# Introduction to Organic Chemistry | Part [B]

## RESONANCE & AROMATICITY Section - 5

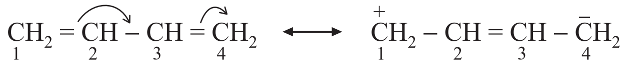
### Resonance

When a molecule or ion can be represented by two or more structures which have the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance. The various structures are called *contributing* or *resonating structures*. None of these structures truly represents all the properties of that molecule or ion. The actual structure is a *resonance hybrid* of several contributing structures.

It generally occurs when there is a conjugation of π - bonds (alternate double - single - double bond arrangement) known as *conjugated system*. It also takes place when there is double bond (C = C or C = O) alongwith a group (G) present in the carbon chain having a lone pair.

*Consider resonance in* 1, 3-*Butadiene* (having a conjugated system) :

- π - electrons moves from first carbon atom to last carbon atom resulting in different structure.



$$\underset{1}{CH_2} = \underset{2}{CH} - \underset{3}{CH} = \underset{4}{CH_2} \longleftrightarrow \overset{+}{\underset{1}{CH_2}} - \underset{2}{CH} = \underset{3}{CH} - \overset{-}{\underset{4}{CH_2}}$$

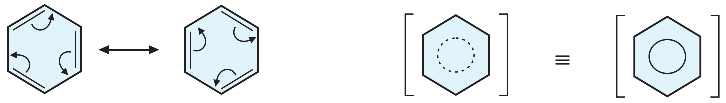
(I) (II)

Note that the relative atomic arrangement of four carbon atoms is same in both the structures (I) and (II).

Resonance hybrid (actual structure) of butadiene is represented as follows (in square brackets) :

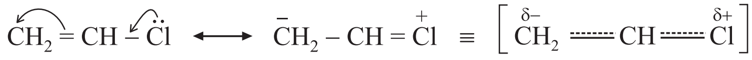
$$\left[ H_2\overset{\delta+}{C} \text{-----} HC \text{-----} CH \text{-----} \overset{\delta-}{CH_2} \right]$$

- *Consider resonance in Benzene* ($C_6H_6$) :



Kekule structures Resonance Hybrid

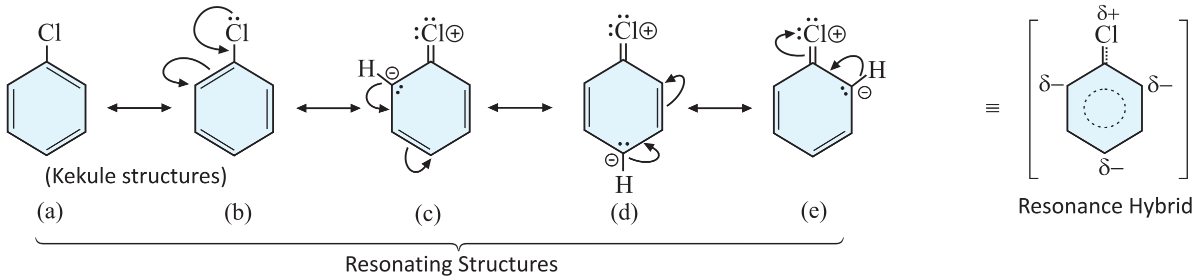
- *Consider resonance in Vinyl Chloride* : Observe that group having a lone pair i.e., Cl is in conjugation with double (C = C).

