Nature of Bonding in Organic Molecules

INTRODUCTION

Organic compounds have great importance in human's life. The carbon comes from a variety of sources like plants, animals and vegetables etc. What are these products? How they are formed? By the term "organic," we actually mean about the molecules that are created from the carbon element (C). Carbon shows striking flexibility in its ability to form various different bonding arrangements with other carbon atoms as well as with elements such as nitrogen (N), oxygen (O), sulfur (S), and phosphorus (P). As such, the presence of covalent bonds is the characteristic of organic (carbon) compounds. The linkages in carbon chemistry are called bonding which is chiefly responsible for the synthesis of various organic products.

DELOCALIZED CHEMICAL BONDING

In organic chemistry, it has been realized that the concept of having delocalized electrons is invoked repeatedly to explain the behavior as well as different properties of organic compounds. Indeed, the electronic delocalization is a very important concept. The electrons that are limited to a particular region are generally called localized electrons. The localized electrons are confirmed between two atoms or belong to a single atom while some electrons are not confirmed to a single atom or bond. The electrons which neither belong to a single atom nor are limited to a bond between the two atoms, but are shared by three or more atoms are known as delocalized electrons. Thus, delocalization is a characteristic feature of π-electrons, where the π-electrons changes their locations (in between different sub-orbitals). The main factor which influences delocalization is the extra availability of sub-orbitals of about same energy than those of the number of electrons. The delocalization usually involves sp2, sp3, and other complex hybridizations. It chiefly occurs due to the presence of double and triple bonds which are the characteristics of hybridization.

Types of delocalization

The delocalization in chemical bonds can be carried out in different ways, and in different systems. Some of these systems are briefly discussed as follows.

1. Isolated systems: The delocalization of electrons occurs in those compounds in which double bonds are separated by more than one single bond.

2. Conjugated systems: The systems in which alternate single and double bond exist. For example, benzene.

3. Cumulated systems: If double bonds are adjacent to each other as in 1,2-dipropene ($H_2C=C=CH_2$).The delocalization is carried out by forming a delocalized bond to uphold the stability of the molecule. Hyperconjugation is also the result of delocalization.

Consequences of electron delocalization:

a) Intermediate bond length: In simple molecules, C-C (alkanes) and C=C (alkenes) bond lengths are 1.54 and 1.34 Å, respectively but in case of benzene, all C-C bond lengths (single, double, and delocalized) are 1.39 Å (see below). 1.54 1.34 1.39 1.39

b) Stability of diene: Compounds having delocalized bonds are more stable than those of normal compounds. For instance, 1,3-pentadiene is more stable than 1,4-pentadiene by 28KJ/mol as shown below.

c) Acidity: Delocalization increases the acidity of compounds e.g. carboxylic acids (RCOOH) are much more acidic than those of alcohols (ROH).

d) Stability of carbonium ion: It contributes toward the stability of a carbocation intermediate. e.g. allylic and benzylic carbocations have delocalized electrons, and thus they are more stable than other primary carbocations.

e) Dipole moment: Dipole moment also increases due to the delocalization of electrons, which are involved in resonance.

Orbital picture of delocalization:

The orbital picture of delocalization can get somewhat complicated. We start by noting different varieties of sp2-hybridized carbon atoms. The most important and common sp2hybridized carbons are neutral and positively-charged sp2 carbons. Substances having neutral sp2 carbons are regular alkenes. Species containing positively-charged sp2 carbons are called carbonium ions. The central carbon in a carbocation has trigonal planar geometry with an unhybridized empty p orbital. A combination of Lewis and orbital or 3D formula is a popular means of representing certain features that we may want to highlight. For example, if we omit sp2 orbitals and just focus on the role of p orbitals, we can use the following notation. Let’s now focus on two simple systems where the delocalization of π-electrons exists. In particular, one of these systems contain two π-bonds in conjugation while the other has a π-bond next to a positively-charged carbon atom. The line drawing along with the orbital picture of these systems can be presented as follows. The two π-molecular orbitals shown in blue color on the left below are close enough to overlap. Indeed, the overlapping of orbitals is a good sign as it helps in the delocalization of the electrons and spreads them over a larger area, and thus imparts stability to the system. It is however time consuming to draw orbitals all the time, and a delocalized system can be presented as shown on the right below. An analogous process applicable to the carbocation can lead to a similar picture. It would be worthwhile to mention here that the resonance representation conveys the idea of delocalization of charge and electrons rather well (see below). Me Me On a final note, the following representations are sometimes also used, but again, the simpler they are, the less accurately they represent the delocalization picture

CONJUGATION AND CROSS-CONJUGATION

A system or molecule which has alternate single and double bonds simply serves as a conjugated system. Conjugation relies on the partial overlap of p-orbitals on adjacent double or triple bonds. A very familiar conjugated system is 1,3-dienes such as 1,3-butadiene. In a conjugated system, overlap of p-orbitals allows electrons to be delocalized over a larger portion of the molecule, thus lowering the energy of the molecule and making it more stable. The conjugation effect is at a maximum when the axes of the orbitals are aligned in a parallel style because this allows a maximum orbital overlap. The word "conjugation" is derived from a Latin word that means "to link together". Conjugation provides an electron highway for electrons to delocalize from one side of a molecule to another. Due to delocalization of electrons, a delocalized bond is formed by fluctuation of π-bonds resulting in different structures, which are known as resonance or contributing structures. Notably, any atom that is capable of donating a p orbital can be the part of a conjugated system

Conjugation is broken completely by the introduction of saturated (sp3-hybridized) carbon atom. Systems containing conjugated double bonds are more stable than those containing non-conjugated double bonds, i.e. 3-Cyclohexenone is less stable than 2-Cyclohexenone. Figure 4 Examples of different conjugated systems; (a) cyclic, (b) linear, (c) mixed, and (d) cross-conjugated systems Alongside of conjugation phenomenon, it would be worthwhile to know about cross-conjugation. Specifically, cross conjugation is a special type of conjugation in which three double bonds are present; out of which two double bonds are not conjugated with each other although each one is conjugated with the third double bond (Figure 4d). i.e interruption of the strict alteration of single and double bonds.

RESONANCE

Most of the organic covalent compounds have a single Lewis structure (dot structure).The Lewis structure explains the bonding in that molecule, but for many molecules, two or more dot structures are also possible. To explain the structure and physico-chemical properties of such covalent compounds that could not be represented by a single structure, Heisenberg introduced the phenomenon of resonance. Specifically, resonance is a situation in which more than one plausible structures can be written for a species but not the true structure at all. For example, the acetate ion can be represented by two equivalent structures, (a) and (b) as shown below Resonating structures (a) and (b) of an acetate anion Of the above two structures, one structure cannot exactly describe all the properties of acetate ion, and thus each of these two structures can contribute to the true structure of the acetate ion. These types of different structures are called ‘resonance or canonical structures’. The structure with localized electrons is called a resonance contributor, a resonance structure, or a contributing resonance structure while the actual structure with delocalized electrons is called a resonance hybrid as shown for benzene (Figure 5). The resonance structures are just alternate Lewis structures for a given ion or molecule. The stability of a real molecule is usually measured in terms of resonance energy or resonance stabilization energy. The resonance energy is defined as the energy difference between the most stable resonating structures and the resonance hybrid form. In benzene, the experimentally measured carbon-carbon bond length is 140 pm, which is intermediate of C-C (154 pm) and C=C (134 pm) bond lengths, suggesting that a resonance hybrid is a true representation. Figure 5 Resonating structures (A and B) and resonance hybrid form (C) of benzene Resonance is very important and significant feature of many organic molecules. Resonance influences the structure, chemical reactions and physical properties of such molecules. In order to fully understand this phenomenon, one must be able to draw the contributing resonance structures as well as the resonance hybrid form. Characteristics of resonance/resonance structures

- All the atoms in the molecules taking part in resonance must be coplanar. This is essential for successful overlap of the p-orbitals.

