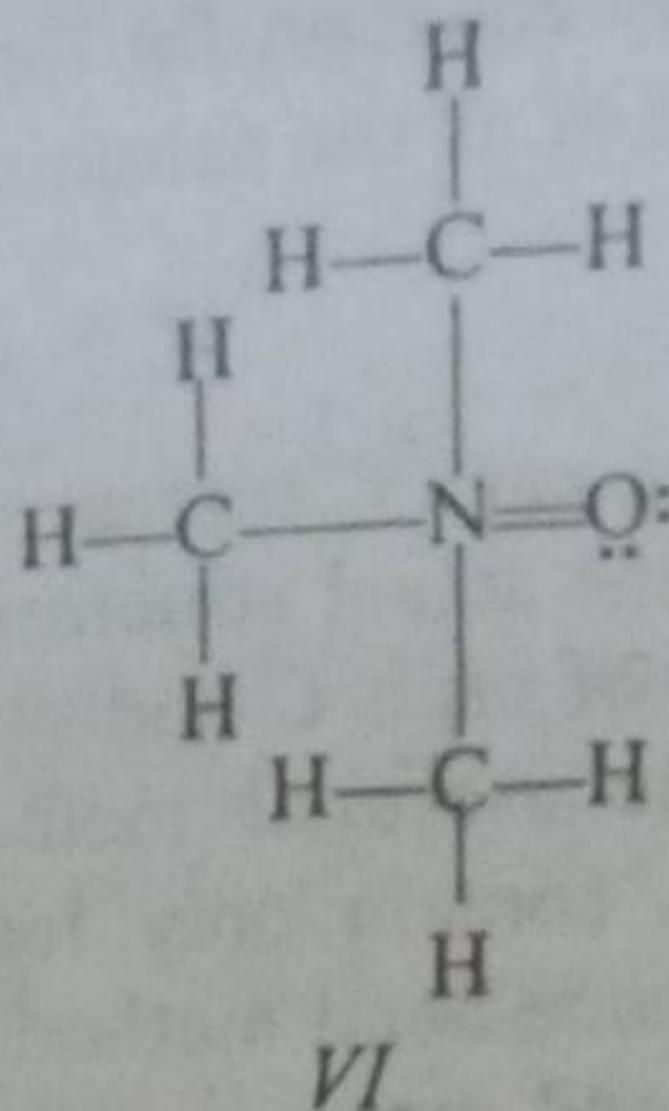
VI.

To calculate the number of electrons in the outer shell (valence shell) of an atom in a molecule, all the shared (bonding) electrons (two for a single bond, four for a double bond and six for a triple bond) are counted for each of the bonded atoms because they surround both the bonded atoms. The unshared (nonbonding) electrons, if there are any, in an atom are counted only for that particular atom. Thus, in the structure VI written for trimethylamine oxide, the number of electrons calculated for the outer shell of nitrogen comes out to be ten (all shared) which is more than the maximum permissible number of electrons for the outer shell of the second-row elements (eight). This is why it is not considered as a valid Lewis structure of trimethylamine oxide.

The valid Lewis structure of trimethylamine oxide (shown above) carries a positive charge on nitrogen and a negative charge on oxygen. These charges are called **formal charges**. A formal charge is assigned to an atom in a Lewis structure by counting the electrons 'belonging' to that atom and comparing them with the valence electrons in the neutral atom. For counting the electrons belonging to an atom for the purpose of assigning a formal charge, the shared electrons are divided equally between the bonded atoms. Only half of the shared electrons are considered to belong to each of the bonded atoms. Unshared (nonbonding) electrons belong entirely to the atom in which they are found.

If the number of electrons belonging to an atom is more than its valence electrons, the atom is assigned a negative charge and if less than its valence electrons, then it is assigned a positive charge. If the number of the belonging electrons is equal to the valence electrons, then the atom is neutral and bears no charge.

Let us now determine the formal charge assigned to the atoms in the structure of trimethylamine oxide.

| Atom	Valence electrons	Electrons belonging to the atom	Formal charge
H (each)	1	1	Zero
C (each)	4	4	Zero
N	5	4	+1
O	6	7	−1

So, in the structure of trimethylamine oxide, nitrogen is assigned a positive charge and oxygen a negative charge.