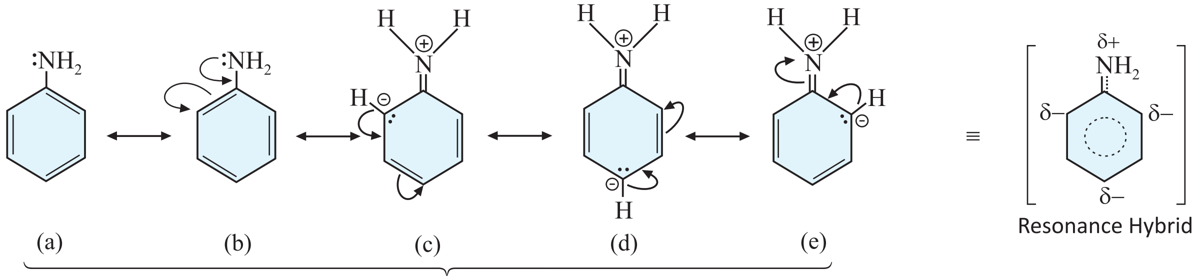


$$CH_2 = CH - \ddot{C}l \longleftrightarrow \overset{-}{C}H_2 - CH = \overset{+}{C}l \equiv \left[ \overset{\delta-}{CH_2} \text{-----} CH \text{-----} \overset{\delta+}{Cl} \right]$$

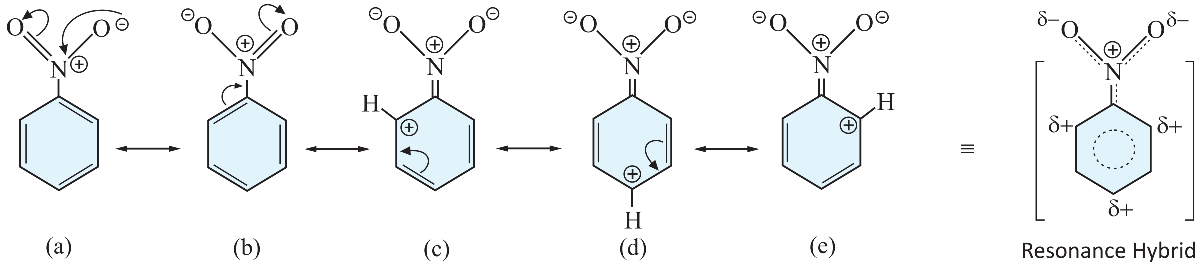
(I) (II) Resonance Hybrid

The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams.





Resonating Structures

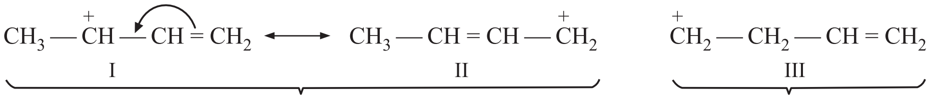


Resonating Structures

## Rules for Resonance

1. **No real existence of Resonance structures :** Although the resonating structures have no real existence of their own, these structures are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonating structures or contributing structures. We connect these structures by double-headed arrows (↔), and we say that the real molecule or ion is a hybrid of all of them.

2. **While writing Resonance structures we are only allowed to move electrons :** The relative positions of the nuclei of the atoms must remains the same in all of the structures. Structure III is not a resonance structure of I or II, in the given example, because in order to form it, we would have to move a hydrogen atom and this is not permitted :



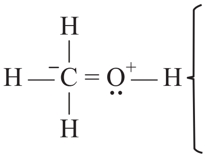
$$\underbrace{\underset{\text{I}}{CH_3-\overset{+}{C}H-CH=CH_2} \longleftrightarrow \underset{\text{II}}{CH_3-CH=CH-\overset{+}{C}H_2}}_{} \qquad \underbrace{\underset{\text{III}}{\overset{+}{C}H_2-CH_2-CH=CH_2}}_{}$$

These are resonance structures

This is not a proper resonance structure of I or II because a hydrogen atom has been moved

Actually speaking, when we move electrons, we move only those of $\pi$ bonds (as in the example above) and those of non-bonding electron pairs (such as lone pairs).

3. **All of the structures must be proper Lewis structures :** We should not write structure in which carbon has five bonds, for example :

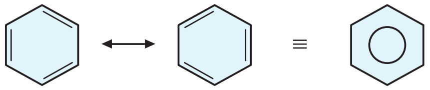


This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the First major row of the periodic table cannot have more than eight electrons in their valence shell.

**4.** **Resonance Stabilisation :** The energy of the actual molecule (Resonance hybrid) is lower than the energy of any one of all the contributing structures. Hence the resonance hybrid is more stable form.

