

DELOCALIZED CHEMICAL BONDING

When a Lewis structure is written for an organic compound, a short line represents one electron pair, two short lines ($=$) symbolize two electron pairs, and three short lines (\equiv) stand for three electron pairs between the two bonded atoms. This is shown for carbon-carbon bond in ethane, ethene and ethyne below.



We have seen that a one electron pair bond or single bond is called a sigma (σ) bond, a two electron pair bond or double bond ($=$) consists of a σ bond and a pi (π) bond, and a three electron pair bond or triple bond (\equiv) is made of a σ bond and two π bonds. In each case the electron density is concentrated between *only two atoms*. Therefore, electrons in σ and π orbitals, discussed earlier in this chapter, give rise to what is known as **localized bonding**. Many organic compounds are fully described by a single *Lewis structure* based on the concept of localized bonds. From experience σ and π bonds, between various kinds of atoms are assigned known values of bond lengths, bond energies and dipole moments. Their chemical reactivity and spectral behaviour is also predictable. Thus when a single Lewis structure represents an organic molecule fully, it means that it should be possible to calculate its heat of atomization from the known bond energies. Also the predicted bond lengths, dipole moment or spectral behaviour should correspond closely with the experimentally found values.

Consider the molecule of 1,4-pentadiene, $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2$. It has two carbon-carbon double bonds, two carbon-carbon single bonds and eight C — H bonds. From the bond energies listed earlier, the heat of atomization is calculated as follows:

$$2\text{C}=\text{C bonds} = 2 \times 630 = 1260 \text{ KJ mol}^{-1}$$

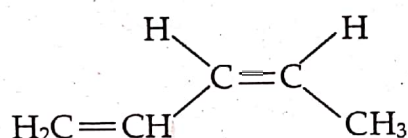
$$2\text{C}-\text{C bonds} = 2 \times 345 = 690 \text{ KJ mol}^{-1}$$

$$8\text{C}-\text{H bonds} = 8 \times 415 = 3320 \text{ KJ mol}^{-1}$$

$$\text{Total} \quad 5270 \text{ KJ mol}^{-1}$$

The experimentally determined value is 5270 KJ mol^{-1} . The bond distances are also those expected for $\text{C}-\text{C}$, $\text{C}=\text{C}$ and $\text{C}-\text{H}$ bonds. Thus the structural formula given above, adequately represents the molecule of 1,4-pentadiene.

There are, however, many organic compounds in which one or more bonding orbitals are spread out over *more than two atoms*. The resulting bonds are said to be delocalized. Organic compounds which have **delocalized bonding** cannot be adequately represented by a single *Lewis* structure. For example, if we write the following *Lewis* structure of cis-1,3-pentadiene

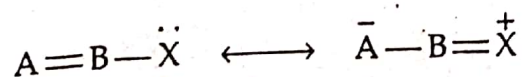
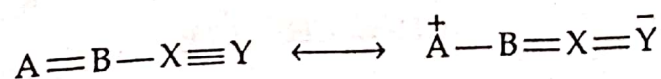
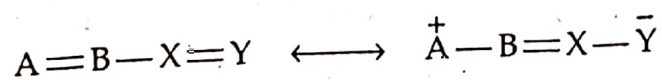


Its expected heat of atomization may be calculated as follows:

		KJ mol ⁻¹
1	$\text{C}=\text{C}$ bond (from 1-pentene)	= 630
2	$\text{C}=\text{C}$ bond (from cis-2-pentene)	= 637
2	$\text{C}-\text{C}$ bonds : 2×345	= 690
8	$\text{C}-\text{H}$ bonds : 8×415	= 3320
	Total	<hr/> 5277

The observed value, however, is 5296 KJ mol^{-1} . The above structure, therefore, does not fully describe the behaviour of the molecule. The $\text{C}=\text{C}$ double bonds are longer than 1.34 \AA ($\text{C}=\text{C}$ bond length) and the $\text{C}-\text{C}$ bond length (between carbon atoms number 2 and 3) is shorter than 1.54 \AA , the normal $\text{C}-\text{C}$ bond length.

The main type of structures which exhibit delocalized bonding are shown below:



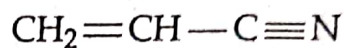


Examples of each type are:

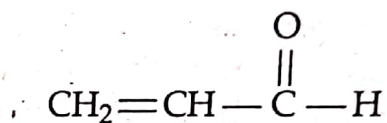
1,3-butadiene



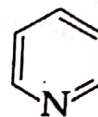
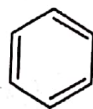
Acrylonitrile



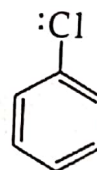
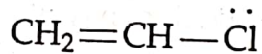
Acrylaldehyde



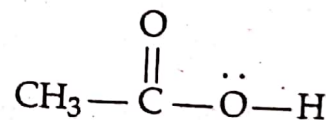
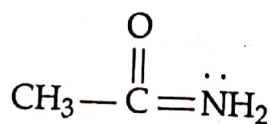
Benzene and pyridin



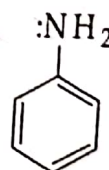
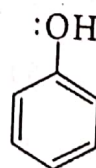
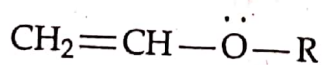
Vinylchloride and chlorobenzene



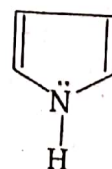
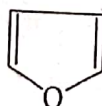
Acetamide and ethanoic acid



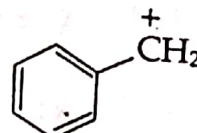
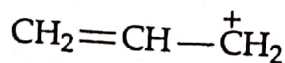
Vinyl ether, phenol and aniline

