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CHEMISTRY
PAPER 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)
MODULE 2: Resonance, conjugation and cross-conjugation

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CHEMISTRY

PAPER 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)

MODULE 2: Resonance, conjugation and cross-conjugation

1. Learning Outcomes

After studying this module you shall be able to:

- Revise what is resonance?
- Understand the terms conjugation and how it leads to resonance
- Learn about cross-conjugation
- Differentiate between conjugation, cross-conjugation and non-conjugation

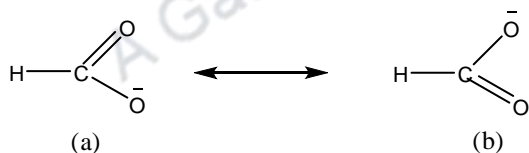
2. Introduction

Resonance, Conjugation and Cross Conjugation seem to be very similar terms. But we should be very clear in understanding what is resonance, how conjugation leads to resonance and how the cross- conjugation differs from conjugation. Further, we must also know what are the requirements that resonance is exhibited in the molecule and how it brings stability? Let us try to explore all this in detail.

3. Resonance

Most covalent molecules have a unique Lewis formula (dot structure). These Lewis formula explain the bonding in that molecule, but for many molecules, two or more dot structures are feasible, rather than only one structure. The phenomenon of resonance was put forward by Heisenberg to explain the properties of such covalent molecules/species that could not be represented by a single structure.

For example, the formate ion can be represented by two equivalent structures, (a) and (b), as shown below:



Of the above structures, (a) and (b) for formate ions, none exactly describe all the properties of the molecule. Here, each of the two structures contribute to the true structure of the molecule. Such different structures are called 'resonance structures' and the actual molecule is termed as the 'resonance hybrid' of all these structures. Resonance structures are simply alternate Lewis structures for a given ion or molecule.

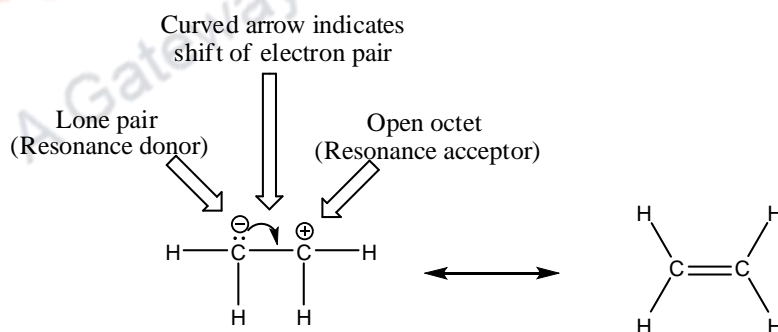
The actual molecule is found to be energetically more stable than would be expected from any of its resonance structures. This difference is measured in terms of resonance energy. Resonance energy is defined as the energy difference between the most stable resonating structure and the resonance hybrid structure.

Resonance is very common and significant feature of many organic molecules. Due to its presence, there is a pronounced influence on the structure, chemical reactions and physical properties of such molecules. In order to understand resonance, one must be able to draw **contributing resonance structures** and the resonance hybrid structure.

Let us now try to understand some characteristics of resonance and resonance structures.

3.1 Characteristics of Resonance/Resonance Structures

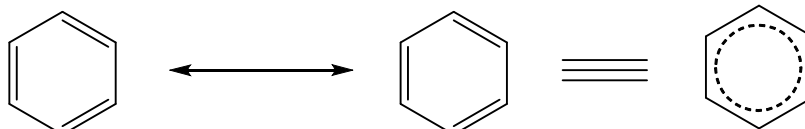
- Resonance exists only in those parts of molecules that are composed of sp or sp^2 atoms; p orbitals are an absolute requirement for resonance. Hence it does not occur in sp^3 hybridised atoms.
- All the atoms in the molecules taking part in resonance should be coplanar. This is necessary for effective overlap of the p orbitals.
- While making a resonance structure from other, electrons move between adjacent atoms. Type of electrons that can be moved are lone pairs or n electrons (or a negative charge) or the unpaired electron present on radicals. These electrons reside on a 'resonance donor atom' and move to the 'resonance acceptor atom' which must be adjacent to the donor atom. The acceptor atoms must also have an open octet, be able to or have another electron pair (lone pair or n electrons) that can be displaced. 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) do not have real existence as individual species. These are only imaginary structures, proposed to explain the properties of the molecule. None of these 'resonance structures' can be prepared in the laboratory. In real sense, the resonance hybrid is the real structure. Due to the resonance

phenomenon, the bond lengths in resonating structures exhibit equal values, i.e become equal.