**5.** **The more stable a structure is, the greater is its contribution to the hybrid.**

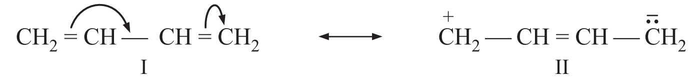
For example, benzene is highly resonance stabilized because it is a hybrid of the two equivalent forms that are highly stable.


Resonance structures

Resonance Hybrid
(highly stable)

**6.** The following rules will help us in making decisions about the relative stabilities of resonance structures.

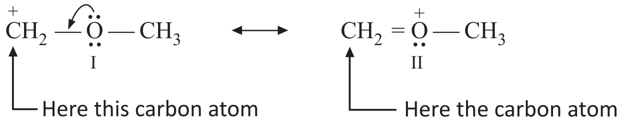
**(a)** **The more covalent bonds a structure has, the more stable it is :** This is because a covalent bond lowers the energy of atoms. This means that out of the following two structures for 1, 3-Butadiene, I is the most stable and hence imparts greater contribution to the stability of resonance hybrid.



$$\underset{\text{I}}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2-CH=CH-\overset{-}{\ddot{C}}H_2}$$

Most stable (more covalent bonds)

**(b)** **Structures in which all of the atoms have a complete valence shell of electrons are especially stable and make large contributions to the hybrid :** In the following example, the structure II makes a larger stabilizing contribution to the cation than the structure I because all of the atoms of structure II have a complete valence shell. Also note that structure II has more covalent bonds than structure I.

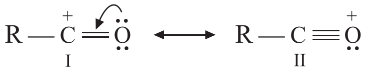


$$\underset{\text{I}}{\overset{+}{C}H_2-\ddot{\underset{..}{O}}-CH_3} \longleftrightarrow \underset{\text{II}}{CH_2=\overset{+}{\underset{..}{O}}-CH_3}$$

Here this carbon atom has only six electrons.

Here the carbon atom has eight electrons

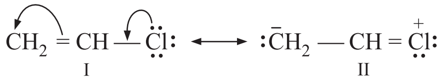
On the same pattern the structure II of the acyl carbonium ion is more stable than I



$$\underset{\text{I}}{R-\overset{+}{C}=\ddot{\underset{..}{O}}} \longleftrightarrow \underset{\text{II}}{R-C\equiv\overset{+}{\underset{..}{O}}}$$

(acyl carbonium) (more stable)

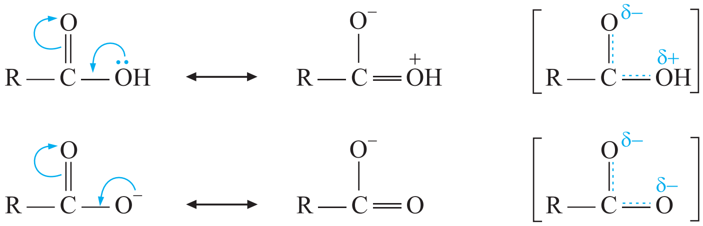
**(c)** **Charge separation decreases stability :** Separating opposite charges requires energy, hence the structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation. This means that of the following two structures for vinyl chloride, structure I makes a larger contribution because it does not have charge separation (This does not mean that structure II does not contribute to the hybrid ; it just means that the contribution made by II is smaller).



$$\underset{\text{I}}{CH_2=CH-\ddot{\underset{..}{Cl}}:} \longleftrightarrow \underset{\text{II}}{:\overset{-}{C}H_2-CH=\overset{+}{\underset{..}{Cl}}:}$$

**(d) Resonance contributors with negative charge on highly electronegative atoms are more stable than ones with negative charge on less or nonelectronegative atoms :** Conversely, resonance contributors with positive charge on highly electronegative atoms are less stable than ones with positive charges on nonelectronegative atoms.