2. *The positions of the atomic nuclei must be the same in all the canonical forms.* The canonical forms of the same molecule differ only in the location of the electrons which are actually delocalized, e.g., VII and VIII.
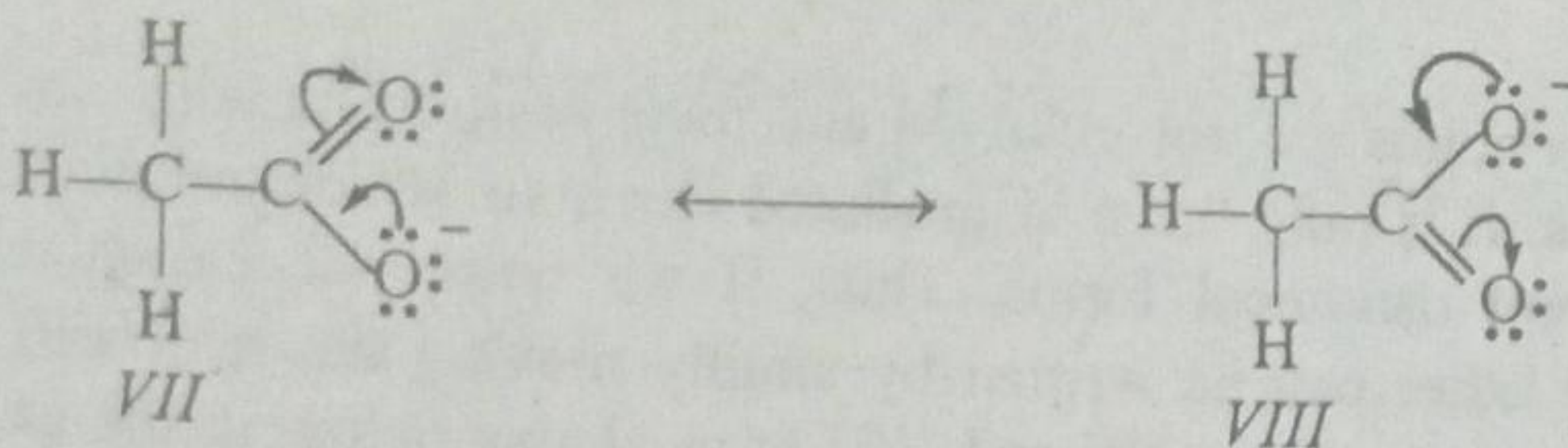
The structures IX and X are not the canonical forms of the same molecule. In fact, these are two different compounds.

Acetaldehyde	*Vinyl alcohol*
IX	X
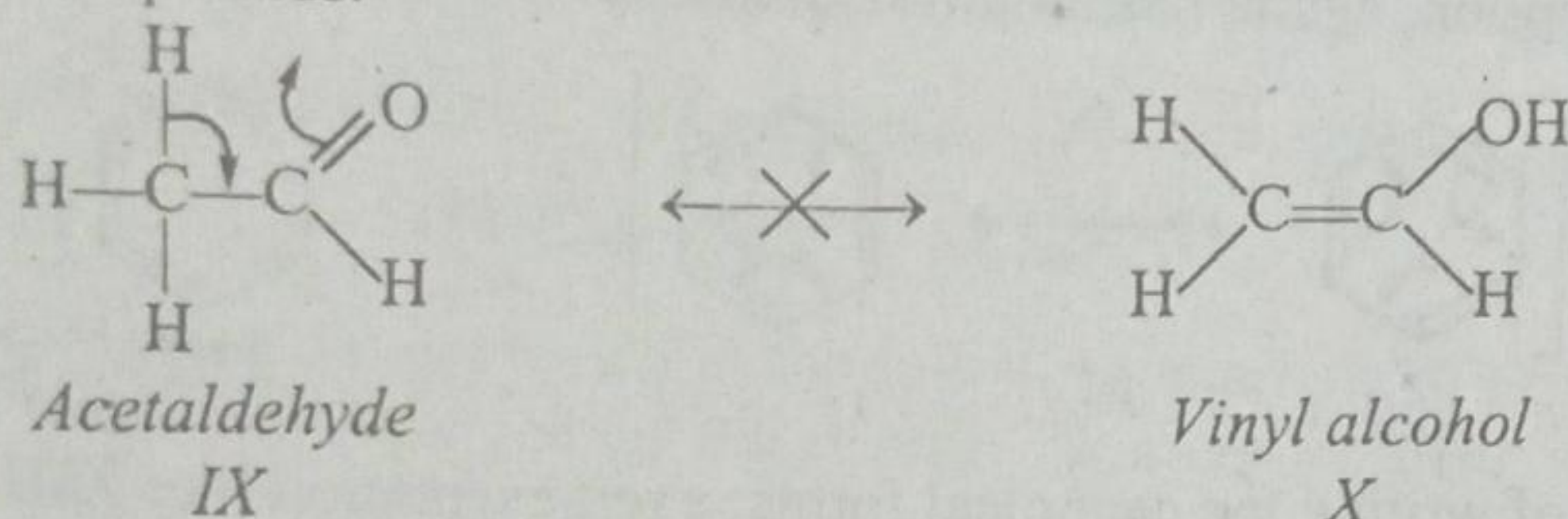
3. *All atoms involved in the resonance must lie in the same plane.* This is necessary to allow maximum overlap of the p orbitals for the delocalization of electrons. Cyclooctatetraene which has alternate single and double bonds, like benzene, does not show resonance similar to that shown by benzene (I and II).
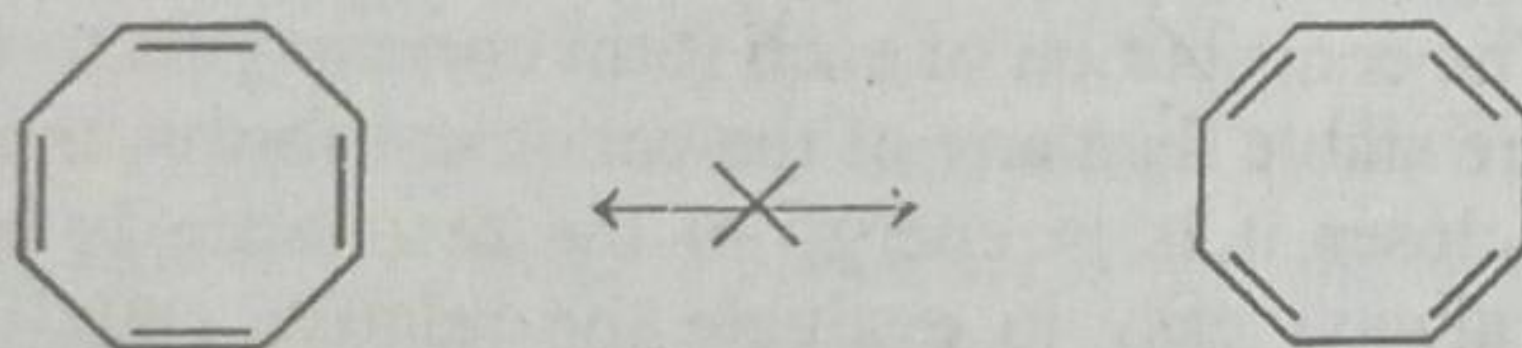