For example, in case of benzene, in the resonance hybrid structure, the C-C bonds are not alternate single and double bonds, rather all of them are intermediates of single and double bonds and the bond lengths are equal.

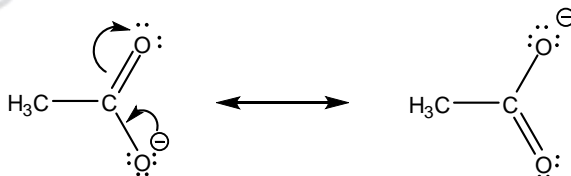


Resonance hybrid

- The resonance hybrid has lower energy and thus greater stability than any of the contributing structures. Also, greater the resonance energy, greater is the stability of the molecule.
- For the resonating structures, the position of the nuclei must be the same in all structures and the total charge must also be constant.
- Those structures have little contribution where negative charge (when separating charge giving rise to ions) is on less electronegative elements. All resonance structures must have the same number of unpaired electrons and the structures with similar charges on adjacent atoms are insignificant due to electrostatic repulsion and consequent instability.
- Resonance structures with greater number of covalent bonds are more stable. Thus, non-polar structure of formic acid is more stable than any other resonance structure.

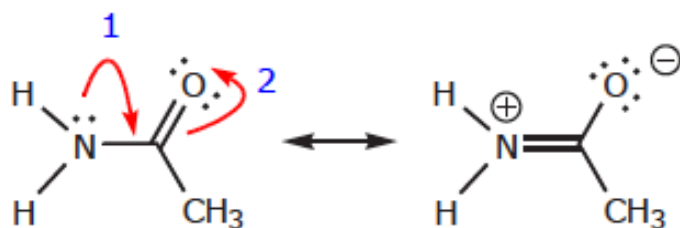
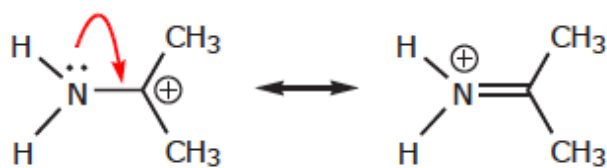
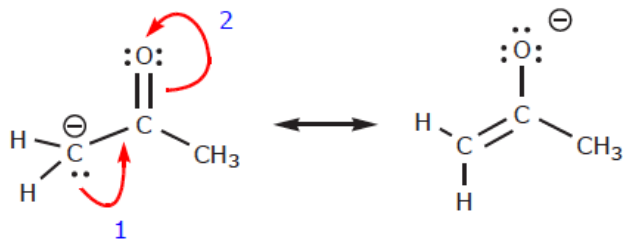


- Charge separation structures are less important than those in which the charge is delocalized. This is due to electrostatic attraction between unlike charges.

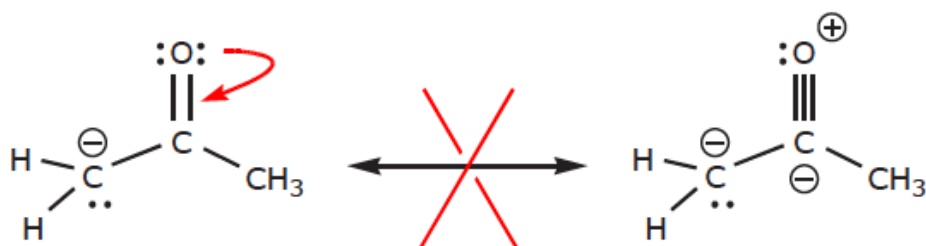


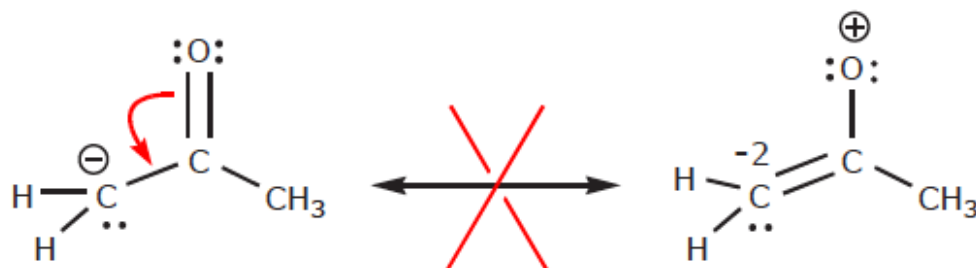
Examples:

Correct way of moving electrons:



Examples : How not to move electrons?