- Observe the rules (c) and (d) above are illustrated beautifully in the following illustrations :

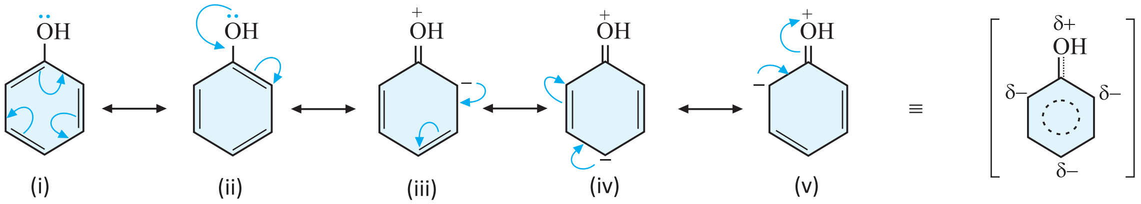


Weakly stabilised by Resonance

Strongly stabilised by Resonance

Carboxylic acids (RCOOH) are less stable than carboxylate ions ($RCOO^-$) because in carboxylic acids, there is charge separation in one of the resonating structure.

Structures where *formal charges* don't suit the electronegativity of the atom on which they rest, are less stable e.g., consider the resonating structure of phenol.



Resonating Structures

Hybrid Structure

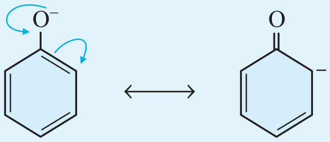
Structure (i) and (ii) are more stable than the others. These are also known as Kekule Structures.

Structures (iii), (iv) and (v) are less stable due to :

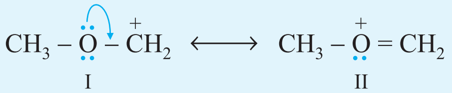
**(a)** charge separation **(b)** +ve charge over Oxygen atom

**Illustration - 9** *In each of the following pairs showing resonating structures, identify which is more stable and why ?*

**(A)**

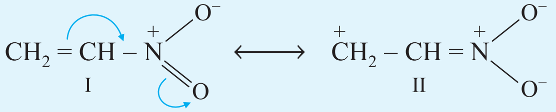


**(B)**

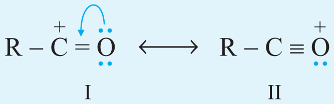


$CH_3-\ddot{O}-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{\underset{\cdot\cdot}{O}}=CH_2$

**(C)**



**(D)**



$R-\overset{+}{C}=\underset{\cdot\cdot}{\ddot{O}} \longleftrightarrow R-C\equiv\overset{+}{\underset{\cdot\cdot}{O}}$

**SOLUTION :**

**(A)** I is more stable than II, because in II, the formal charge (–) is on carbon atom which does not suit its electronegativity.

**(B)** II is more stable than I. In II, all atoms (except H-atom) have an octet,whereas in I, carbon has sixet (incomplete octet).

**(C)** I is more stable than II, since in I all have complete octets.

**(D)** II is more stable than I because in the former, all the atoms have complete octet.

## Aromatic (Hückel Rule), Anti-aromatic and Not Aromatic

Among planar, monocyclic, fully conjugated polyenes, only those possessing $(4n + 2)$ $\pi$ electrons, where n is a whole number, will have special stability ; that is, be aromatic.

Condition for a compound to be :

**(i) Aromatic :** Cyclic, Planar, Complete Conjugation, $(4n + 2)$ $\pi$ $e^-$s $(n = 0, 1, 2 \ldots)$

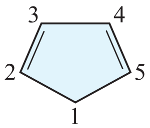
**(ii) Anti-aromatic :** Cyclic, Planar, Complete Conjugation, $4n$ $\pi$ $e^-$s $(n = 1, 2 \ldots)$

**(iii) Not aromatic :** Not cyclic OR Not Planar OR Not Completely Conjugated.

What is Complete Conjugation? Alternate single and double bonds. In other words, every Carbon has to be $sp^2$ hybridised.

**Examples :**

(a)

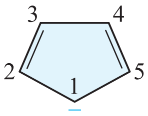


Cyclo Pentadiene

: Cyclic, Planar but not completely conjugated. Carbon-(1) is $sp^3$ hybridised.