This is because its molecule is not planar but tub-shaped, as shown below, and the two p orbitals forming a double bond are not parallel to the p orbitals of the next double bond. This hampers delocalization of the π electrons.
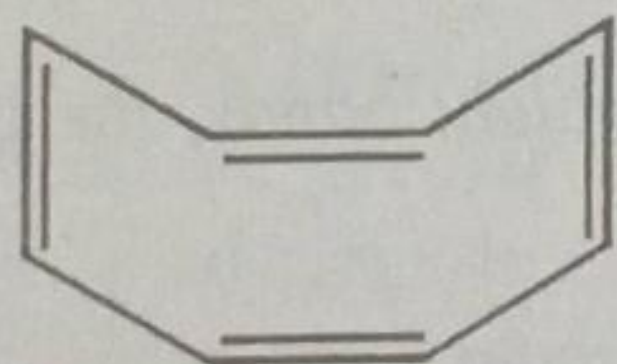

Cyclooctatetraene

4. *The number of unpaired electrons must be the same in all the canonical forms.* Thus, structure XI is not a valid canonical form for ethylene. It is rather an excited state of ethylene which is a different type of molecule.

$$CH_2{=}CH_2 \quad \longleftrightarrow\!\!\!\times\!\!\!\longrightarrow \quad \overset{\bullet}{C}H_2{-}\overset{\bullet}{C}H_2$$

Ethylene XI
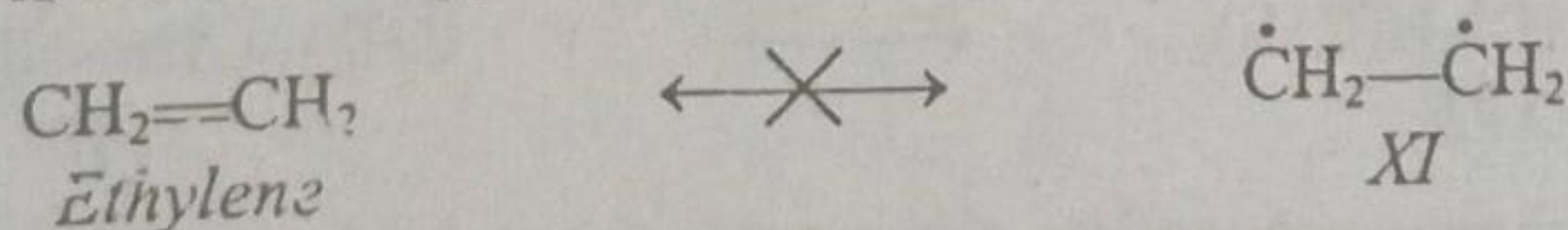
5. *Structures with distorted bond angles or bond lengths will not contribute or will make little contribution to the resonance hybrid.* Thus, the structure XII is not considered as a canonical form for acraldehyde.

$$CH_2{=}CH{-}CH{=}O \quad \longleftrightarrow\!\!\!\times\!\!\!\longrightarrow$$

Acraldehyde

XII
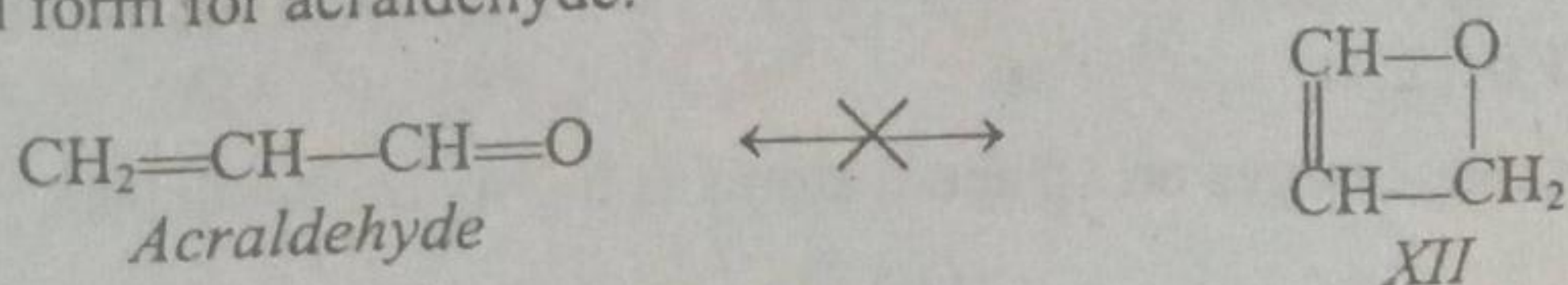
Similarly, the structures III, IV and V make only a little contribution to the resonance hybrid of benzene because they have one bond each which is expected to be longer than a normal covalent bond.

In resonance, σ bonds are not involved and their position remains unchanged in all the canonical forms. It is only the π or unshared electrons which are placed at different positions in different canonical forms. Thus, if we write one canonical form for a molecule, then the other can be written by simply moving the π or/and the unshared electrons, as shown in structures VII and VIII or as shown below in the case of benzene (only the two main contributing structures are shown); the formal movement of electrons in resonance description, again, has no physical reality.
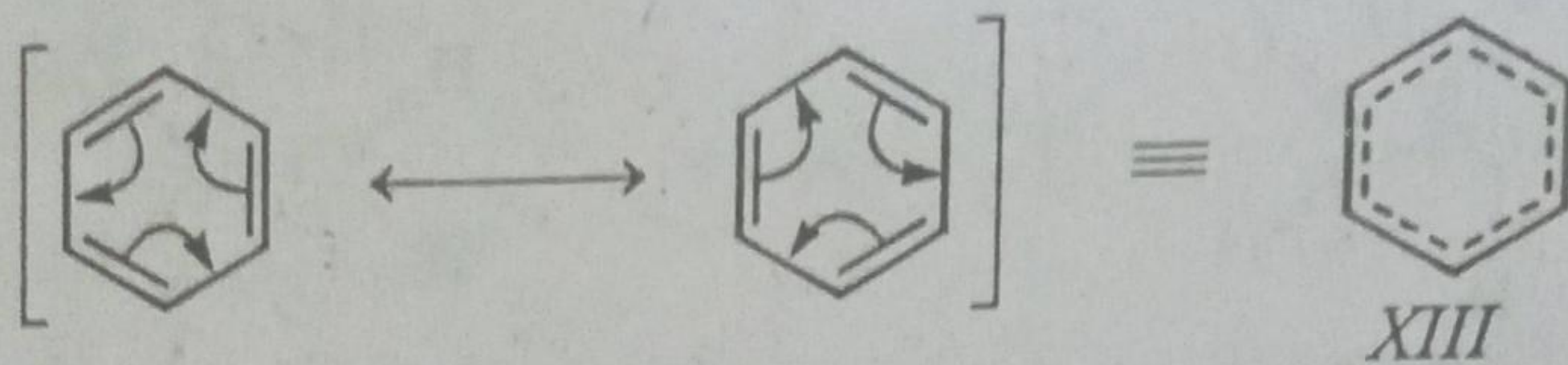
XIII

However, instead of writing the canonical forms, a representation like XIII can be used to express the resonance hybrid. In such representations, the bonds that are present in all the canonical forms, are drawn as solid lines while the bonds that are not present in all the canonical forms are drawn as dotted lines.