3.2 Most Important Resonance Contributor

During an organic reaction, many molecules or exhibit **resonance**. When writing the mechanism for the reaction, the best representation of reality can be depicted by using the **resonance hybrid structure**. However, because the resonance hybrid does not show explicitly the electron pairs that are shared by resonance, its use in mechanisms can be unclear and confusing. Thus we often use a single resonance contributor instead of the hybrid. But which one has to be used?

When deciding which resonance contributor to be used, we must consider the one that makes the greatest contribution to the resonance hybrid. That would be one which is most stable of the possible canonical structures. Let us try to understand how to compare the resonating structures in terms of their stability? For this, we need a set of rules to determine the most important resonance contributor.

These rules are based on the assumption that had the resonance contributors actually existed, the most thermodynamically stable structures would have made more significant contributions to the resonance hybrid. Factors that increase the thermodynamic stability are maximization of covalent bonding and minimization of charge. Resonance increases stability by increasing the bonding between adjacent atoms and by distributing charge over a greater number of atoms.

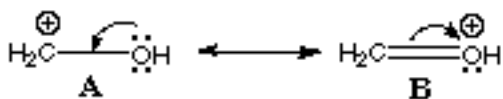
Note that the following are checked in sequence:

1. A neutral molecule is more stable than a charged one.

This is obvious that a neutral molecule shall be more stable than its resonating species in which charge separation is there.

2. A species having maximum number of atoms with full octets is more stable than others.

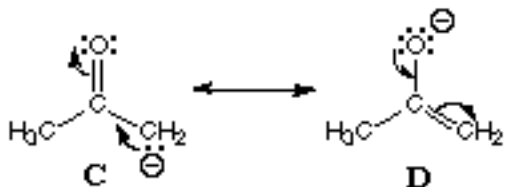
This preference gets priority over the other three rules for determining the most important resonance contributor.



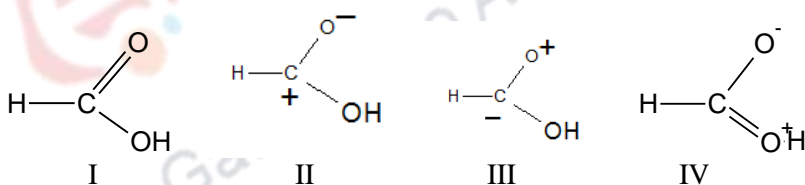
The carbon of structure **A** has an open octet. All the atoms of structure **B** have full octets. Therefore contributor **B** is more important than contributor **A**, although the positive charge is on the more electronegative oxygen atom instead of the less electronegative carbon atom.

3. Electronegative atoms having negative charge is more stable than having positive charge over them. Electropositive atoms having positive charge is more stable than having negative charge over them.

For example, out of C and D, D is more stable as electronegative oxygen atom is having negative charge over it rather than electropositive carbon having negative charge as in C.



Example: Compare the stability of the following resonating structures of formic acid



Of the four, clearly, I is the most stable as it is neutral molecule and rest are charged species. (**Parameter 1**)

Of the remaining, IV is more stable as it has all the atoms with complete octet. (**Parameter 2**) (CAUTION: Don't get carried away by the positive charge on oxygen atom to mark it as least stable!)

Of II and III, II is more stable as it contains electronegative atom oxygen having negative charge and electropositive carbon having positive charge and other way round in III. (**Parameter 3**)

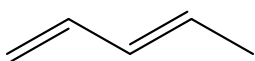
Hence the overall stability order is

I > IV > II > III

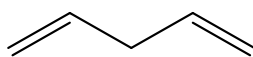
4. Conjugation

Conjugation is the overlap of one p-orbital with another across an intervening sigma bond (in larger atoms d-orbitals can be involved). In molecules that contain more than one multiple bond, e.g. dienes with two C=C bonds, it is found that compounds in which the bonds are conjugated (alternating multiple and single bonds) are slightly more stable than those in which they are isolated.

For example, out of the following dienes, the conjugated one (I) is more stable than (II).