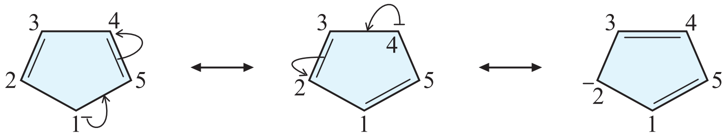
$\Rightarrow$ Compound is "Not aromatic"

(b)



Cyclopentadienyl anion

: Cyclic, Planar, Completely Conjugated. Carbon-(1) is $sp^2$ hybridised as it is clear from its resonating structures



Now count the number of $\pi$ $e^-$s in the compound as per the following rules :

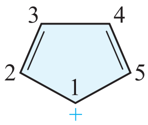
(i) Each '=' bond is counted as $2\pi$ $e^-$s (ii) Count the number of lone pairs.

If the number of lone pairs is :
- = 1 : Check bonding of atom with lone pair
  - Singly Bonded : Count as 2 $\pi e^-$s
  - Doubly Bonded : Do not count
- > 1 : Count them as exactly one lone pair and go back to the above condition corresponding to 1 lone pair.

Number of $\pi$ $e^-$s = 4 (From 2 double bonds) + 2 (one lone pair at C – 1 and is single bonded)

= 6 $e^-$s $\Rightarrow$ Compound is "Aromatic"

(c)



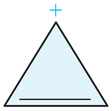
Cyclopentadienyl cation

: Cyclic, Planar, Completely Conjugated (See Resonating Structure)

*However, in anti-aromatic species delocalisation of $\pi$-electrons does not take place. i.e., they have conjugation but no delocalisation.*

Now, count the number of $\pi$ $e^-$s : 4 (From 2 double bonds)

$\Rightarrow$ Compound is "Anti-aromatic"

(d) 

Cyclopropenyl cation

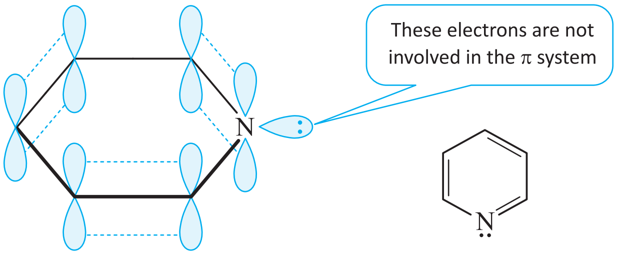
: Cyclic, Planar, Completely Conjugated.

Now, count number of $\pi$ $e^-$s : 2 (From 1 double bond)

⇒ Compound is "Aromatic"

***Note :*** Cyclopropenyl cation is smallest aromatic species.

**(e) Pyridine : ($C_5H_5N$) :**



Cyclic, Planar, Completely Conjugated.

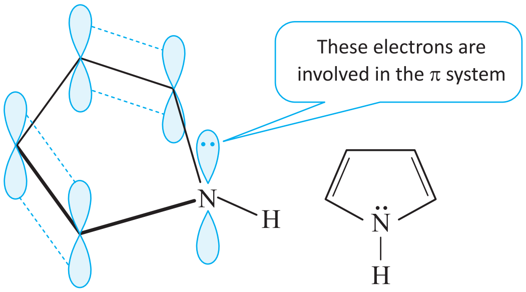
6 $\pi$ $e^-$s (From 3 double bonds)

**Note :** 'N' has 1 lone pair and is doubly bonded.

So, this will not be counted.

⇒ Compound is "Aromatic"

**(f) Pyrrole : $C_4H_4NH$**



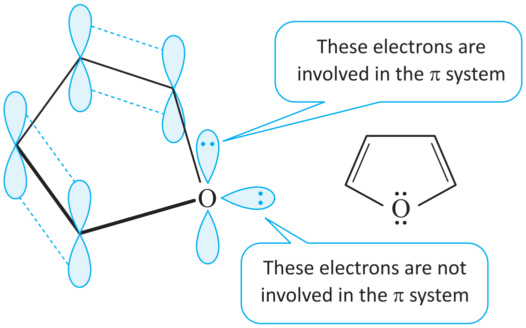
Cyclic, Planar, Completely Conjugated.