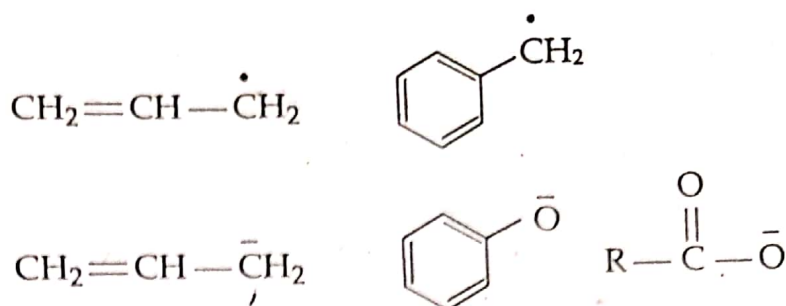


Furon and pyrrole



Allylic and benzylic cations, anions and free radicals

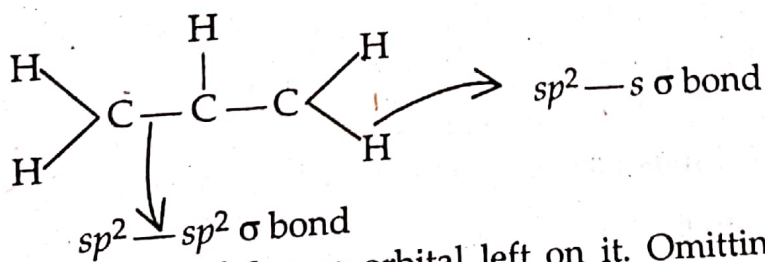




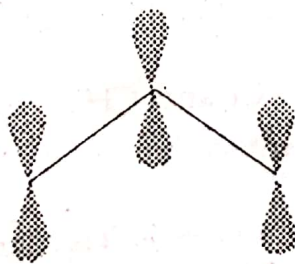
If molecular orbitals are drawn for any one of these structures for all the σ bonds involved, a common feature will be that the structures have p-orbitals on at least three adjacent atoms, the atoms bearing the p-orbitals being in one plane. Systems having **three or more than three p-orbitals on adjacent atoms** are said to be **conjugated**. No conjugated system is fully described by a single *Lewis* structure. To explain the structures of conjugated system two methods are available, viz., the *molecular orbital method* and the *resonance method*.

The Molecular Orbital Method

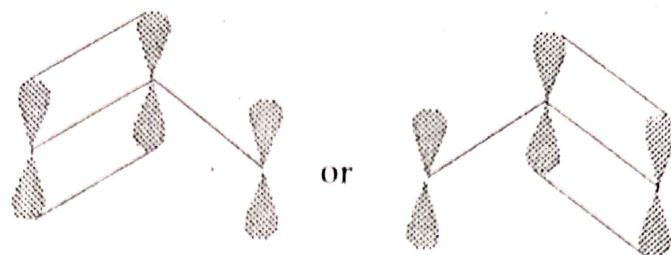
In molecular orbital theory the delocalized bond in conjugated systems are described in terms of delocalized molecular orbitals (orbitals which are spread out over more than two atoms). For example, in the carbocation, $\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}_2$ all the three carbon atoms are sp^2 hybridized (because each one is bonded to only three other atoms), the bonds between carbon atoms being sp^2-sp^2 σ bonds and the C—H bonds being sp^2-s σ bonds:



Each carbon atom has a p-orbital left on it. Omitting the C—H bonds the carbon skeleton can be pictured as:



A localized π orbital picture will be:



Since there is no reason why the central p -orbital may not overlap equally with both the terminal p -orbitals, any one of the above orbital pictures is inadequate. Instead a linear combination (addition and subtraction of their wave functions) of the three p -orbitals will give rise to three molecular orbitals, as shown in Fig. 1.18.

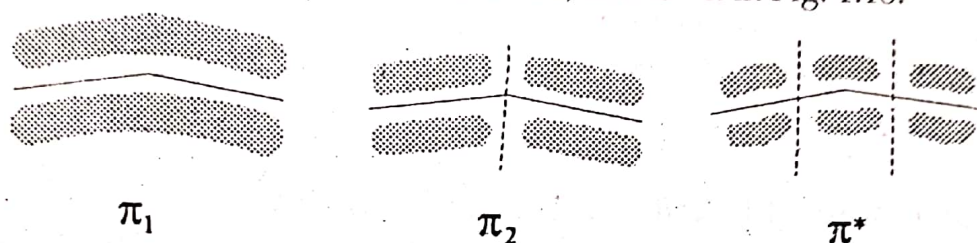


Fig. 1.18 π molecular orbitals of allylic system

The π_1 and π_2 orbitals are bonding molecular orbitals and have energies lower than the p orbitals from which they were made. The π^* orbital is an antibonding molecular orbital and has energy higher than that of the p orbitals from which it was made. Note that the π_2 orbital has one node more than π_1 and the π^* orbital has two more nodes than π_1 . If a plane is passed through the node (dotted line) the probability of finding the electrons in the nodal plane is zero. Thus π^* , which has two nodal planes, has the highest energy of the three and π_1 is the most stable orbital, *i.e.*, it has the lowest energy. These orbitals which are spread out over more than 2 atoms are called **delocalized molecular orbitals** and are filled according to the same rules as applied to atomic orbitals. In the allylic carbocation, $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$, there are only two p electrons available and these will occupy the most stable π_1 orbital. The orbitals π_2 and π^* will remain empty. Since the π_1 electrons are attracted by three nuclei rather than only two (as in the case of a localized π orbital), the allylic carbocation has special stability.

Molecules such as $\text{CH}_2 = \text{CH} - \ddot{\text{Cl}}$ and $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$ have molecular orbital pictures similar to the allylic carbocation, with the exception that there are three p -electrons available in $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$ and four in $\text{CH}_2 = \text{CH} - \ddot{\text{Cl}}$. In $\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2$ there will be 2 electrons in π_1 and one in π_2 . Whereas in $\text{CH}_2 = \text{CH} - \ddot{\text{Cl}}$, there will be an electron pair each in π_1 and π_2 . Thus the electrons in these systems are spread out over more than two nuclei. The electron density between any two atoms will be more than that of a single bond (one electron pair) but it will be less than that of a localized double bond (2 electron pairs). Thus we see that

$\text{CH}_2=\text{CH}-\text{Cl}$ has a smaller dipole moment ($\mu = 1.43\text{D}$) than that of $\text{CH}_3-\text{CH}_2-\text{Cl}$ (2.05D), the $\text{C}=\text{C}$ bond length is 1.38 \AA (longer than $\text{C}=\text{C}$ which is 1.34 \AA) and the $\text{C}-\text{Cl}$ bond length is 1.69 \AA (shorter than a normal $\text{C}-\text{Cl}$ bond length of 1.78 \AA).

In a similar treatment of the 1, 3-butadiene molecule, in which the four carbon atoms are sp^2 hybridized, linear combination of the four atomic p orbitals gives four π molecular orbitals Fig. 1.19.

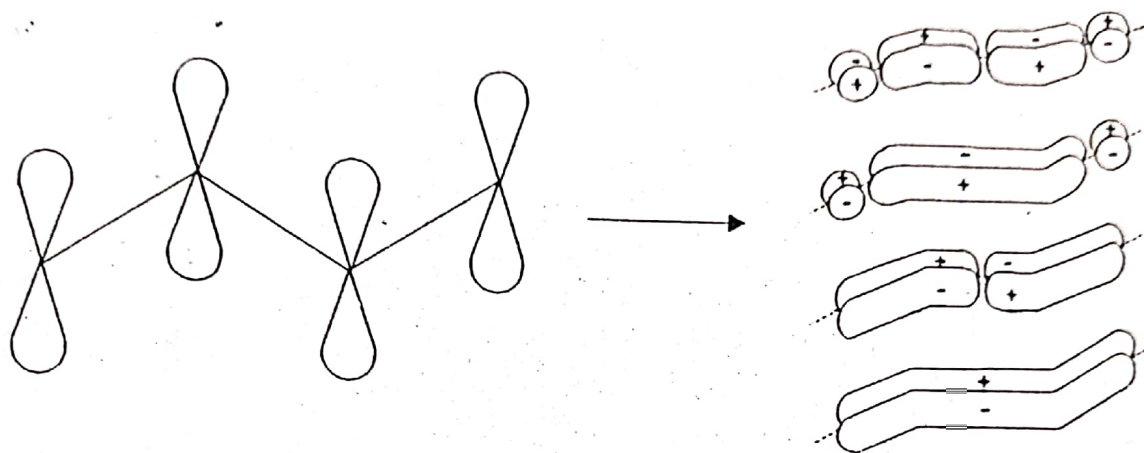
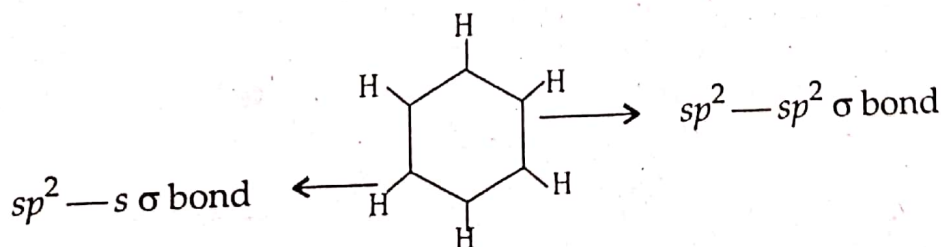


Fig.1.19 Four p atomic orbitals give four π molecular orbitals in 1,3-butadiene.

The π_1 and π_2 are bonding molecular orbitals and π_1^* and π_2^* are anti-bonding orbitals. The four available electrons fill the two bonding orbitals, the antibonding (π^*) orbitals being unoccupied. Note that as we go from π_2 to π_2^* each orbital has one more node than the one of next lower energy. The butadiene molecule has lower energy than that predicted from a single structure in which π electrons are in two localized π orbitals.

In benzene, again, the six carbon atoms are sp^2 hybridized. The carbon-carbon bonds are $\sigma\ sp^2-sp^2$ and $\text{C}-\text{H}$ bonds are $\sigma\ sp^2-s$. There remains one p orbital on each carbon.



Linear combination of the six atomic p orbitals, one on each carbon atoms, give six π -molecular orbitals. These six molecular orbitals are arranged in order of increasing energy as follows, Fig.1.20.

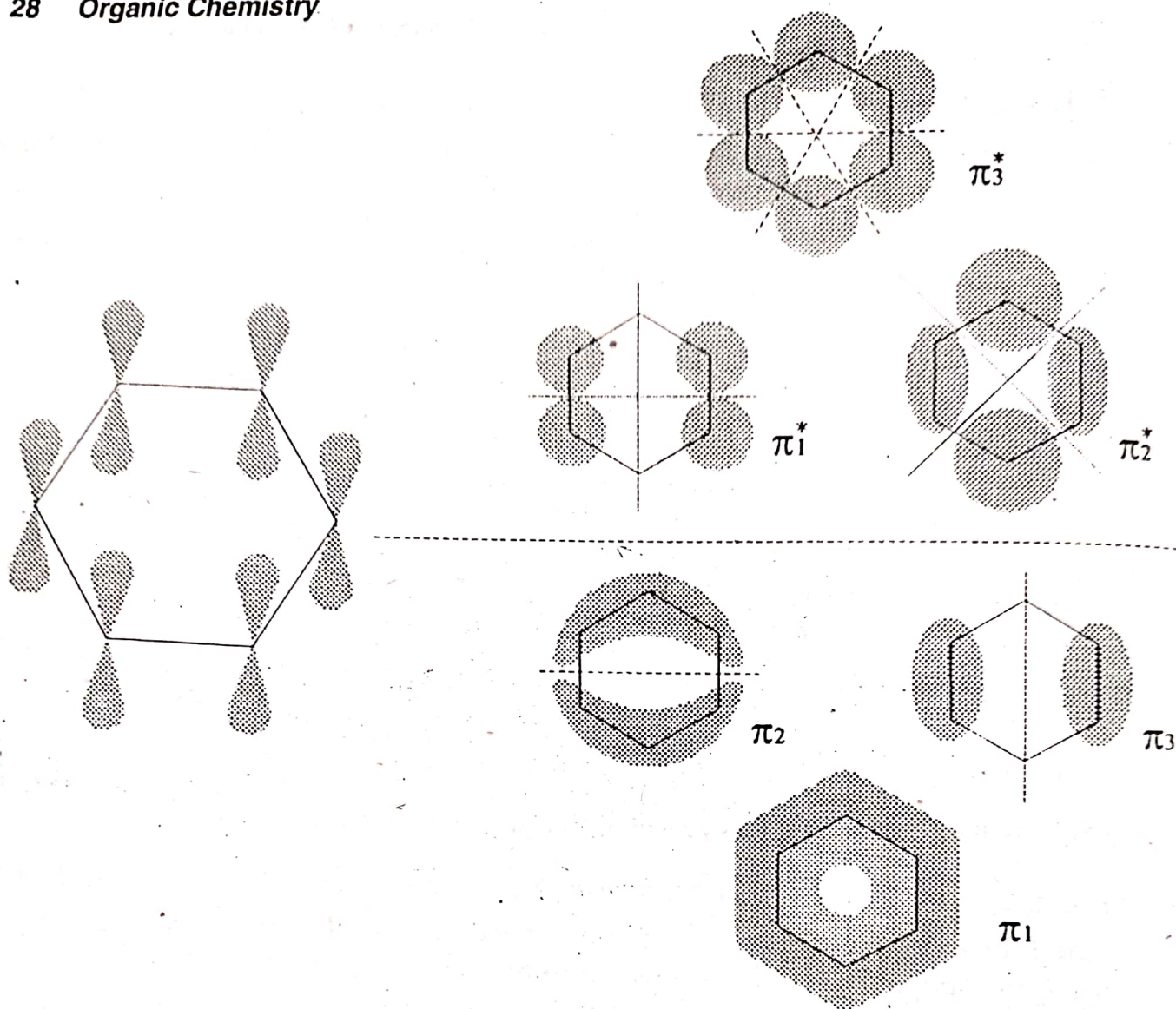
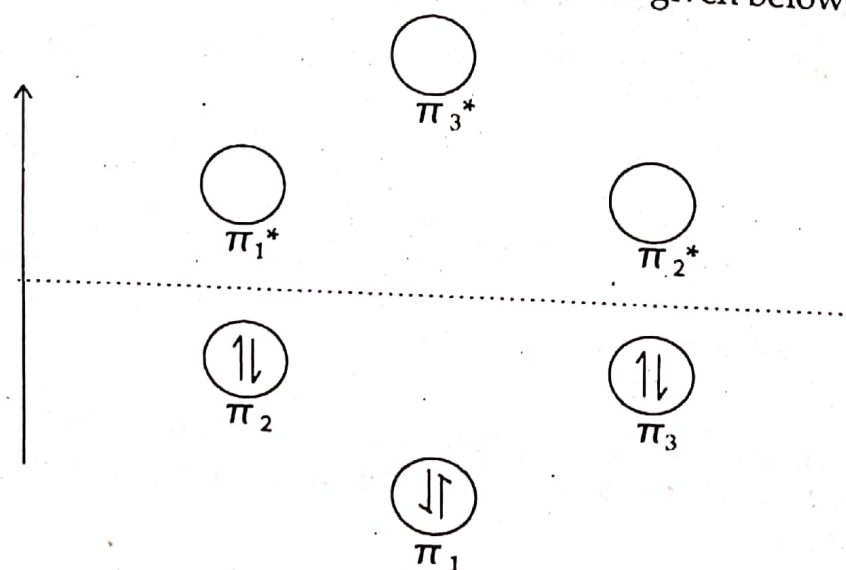


Fig. 1.20 Six π molecular orbitals of benzene

The relative energy levels of these orbitals are given below:



The six available electrons fill the three lowest energy orbitals, π_1 , π_2 and π_3 while, the three antibonding orbitals (π_1^* , π_2^* and π_3^*) are empty when the benzene molecule is in its ground state (most stable state).

The most stable bonding orbitals, π_1 has no node. It concentrates electron density between each pair of nuclei. The least stable antibonding orbitals (π_3^*) has three nodes between the nuclei. The bonding orbitals π_2 and π_3 are of equal energy, each having one node. Similarly, the two antibonding orbitals π_1^* and π_2^* are of equal energy, each having two nodes.

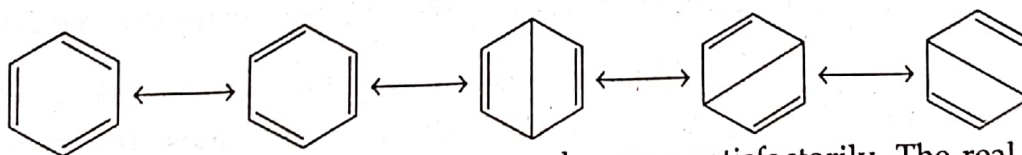
According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full σ (2 electrons) and half a π bond. The carbon-carbon bond length in benzene is 1.397\AA , which lies between the C—C and C=C bond lengths. The accepted structural formula of benzene in accordance with this molecular orbital picture is



The Resonance Method

The molecular orbital approach used in the previous sections is not unique.

In another method, which is extensively used by organic chemists to describe structures of conjugated systems, two or more *Lewis structures* are written to represent a compound and the actual molecule is taken to be a weighted average of them. This representation of a real structure as a weighted average of two or more forms is called *resonance*. When two or more Lewis structures can be written for a compound, these structures are called *resonance contributing structures* or *canonical structures* and the real structure is a *hybrid* of these contributing structures. The resonance hybrid is similar to each of the contributing structures but identical to none of them. For example the various contributing structures of benzene are:

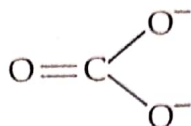


None of these structures represents benzene satisfactorily. The real structure of benzene is a resonance hybrid of these contributing structures. No molecule of benzene has any one of the contributing structures at any time. The contributing structures exist only in our imagination. The molecule of benzene has just one structure which cannot be drawn but which resembles the contributing structures to varying degrees. The energy of the actual molecule, the resonance hybrid, is less than that of any one contributing structure. The difference of energy between the actual molecule and the contributing structure of the lowest energy is called the resonance energy.

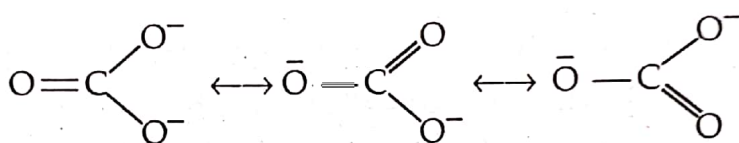
The double headed arrow, \longleftrightarrow , symbolizes resonance and should be distinguished from symbols such as \rightleftharpoons or \rightleftarrows which indicate that a reaction is reversible. The double headed arrow, \longleftrightarrow , does not imply that the structures joined by it are in equilibrium with each other. It simply means that the molecule is better represented by several Lewis structures than by one. Also it is not necessary that the hybrid (the actual molecule) should resemble each contributing structure more than it does another. Since the hybrid has energy lower than any of the contributing structures, it is obvious that it will resemble those structures more closely which have lower energy. Of the several structures that might be written for a molecule, those having lowest

energy are the most important contributors. Structures with relatively higher energy are less important, i.e., their resemblance to the hybrid is small.

Consider, now, the carbonate ion, CO_3^{2-} . According to the Lewis theory it may be represented by the following structure.



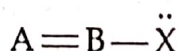
However, there is physical evidence that all the C — O bonds have the same length in the carbonate ion. According to the resonance method the equivalence of the three C — O bond lengths is accounted for by writing a set of three structures for the carbonate ion as under.



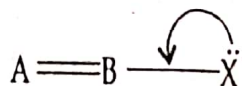
In any one of these structures the negatively charged oxygen atoms are different from the doubly bonded oxygen atom implying that the negative charges are localized on only two oxygens, while the π bond is restricted between the third oxygen and carbon. The resonance picture, however, shows that the electrons comprising the π bond and two negative charges are delocalized over the entire molecule and that in the actual carbonate ion all the three oxygen atoms are equivalent and therefore equidistant from the carbon atom.

The technique of writing the resonance contributing structures may be illustrated by a few examples. For conjugated systems of the type $\text{A}=\text{B}-\ddot{\text{X}}$, where the two dots represents an unshared electron pair on the atom X, the following steps are involved:

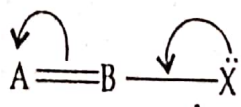
1. Write down a single conventional structure showing also the unshared electron pair.



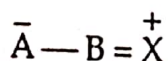
2. Move the unshared electron pair on X toward the double bond to make a new bond between X and B as shown by the direction of the arrow:



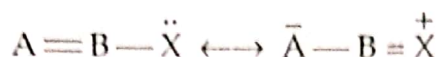
3. Move the bonding π electron pair between B and A toward A:



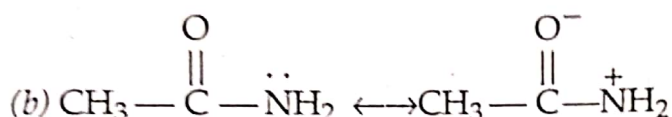
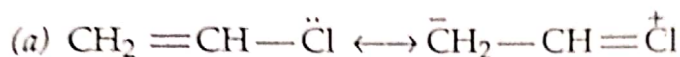
4. Write a unit positive charge on X and a unit negative charge on the atom A:



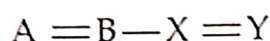
The two contributing structures that will result from the above operations are:



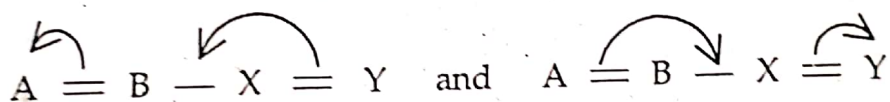
The resonance pictures of vinyl chloride (a) and acetamide (b) which are of $A=B-\ddot{X}$ type, as derived by the above technique are:



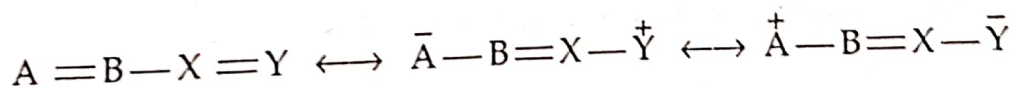
For compounds for which one conventional structure is of the type:



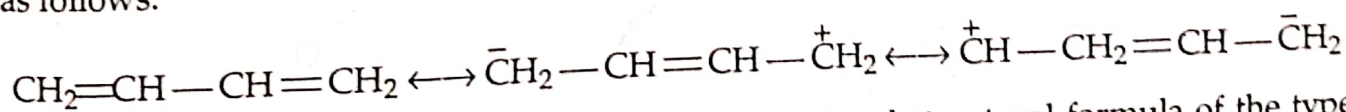
Other structures are drawn by moving electrons in the direction of the arrows:



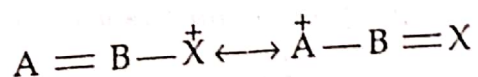
In the first case a unit positive charge on Y and a unit negative charge on A is written and in the second case the charges are reversed. The three resonance structures of the above molecule, therefore will be:



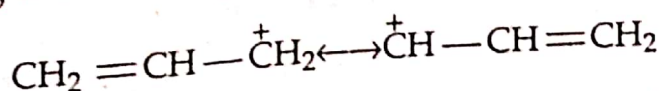
1, 3-Butadiene is a compound of the above type and its resonance description is as follows:



For compounds which might have a conventional structural formula of the type $A=B-\overset{+}{X}$, other contributing structures are written by moving the π -electrons between A and B towards the positively charged atom X to make a new bond between B and X. Atom A, then, gets a unit positive charge:



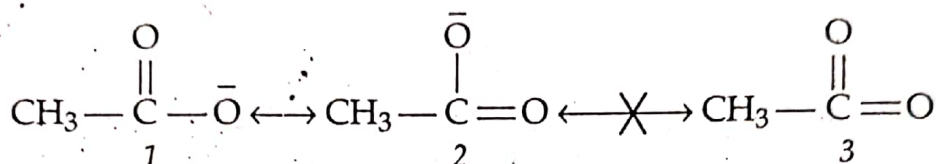
Allylic action is typical of this category and is considered to be a resonance hybrid of the following two structures:



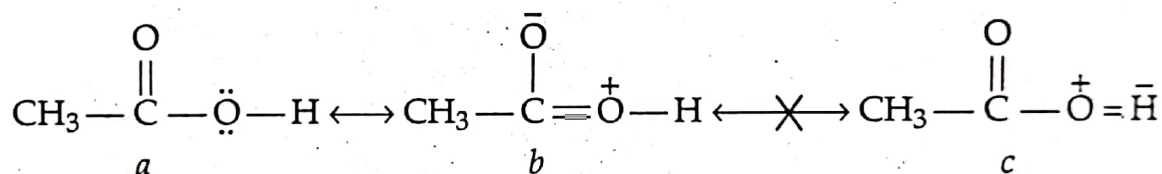
The Rules of Resonance

The selection of the canonical structures, which contribute to a resonance hybrid, is guided by the following rules:

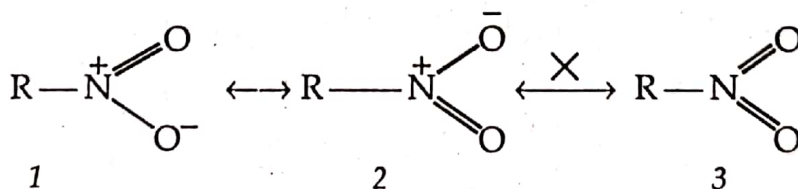
1) *All the contributing structures should be Lewis structures.* For instance, in any canonical structure the *maximum* number of covalent bonds that an atom may have is *one* for hydrogen, *four* for carbon, *four* for nitrogen, *three* for oxygen and *two* for halogens. The following example illustrates this rule:



Structure 3 is *not* a contributor because the carboxylic carbon atom has five covalent bonds. Also note that when the oxygen atom has one covalent bond it bears a unit negative charge while the divalent oxygen atom is electrically neutral. When three bonds are written for an oxygen atom it has a unit positive charge on it, e.g.,

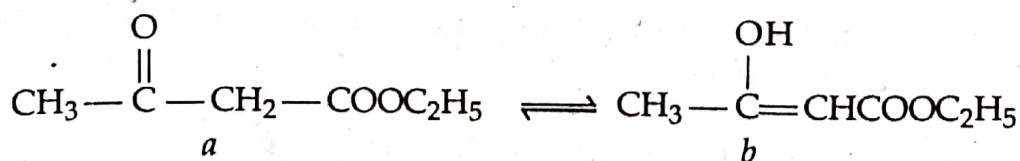


The structure *c* is *not* allowed because the hydrogen atom has two covalent bonds. Again consider the resonance picture of a nitro compound:



Structure 3 has five covalent bonds for the nitrogen atom and, therefore, is not allowed. Note that when the nitrogen atom has four covalent bonds it has a unit positive charge on it.

2) *The various contributing structures of a compound may differ only in the distribution of electron, the relative positions of atoms remaining unchanged from structure to structure.* In the following case, i.e.,



Structures *a* and *b* represent two different compounds which are in equilibrium with each other; they are *not* canonical forms of the same compound as the position of a hydrogen atom has changed in going from *a* to *b*.

paired

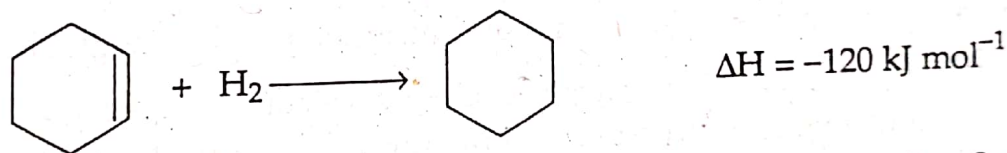
- 3) All the contributing structures of a given resonance hybrid must have the same number of unpaired electrons. For example, the following structure *does not* contribute to the molecule of 1,3-butadiene as it has two unpaired electrons.



The valid canonical forms of butadiene such as $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ and $\overset{+}{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \overset{-}{\text{C}}\text{H}_2$ have no unpaired electrons.

- 4) The real molecule, i.e., the resonance hybrid, is always more stable than any of the canonical forms. This is obvious because in any one canonical form each pair of bonding electrons is localized between two atoms only, whereas in the hybrid the π electrons are delocalized over three or more atoms. The **resonance energy** of a compound is the difference of energy between the actual molecule (the hybrid) and the most stable canonical form.

One can calculate the resonance energy of benzene from its heat of hydrogenation. The heat of hydrogenation of cyclohexene (which adds one mole of H_2 molecule) is 120 kJ mol^{-1} .



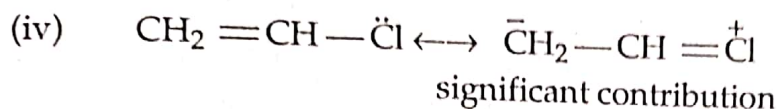
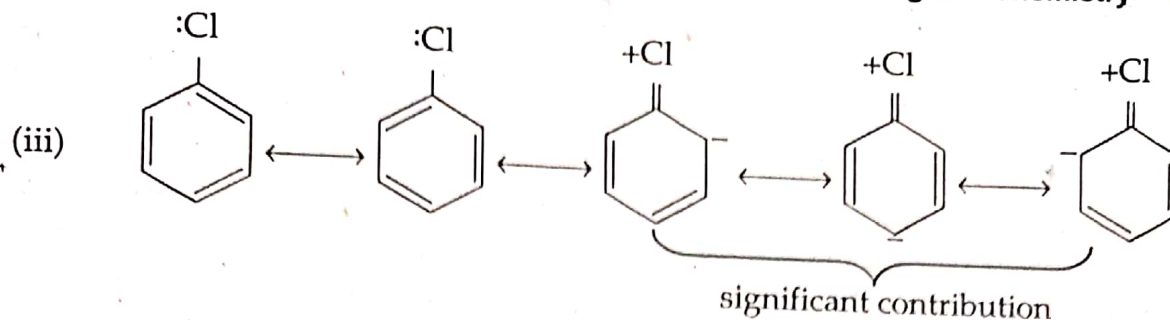
Benzene, which also gives cyclohexane on hydrogenation, by adding 3 moles of H_2 , has expected heat of hydrogenation three times that of cyclohexene. In other words if there were a compound which could be represented by the following single structure,



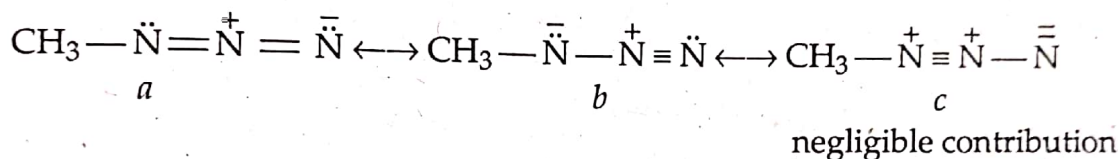
would have an expected heat of hydrogenation $3 \times 120 = 360 \text{ kJ mol}^{-1}$. The observed heat of hydrogenation of benzene is 208 kJ mol^{-1} . The resonance energy of benzene, therefore, is $360 - 208 = 152 \text{ kJ mol}^{-1}$, showing that benzene has extra stability of 152 kJ mol^{-1} due to delocalization.

In short all compounds which are not fully described by a single structure but a combination of contributing structures have extra stability and are said to be resonance stabilized.

- 5) All canonical forms do not contribute equally except when they have the same energy; the most stable canonical forms are the most important contributors, e.g.,

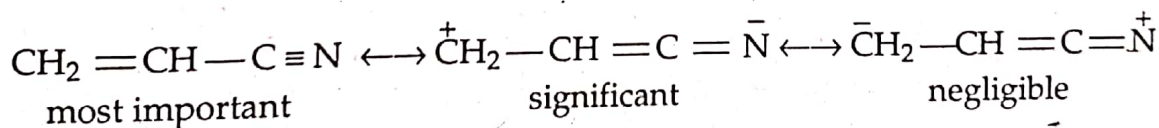


(c) Structures with like charges on the same atom or on two adjacent atoms are highly unstable, e.g.,

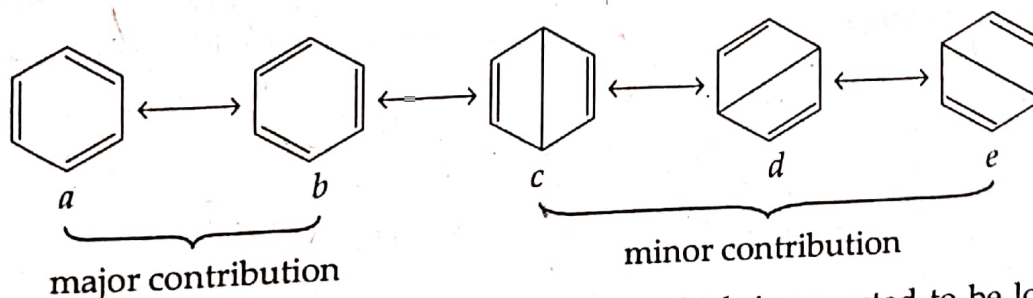


Structures *a* and *b* are the important canonical forms of CH_3N_3 (methyl azide), but structure *c* is negligible contributor because it has two negative charges on the same nitrogen atom and two positive charges on two adjacent atoms. The forces of repulsion between the like charges increase the energy of this structure considerably, making its contribution of no importance.

(d) Structures with a negative charge on a more electronegative atom are more stable than those in which the negative charge is on the less electronegative atom, e.g.,

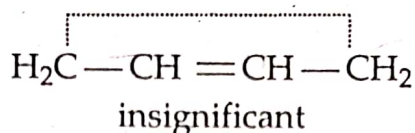


(e) Structures in which bond angles and bond lengths resemble closely with the resonance hybrid are more stable than those with distorted bond angles and bond lengths, e.g.,



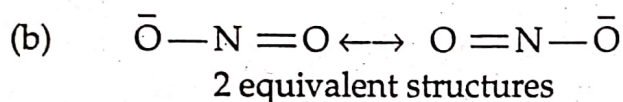
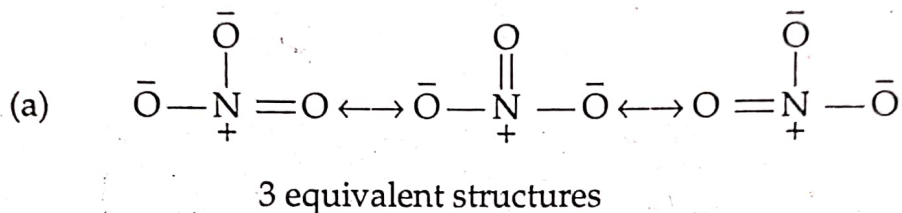
Structures *c*, *d* and *e* have one bond each which is expected to be longer than a normal covalent bond and therefore make only about 7% contribution each whereas the structures *a* and *b* with normal bond lengths make about 40% contribution each.

The following structure for butadiene is of negligible importance because one bond (dotted) is expected to be much longer than a normal covalent bond.

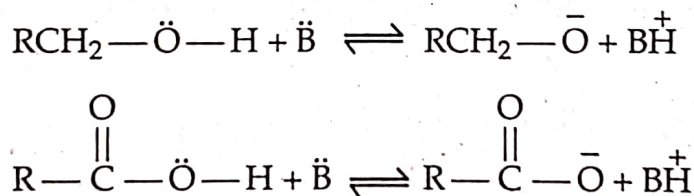


6) Compounds for which a large number of significant structures can be written have greater resonance energy (are more stable) especially if the contributing structures are of equal energy.

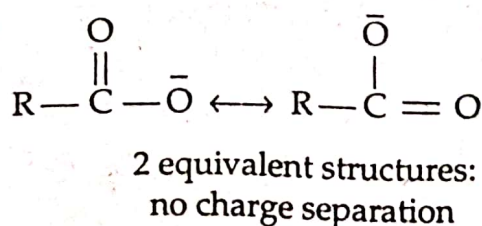
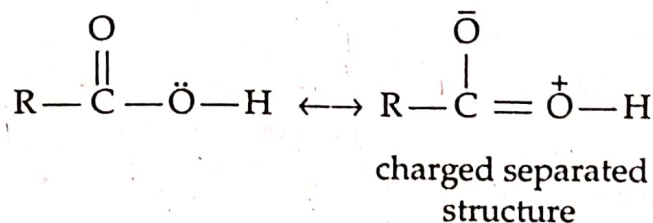
Thus butadiene has resonance energy of only 17 kJ mol^{-1} whereas benzene, for which two equivalent structures make significant contribution, has a resonance energy of 152 kJ mol^{-1} . The greater acidity of nitric acid, HNO_3 , as compared to nitrous acid is also attributed to a similar effect; the nitrate ion is more stable than the nitrite ion:



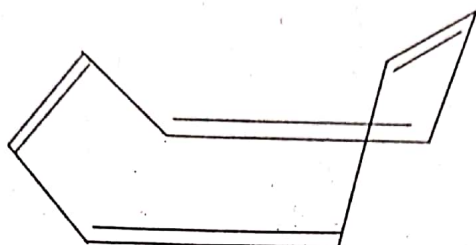
Again the greater acidity of carboxylic acids as compared to alcohols is attributed to the larger resonance stabilization of the anions of the carboxylic acids relative to the unionized acids.



For the unionized alcohol as well as the anion of the alcohol a single Lewis structure is sufficient to describe the molecule. In other words there is no resonance either in RCH_2OH or in RCH_2O^- and the loss of proton does not add to the stability of the molecule. On the other hand, the anion of a carboxylic acid has greater resonance stabilization than its unionized form:

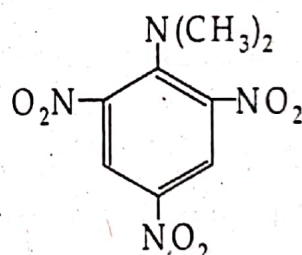
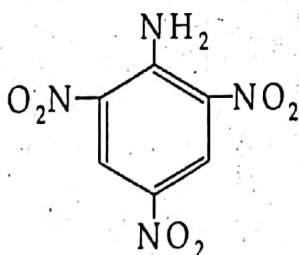
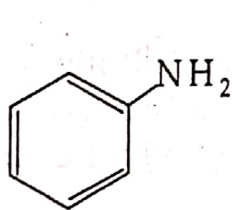


7) *Delocalisation of electrons over more than two adjacent atoms is maximum if these atoms are in one plane.* Thus benzene, butadiene, vinyl chloride and other molecules for which sets of resonance structure were previously written are all planar molecules. There is no delocalisation of electrons if one pair of doubly bonded atoms lies in a plane which is perpendicular to the plane of another pair of doubly bonded atoms or another atom with an unshared pair of electrons, a positive charge or a negative charge. For example cyclooctatetraene is fully described by the following non-planar single structure:



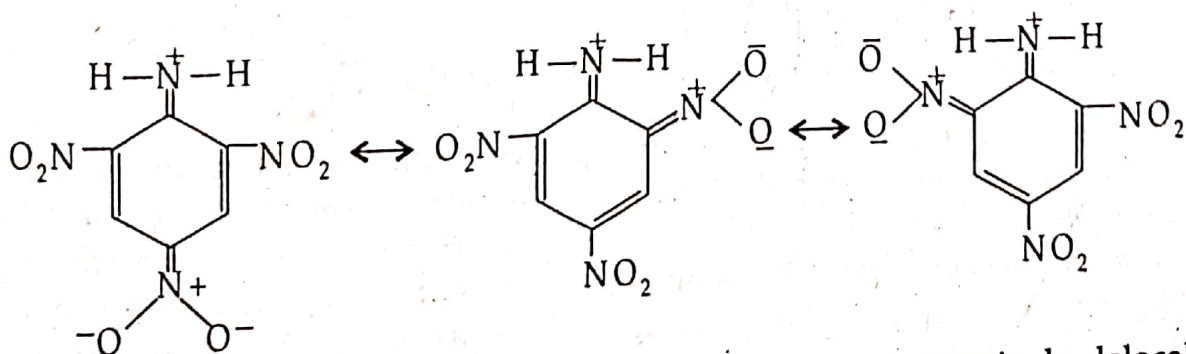
There are four localized double bonds in the molecule. Since one doubly bonded pair of atoms lies in a plane which is perpendicular to the plane of the next pair of doubly bonded atoms, resonance contributing structures, which would imply delocalization of the π -electrons, cannot be written for this molecule.

Compare the following compounds for their strength as bases.



The decreasing order of their basicities is aniline > N, N-dimethyl-2,4,6-trinitroaniline > 2,4,6-trinitroaniline.

The weakest base, i.e., trinitroaniline has, amongst others, the following structures as significant contributors:



Thus the electrons of the amino nitrogen atom are extensively delocalized over all the oxygen atoms of the nitro groups. The electron density on the amino nitrogen is greatly reduced making it a poor electron-pair donor in an acid-base reaction.