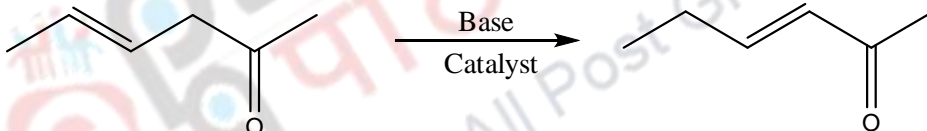
(More stable)
(I)



(Less stable)
(II)

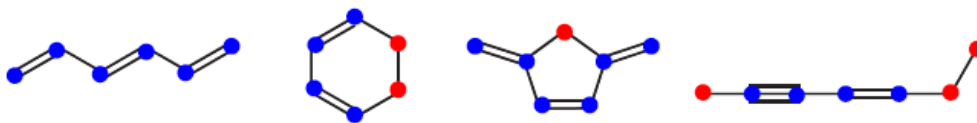
The largest conjugated systems are found in graphite, conductive polymers, and carbon nanotubes. A conjugated diene has a lower heat of combustion and a lower heat of hydrogenation.

Also, isolated double bonds can often be made to migrate quite readily so that they become conjugated.



Examples:

The atoms that form part of a conjugated system in the examples below are shown in blue, and the ones that do not are shown in red. Notice that, it is sp^3 hybridized atoms that break a conjugated system.



The electrons in a conjugated polyene are said to be *delocalized*, as they are now held in common by the whole of the conjugated system rather than being localized over two carbon atoms in π bonds.

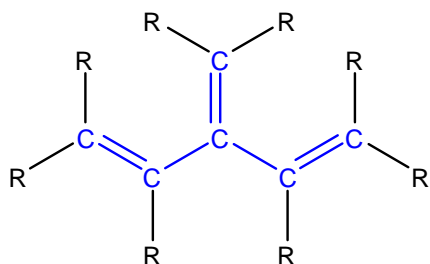
Delocalization is involved in stabilizing the excited states of dienes, and of polyenes in general, i.e. in lowering the energy level of their excited states. The effect of this is to reduce the energy gap between ground and excited states of conjugated molecules, as compared with those containing isolated double bonds, and this energy gap is progressively lessened as the extent of conjugation increases. This means that the amount of energy required to effect the promotion of an electron, from ground to excited state, decreases with increasing conjugation, i.e. the wavelength at which the necessary radiation is absorbed increases. Simple dienes absorb in the ultra-violet region, but as the extent of conjugation increases, the absorption moves towards the visible range and the compound appears coloured.

Consider the series of $\alpha\omega$ -diphenylpolyenes: $C_6H_5(CH=CH)_n C_6H_5$

$n = 1$	Colorless
$n = 2-4$	Yellow
$n = 5$	Orange
$n = 8$	Red

5. Cross-conjugation

Cross-conjugation is a special type of conjugation in a molecule. Here, out of a set of three π bonds only two interact with each other by conjugation, while the third one is excluded from interaction. A *cross-conjugated system* has a double-bonded unit single-bonded to one of the middle atoms of another conjugated chain. On the other hand, a normal conjugated system such as a polyene typically has alternating single and double bonds along consecutive atoms.

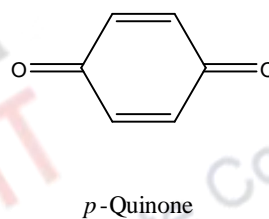
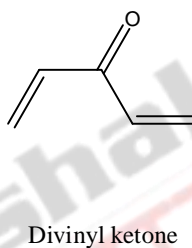
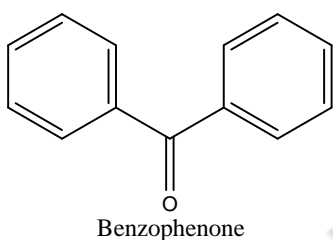


In other words, one of the double-bonds branches off rather than continuing consecutively. Hence, the main chain is conjugated, and part of that same main chain is conjugated with the side group, but all parts are not conjugated together.

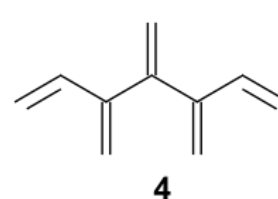
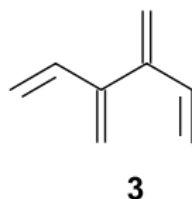
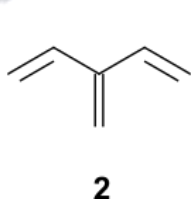
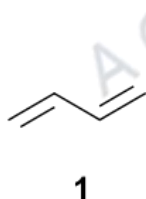
This type of conjugation has an impact on reactivity and molecular electronic transitions.