- The sp3-hybridized atoms do not participate in resonance. They exist only in those parts of molecules that are composed of sp or sp2 atoms; p-orbitals are an absolute requirement for resonance.

- While making a resonance structure, electrons (lone pairs/π-electrons/a negative charge or the unpaired electrons present on radicals) move only between the adjacent atoms. In particular, these electrons move to the 'resonance acceptor atom' from a 'resonance donor atom', which must be adjacent to the acceptor atom. An atom with a formal positive charge, can also be a resonance acceptor atom as long as the atom does not accept more electrons than it can normally accommodate.

- The resonance structures (or contributing structures) are only the imaginary structures. Thus, the resonance structures do not have a real existence as the individual species. These imaginary structures only proposed to explain the properties of a molecule, and none of these 'resonance structures' can be prepared in the laboratory.

- The resonance hybrid is the real structure. Due to the resonance conjugation fact, the bond lengths in resonating structures exhibit equal values.

- In different resonating structures, the position of the nuclei must be the same in all the structures and the total charge should also be constant.

- The resonance hybrid has lower energy and thus greater stability than any of the contributing structures.

- Greater the resonance energy, greater is the stability of the molecule.

- The structures with similar charges on adjacent atoms are irrelevant due to electrostatic repulsion, and consequently, show instability.

- Those structures have small contribution where negative charge (when separating charge giving rise to ions) is on the less electronegative elements. For clarity, the resonating or canonical structures of some selected species are given below.

HYPERCONJUGATION

In an elegant work, Baker and Nathan suggested that alkyl groups with at least one αhydrogen atom, when attached to an unsaturated carbon atom, are capable to release electrons by a mechanism similar to that of the electromeric effect. This effect is known as hyperconjugation or Baker-Nathan effect. Hyperconjugation is an unusual type of resonance in which delocalization of electrons takes place through the overlapping between the sigma (σ) bond orbital(usually C-H or C-C) with an adjacent empty or partially filled p-orbital or a π-orbital giving an extended molecular orbital that increases the stability of the system. The stabilization arises because the orbital interaction leads to the electrons being in a lower energy orbital . Hyperconjugation occurs due to the partial overlap of sp3-s σ bond orbital and the empty porbital or π-bond orbital of an adjacent carbon atom.

Hyperconjugation is a factor in explaining why increasing the number of alkyl substituents on a carbocation or radical centre leads to an increase in stability. Examples of Hyperconjugation There are many molecules and reaction intermediates which can show hyperconjugation effect. Some of the common examples are as following.

1. Carbonium ion: In carbocation or carbonium ion such as ethyl carbocation, the σ electrons of Csp3-hydrogen bond are delocalized with an empty p-orbital of positively-charged carbon atom and can show four contributing structures, similar to that of propene as discussed above.

2. Free radicals: Like carbonium ion, free radicals get stabilized through hyperconjugation. The σ electrons of C-H bonds of methyl group next to the carbon atom contain an odd electron and interact with p-orbital having an odd electron. As the number of α-carbonhydrogen bond increases, the number of contributing structures also increases resulting in greater stability.

3. Alkene: In 2-butene, the interaction of π-bond with α-carbon-hydrogen bond can form six resonating structures of 2-butene (not shown here).

4. Nitromethane: The nitrogen-oxygen π-bond can interact with α-carbon-hydrogen bond.

The orientation influence of methyl group in toluene due to hyperconjugation effect Applications of hyperconjugation effect 1. Stability of alkenes and other unsaturated hydrocarbons: The stability of unsaturated hydrocarbons like nitriles and alkenes depends upon hyper conjugation. The more possible contributing structures in hyperconjugation usually increase the stability of the molecule. Since hyperconjugation mainly involves α-carbon-hydrogen σ bond and π-electrons, therefore, as the number ofα-, σ bonds increases, hyperconjugation also increases. For instance, 2-butene consists of six α-carbon-hydrogen σ bonds while there are only two carbon-hydrogen bonds next to the double-bonded carbon atom in 1-butene. Hence 2-butene can shows six contributing structures while 1-butene shows only two structures, making 2-butene more stable over 1-butene (Exercise: can you draw these structures? give a try by yourself). In other words, most- substituted alkenes are more stable than those of less-substituted alkenes. 2. Stability of reaction intermediates Hyperconjugation is also observed in reaction intermediates like carbocations and free radicals which stabilize the intermediates as it helps in the dispersal of positive charge. Thus, we can say that greater the number of alkyl groups attached to a positively-charged carbon atom, the greater is the hyperconjugation interaction, and thus the stabilization of the carbonation. For example; in primary carbocation like ethyl carbocation, there are three α-carbon-hydrogen bonds which can delocalize into an empty p-orbital. However, in secondary (isopropyl) and tertiary (tert-butyl) carbocations, there are six and nine α-carbon-hydrogen bonds, respectively. Consequently, the increasing order of stability of carbocations can be written as: H3C C C H3 (CH3)2CH2 CH3CH2 CH3 Hyperconjugation stability Similarly, the increasing order of stability of free radicals would be primary < secondary < tertiary free radical.

3. Dipole moment & bond length Hyperconjugation induces polarity in the molecule which influences both the dipole moment and bond length of the molecule. As the polarity increases, dipole moment also increases while bond length decreases. 4. Anomeric effect Anomeric Effect may explain as the tendency of anomeric substituents to favor an axial configuration over an equatorial position. The high stability of αα-methyl glucoside than that of ββ-anomer can be explained based on the hyperconjugation effect. Whereas an αα-anomer can show hyperconjugation of lone pair of oxygen atom with axial methyl group, hyperconjugation is not possible in ββ-anomer due to equatorial position.

TAUTOMERISM Tautomerism is defined as the phenomenon in which a single compound exists in two readily interconvertible structures that differ noticeably in the relative position of at least one atomic nucleus, generally hydrogen. The term ‘tautomer’ is made by two words; one is tauto (same) and meros (parts). The term tautomerism is also known as desmotropism (Greek desmos-bond; tropos-turn) based on the interconversion of the two forms involving a change of bonds or dynamic isomerism (as the two forms are in dynamic equilibrium with each other). The most common tautomers exist in pairs, which mean that the proton is located at one of the two positions. In other words or more specifically, the most common form involves a hydrogen changing place with a double bond. The tautomerism is frequently observed in carbonyl or keto compounds and unsaturated hydroxyl compounds or enols. For this reason, the tautomerism is also known as keto-enol tautomerism. In this context, the structural change is the shift of a hydrogen atom between atoms of carbon and oxygen with the rearrangement of bonds. Needless to say that the enol form differs from the keto form in its polarity, acidity, and nucleophilicity. However, the keto form is typically much more stable than the enol form with K's of ca. 10-5. Indeed, this is essential because the C=O bond is much more stable than the C=C double bond. The keto form is also more thermodynamically stable than enol form by 12 kcal/mol (48 kJ/mol). Although the keto form is mainly stable for aldehydes and ketones in most situations yet some factors can shift the equilibrium towards the enol form as mentioned below.

1. Aromaticity: In case of phenol, theoretically keto form should be more stable, but the enol form is greatly favored due to an aromatic stabilization (see left below). 2. Hydrogen Bonding: In the presence of a Lewis basic group, the intermolecular hydrogen bonding stabilizes an enol form (see right below). However, the ratio of the two forms will also depend upon the solvent(s) used. Besides these two factors, three more subtle effects are also observed in keto-enol tautomerism. Solvent: Solvent play an important role in the relative stability of the enol form. For example, the enol form of 2,4-pentanedione predominates over the keto form in benzene. However, the stability reverses completely in the water i.e. the keto form becomes more stable in water as shown below. In a protic solvent, the lone pairs will be occupied in hydrogen bonding with the solvent, making them less accessible to hydrogen bond with the enol form. Conjugation and substitution: The presence of conjugation and substituents in a molecule always shift the equilibrium towards enol form. (Exercise 1: Which enol form will be favored for a given below ketone?)

Types of Tautomerism: The tautomerism can occur in both diad and triad systems. In diad system, hydrogen or any other group migrates from atom no. 1 to an electronegative atom no. 2 as shown below. The same can be applied for a triad system. Some selected examples of triad systems are given in Figure 9.   Figure 9 Keto-enol tautomerism in triad systems. In systems (a-c), all keto forms exist as major (>99.97%) Mechanisms of Tautomerism:

1. Acid-catalysed mechanism: In acid-catalysed enolization, a proton (from an acid) reacts with water molecule and forms hydronium ion (H3O+). A lone pair of electrons is removed from the carbonyl oxygen by the H3O+. Finally, water abstracts a proton from α-carbon atom, resulting in the formation of the enol form (Scheme 1a). However, if the starting compound is an enol, Markovnikov's addition of hydrogen ion occurs (Scheme 1b). Scheme 1 An acid-catalyzed mechanism for keto-enol tautomerism 2. Base-catalyzed mechanism: The formation of an enol under base catalysis involves the formation of an intermediate enolate, the conjugate base of the carbonyl compound. In the first step, hydroxyl group abstract an α-proton and an enolate ion is formed. The enolate ion is stabilized by resonance and accepts a proton from water to form enol compound in the final step (Scheme 2). Scheme 2 A base-catalyzed mechanism for keto-enol tautomerism Differences between tautomerism and resonance: The tautomeric forms are chemically distinct entities and can be separated and characterized. On the other hand, resonating forms differ only in the distribution of electrons and can never be separated from one form to another since neither of them have any real existence. The important differences between resonance and tautomerism are given below. 1. Tautomerism engages a change in the position of atom (generally hydrogen), while resonance involves a change in the position of the bonds and electrons. 2. Tautomers may be separated and isolated. Resonating structures are only imaginary and cannot be isolated. 3. The two tautomeric forms have different functional groups but the various resonating structures have the same functional group. 4. In case of tautomerism, bond length does not change while resonance significantly affects the bond length (single bond is shortened while the double bond becomes longer). 5. Resonance decreases the energy and hence increases the stability of compounds, while tautomerism does not lower the energy of the molecule, and hence does not play any role in stabilizing the molecule. 6. Tautomerism is represented by ( ) but the resonance is represented by ( ) symbol. 7. Tautomerism can occur in planar as well as non-planar molecules while only planar molecules can show the phenomenon of resonance.

HUUCKEL'S RULE AND AROMATICITY Compounds such as benzene having relatively fewer hydrogen atoms than those of carbons are typically found in oils, which, in turn are produced from trees and other plants. Because of their pleasant fragrance (aroma), early chemists called such compounds as aromatic compounds. However, the chemical definition of aromatic now signifies certain kinds of chemical structures. Aromatic compounds are a special class of organic compounds and have attracted considerable attention due to their potential applications in various fields of chemistry. Among them, the formation, reactions and stability of such cyclic (aromatic) compounds are always of particular interest owing to their vast array of potential applications. Aromaticity: Benzene is a planar compound with a cyclic cloud of delocalized electrons both above and below the plane of the ring as shown above. Because its π-electrons are delocalized, all the CC bonds in benzene have the equal length- partway between the length of a typical single and double bonds. We have noticed that the benzene is a particularly stable compound because it has extraordinarily large resonance energy (36

Kcal/mol). The compounds such as benzene with unusually large resonance energies are typically called aromatic compounds, and the cause which explains the extra stability of such cyclic molecules is termed as ‘aromaticity’. In aromatic compounds, resonance phenomenon (for details, see resonance section) typically increases the stability of the molecule, and therefore, the energy is called resonance energy. The concept of aromaticity can be best explained based on the Hückel’s rule as discussed below: Hückel’s rule: For a compound to be aromatic, the following conditions must be followed (i) A compound must have an uninterrupted cyclic cloud of π-electrons. For the πcloud to be cyclic, a compound must be cyclic and planar or nearly planar. (ii) The πcloud must contain an odd number of pairs of π-electron. (iii) The German chemist Erich Hückel was the first to recognize that an aromatic compound must obeys [4n + 2] π-electron rule.