4 $\pi$ $e^-$s (From 2 double bonds) + 2 $\pi$ $e^-$s (From 1 lone pair)

⇒ Compound is "Aromatic"

**Note :** 'N' has 1 lone pair and is singly bonded.

**(g) Furan :**



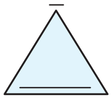
Cyclic, Planar, Completely Conjugated.

Number of $\pi$ $e^-$s

= 4 (From 2 double bonds) + 2 (From 1 lone pair)

**Note :** 'O' has 2 lone pairs. Count only one lone pair.

⇒ Compound is "Aromatic"

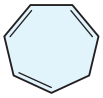
(h) 

Cyclopropenyl anion

: Cyclic, Planar, Completely Conjugated.

Number of $\pi$ $e^-$s = 2 (From 1 double bond) + 2 (From 1 lone pair) = 4

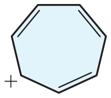
⇒ Compound is "Anti-aromatic"

(i) 

Cycloheptatriene

: Cyclic, Planar, Not Completely Conjugated.

⇒ Compound is "Not Aromatic"

(j) 

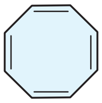
Cycloheptatrienyl cation (Tropylium ion)

: Cyclic, Completely Conjugated.

Number of $\pi$ $e^-$s = 6 (From 3 double bonds)

⇒ Compound is "Aromatic"

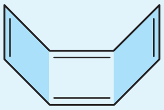
### (k) Cyclo-Octatetraene :



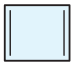
Cyclic, “Not Planar”, Completely Conjugated.

$\Rightarrow$ Compound is “Not Aromatic”

**Note :** It has a tub shape structure



**(l)**



: Cyclic, Planar, Completely Conjugated.

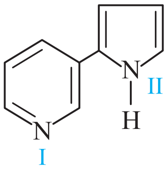
Number of $\pi$ $e^-$s = 4 (From 2 double bonds) $\Rightarrow$ Compound is “Anti-Aromatic”

- If a compound is Anti-aromatic, it is less stable than its open chain counter part i.e., $\pi$ electrons conjugation adds de-stability to the compound, if it is anti-aromatic.
- If a compound is aromatic, it adds stability to the compound through $\pi$ electrons delocalisation.

**Note :** There are thousands of aromatic compounds that are not monocyclic such as naphthalene, azzulene, anthracene etc. are polycyclic aromatic hydrocarbons.

### Illustrating the Concept of Localized and Delocalized Electrons :

Hybridisation of nitrogen I and II in the following compound is :

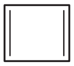


**(A)** $sp^2, sp^3$ **(B)** $sp, sp^2$

**(C)** $sp^2, sp^2$ **(D)** $sp^2, sp$

### SOLUTION : (C)

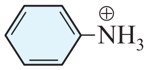
In pyridine ring electron pair of N atom is localized due to $sp^2$ hybridization and it is not the part of close loop. While is pyrrole electron pair of N is delocalized and it is part of close loop, hence hybridization state of this N atom is $sp^2$ not $sp^3$.

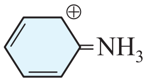
- Cyclobutadiene exist is rectangular form to gain stability, 
- COT readily reduces to form planar $C_8H_8^{2-}$ .

## IN-CHAPTER EXERCISE-C

**Choose the correct alternative. Only One choice is Correct. However, questions marked * may have More than One Correct option :**

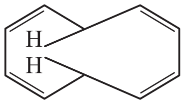
***1.** *Choose the correct statement(s) for the given resonating structures of anilinium ion.*

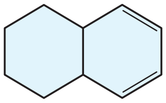
I. 

II. 

**(A)** *II is not correct because carbocations are less stable than ammonium ion*
**(B)** *I is non aromatic*
**(C)** *II is not correct as N* has 10 valence electrons
**(D)** *II is a correct resonating structure.*

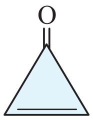
**2.** *Which statement is true for structures I and II ?*

I. 

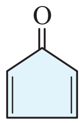
II. 

**(A)** *Compound I is aromatic, II is non aromatic*
**(B)** *Compound II is aromatic, I is non aromatic*
**(C)** *Both compounds I and II are aromatic*
**(D)** *Both compounds I and II are non aromatic*

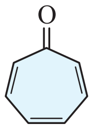
**3.** *Which of the following structure(s) is(are) aromatic ?*
*The correct option is :*



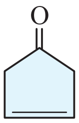
I



II



III

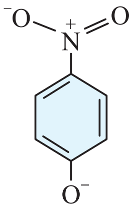


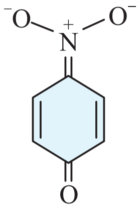
IV

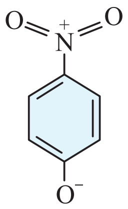
**(A)** *I, II* **(B)** *II, III* **(C)** *I, III* **(D)** *I, III, IV*

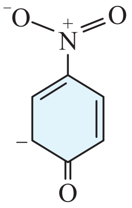
**4.** Which of the following statements about resonance is(are) correct ?
**(A)** Resonance structures may have different energies, but most stable structure determines the overall stability
**(B)** In resonating structures, the constituent atoms must be in the same position
**(C)** In resonating structures, there should not be same number of electron pairs
**(D)** Resonating structure should differ only on the location of electrons around the constituent atoms

**5.** The most unlikely representation of resonance structure of p-nitrophenoxide ion is :

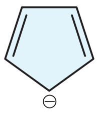
**(A)** 

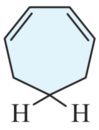
**(B)** 

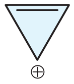
**(C)** 

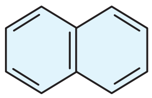
**(D)** 

**6.** Which one of the following substances is not aromatic?

**(A)** 

**(B)** 

**(C)** 

**(D)** 

## For Questions 7 - 8

**(A)** Statement-1 is True, Statement-2 is True and Statement-2 is a correct explanation for Statement-1

**(B)** Statement-1 is True, Statement-2 is True and Statement-2 is NOT a correct explanation for Statement-1

**(C)** Statement-1 is True, Statement-2 is False

**(D)** Statement-1 is False, Statement-2 is True

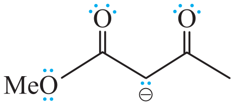
**7.** Statement 1: $\overset{+}{C}H_2-O-CH_3$ is more stable compared to $CH_3-\overset{+}{C}H-CH_3$.

Statement 2: O atom through its +M effect stabilises the positive charge over carbon in $\overset{+}{C}H_2-OCH_3$

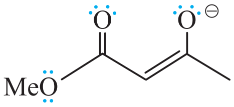
**8.** Statement : 1 $CH_3\ddot{O}-CH=CH_2 \longleftrightarrow CH_3\overset{+}{O}=CH-\overset{\ominus}{C}H_2$ is correct resonating structure.

Statement : 2 Opposite charge separation is energetically unfavourable.

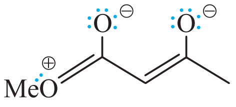
**9.** Which of the following is not a valid resonance structure of the other three?



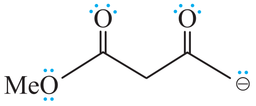
**(A)**



**(B)**



**(C)**



**(D)**

***10.** Which of the following is (are) valid as resonance structures of the pentadienyl cation?

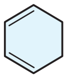
**(A)** $CH_2=CH-CH=CH-\overset{\oplus}{C}H_2$

**(B)** $CH_2=CH-\overset{\oplus}{C}H-CH=CH_2$

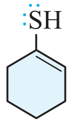
**(C)** $CH_3-CH=CH-CH=\overset{\oplus}{C}H$

**(D)** $CH_2=CH-CH=\overset{\oplus}{C}-CH_3$

**11.** Which of the following species are conjugated ?

**(A)** 

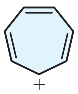
**(B)** $CH_2=C=CH-\ddot{N}H_2$

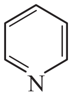
**(C)** 

**(D)** All of these

**12.** Which of the following species contains six pi conjugated electrons ?

**(A)** $CH_2=CH-CH=CH-\overset{-}{C}H_2$

**(B)** 

**(C)** 

**(D)** All of these

**13.** Which is correct for x and y ?

$CH_2=CH-\ddot{C}l:$ ↓ bond length x A°

$CH_3-CH_2-\ddot{C}l:$ ↓ bond length y A°

**(A)** x = y

**(B)** x > y

**(C)** x < y

**(C)** can't be predicted

**14.** Isocyanic acid, HNCO can be represented by the following three contributing structures :

$$\underset{I}{H-\ddot{N}=C=\ddot{O}} \longleftrightarrow \underset{II}{H-\overset{-}{\ddot{N}}-C\equiv\overset{+}{O}:} \longleftrightarrow \underset{III}{H-\overset{+}{N}\equiv C-\overset{-}{\ddot{O}}:}$$

Order of stability of the three contributing structures is :

**(A)** I > II > III

**(B)** I > III > II

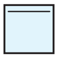
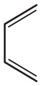
**(C)** I > II = III

**(D)** I = II = III

**15.** Which of the following pairs represent the phenomenon of resonance ?

**(A)** $CH_3-CH_2-CH=O$ and $CH_3-CH=CH-OH$

**(B)** $CH_3\overset{+}{C}HOH$ and $CH_3CH=\overset{+}{O}H$

**(C)**  and 

**(D)** $HC\equiv N$ and $H-N\equiv C$

**16.** Cyanate ion, $CNO^-$ has three important resonating structures :

$$\underset{\text{I}}{O=C=N^-} \longleftrightarrow \underset{\text{II}}{^-O-C\equiv N} \longleftrightarrow \underset{\text{III}}{^+O\equiv C-N^{2-}}$$

Which of the above structures contribute more to the resonance hybrid ?

**(A)** I **(B)** II **(C)** I and II equal **(D)** All equal

**17.** In which of the following, resonance will be possible ?

**(A)** $CH_2=CH-CH_2-CHO$ **(B)** $CH_2=CH-CHO$

**(C)** $CH_2=CH-COOH$ **(D)** $CH_2=CH-CH_2-CH=CH_2$

## ORGANIC REACTIONS [BASICS] Section - 6

Organic compounds are covalent bonded. The carbon atom in these may be $sp^3$, $sp^2$ or $sp$ hybridised. Hydrocarbons are almost non-polar, but their derivatives containing functional groups are polar covalent compounds. To understand and visualise the mechanisms of organic reactions, first we must go into details of various types of electrical effects that monitor the properties of various organic compounds. Then we have to understand various types of Substrates (main organic compound) ; Intermediates formed from these substrates; the various types of Reagents and the Medium (solvent) in which organic reactions occur.

All organic reactions can be classified into one of the following three categories for the purpose of understanding reaction mechanisms :

**(i)** Substitution Reactions **(ii)** Addition Reactions **(iii)** Elimination Reactions

Above three categories of reactions may involve : Rearrangement, Cyclisation (Ring opening & Ring closing) and stereo specific changes (involving optical and geometrical isomers), oxidation and reduction.

**1.** **Substrate :** It is the main organic compound acting as reactant and reacts with a reagent to give an new organic compound as main product. Substrates in general are of two types :

Nucleophilic : The organic compounds which have "electron rich centre or area" are referred to as nucleophilic in nature. They are acted upon by electron seeking reagents.

Alkenes, alkynes and benzene and its derivatives are some of such important substrates.

Electrophilic : The organic compounds which have "electron definicient centre or area" are referred to as Electrophilic in nature. They are acted upon by electron rich reagents usually most of organic derivatives containing functional groups act as electrophilic substrates. Organic Halides, Alcohols, Ethers, Aldehydes & Ketones and Carboxylic Acids & Derivatives are some of the important electrophilic substrates.

$$\text{Electrophilic centre} \rightarrow \overset{\delta+}{C}-\overset{\delta-}{G}$$

**2.** **Reagents :** Based on the attack by the type of attacking reagent, these are further categorised.

The main type of attacking reagents are :

**(a)** **Nucleophile :** Electron rich species, looking to attack a +vely charged centre (Electrophilic substrates).

These are classified as follows :

**Charged :** $H^-, OH^-, RO^-, CH_3^-, X^-, HS^-$ . . . .etc.