Examples:

1. Simple cases:

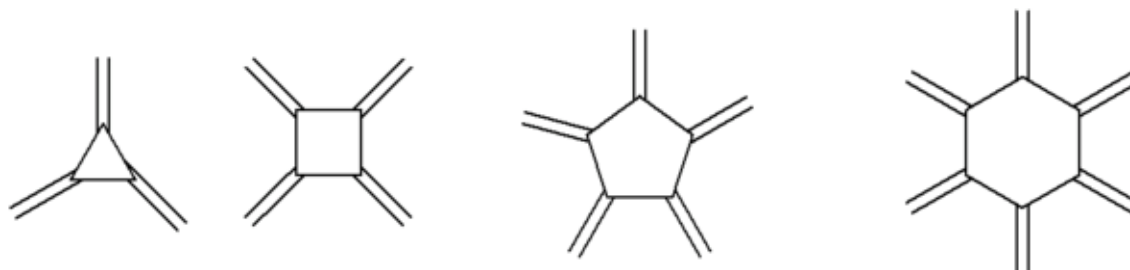


2. **Dendralenes**: A dendralene is a discrete acyclic cross-conjugated polyene. [1][2] The simplest dendralene is buta-1,3-diene (1) or [2]dendralene. The next one is [3]dendralene (2), [4]dendralene (3) and [5]dendralene (4) and so forth. [2]dendralene (butadiene) is the only one not cross-conjugated.



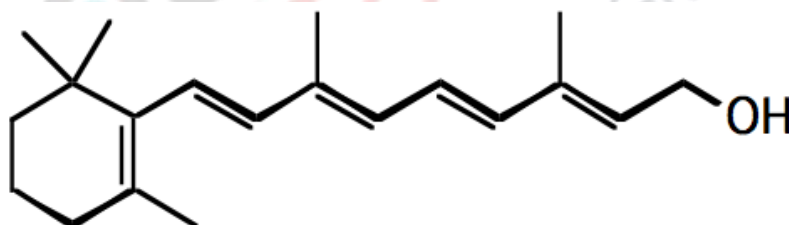
3. **[n]Radialenes** : These are cross conjugated alicyclic organic compounds. They contain n cross-conjugated exocyclic double bonds. The double bonds are commonly alkene groups but

those with a carbonyl (C=O) group are also called radialenes. Shown below are [3], [4], [5] and [6] radialenes.

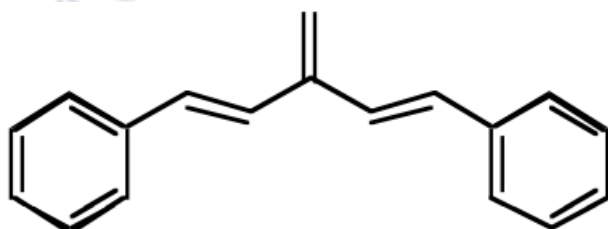


6. Comparison of conjugation, cross-conjugation and non-conjugation

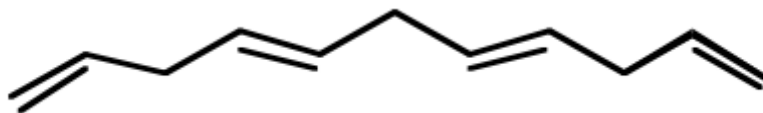
Conjugation comes in three “flavors,” the simplest of which is the normal straight-through (linear) conjugation seen in many biomolecules (such as Vitamin A).



However, it is possible for two systems to be in “cross-conjugation” with each other, as in the example below (the two benzene rings are cross-conjugated, NOT conjugated!):



Conjugation is broken completely by the introduction of saturated (sp^3) carbon: There are a lot of double bonds, but there is NO conjugation in this molecule.



7. Summary

- Resonance is very common and significant feature of many organic molecules. Due to its presence, there is a pronounced influence on the structure, chemical reactions and physical properties of such molecules.
- Resonance energy is defined as the energy difference between the most stable resonating structure and the resonance hybrid structure.
- Resonance increases stability by increasing the bonding between adjacent atoms and by distributing charge over a greater number of atoms.
- *A cross-conjugated system has a double-bonded unit single-bonded to one of the middle atoms of another conjugated chain.* On the other hand, a normal conjugated system such as a polyene typically has alternating single and double bonds along consecutive atoms.
- Conjugation is broken completely by the introduction of saturated (sp^3) carbon: