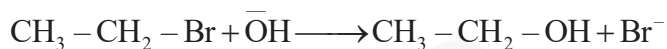


## ELECTRONIC DISPLACEMENT EFFECT

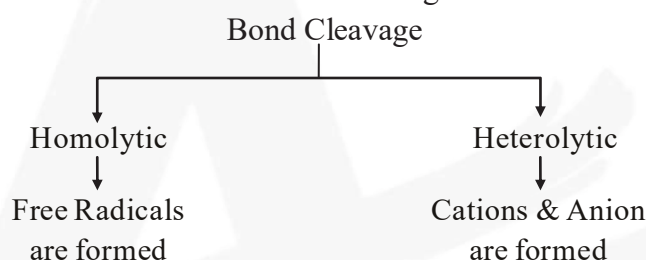
## BOND CLEAVAGE

- Organic reaction is a process in which breaking and formation of covalent bonds takes place.
- In organic reaction, the organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the reactant or substrate and the new compound formed is known as the product.
- The chemical species (more reactive) which causes the change is called reagent.



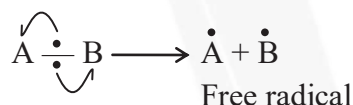
Substrate      Reagent      Product

Breaking of covalent bond is known as bond cleavage. A bond can be broken by two ways :



## Homolytic Fission or Homolysis

- The covalent bond is broken in such away that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.
- Homolytic bond fission gives free radical as the reaction intermediate.



- The factor which favours homolysis is zero or a small difference in electronegativity between A and B.
- Homolytic bond fission takes place in gaseous phase or in the presence of non polar solvents (CCl<sub>4</sub>, CS<sub>2</sub>).

## Heterolytic Bond Fission or Heterolysis

- In heterolysis, the covalent bond is broken in such away that one species (i.e., less electronegative) loss its own electron, while the other species (i.e., more electronegative) gains both the electrons.



- Thus formation of opposite charged species takes place. In case of organic compounds, if positive charged is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.
- The factor which favours heterolysis is a greater difference of electronegativity between A and B.

## REACTION INTERMEDIATES

The formation of reactant intermediate by the breaking of covalent bond of the substance. They are short-lived species (half life  $\geq 10^{-6}$  sec.) and are highly reactive. few important types of reaction intermediates are as follows.

(1) Carbocation              (2) Carbanion              (3) Free radical

**1. Carbocations**

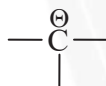
An organic species which has a carbon atom bearing six electrons in its outermost shell and has a positive charge is called a carbocation.

**Characteristics of Carbocation :**

- Carbocation have a positive charge on carbon.
- Positively charged carbocation has only six electrons in the outermost shell. It has an incomplete octet. So it behaves like a Lewis acid.
- Since all electrons are in paired state so carbocations are diamagnetic.
- Carbocations are  $sp^2$  hybridised.
- Carbocations are planar.
- Carbocations are formed in polar solvent.
- It stabilize by presence of electron donating group (EDG)

**2. Carbanions**

Anion of carbon is known as carbanion. Carbanion carries three bond pairs and one lone pair, thus making the carbon atom negatively charged thus carbanion may be represented as

**Characteristic of Carbanions :**

- It is formed by heterolytic bond fission.
- It behaves as charged nucleophile.
- It is diamagnetic in character because all eight electrons are paired.
- Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is  $sp^3$  and geometry is pyramidal



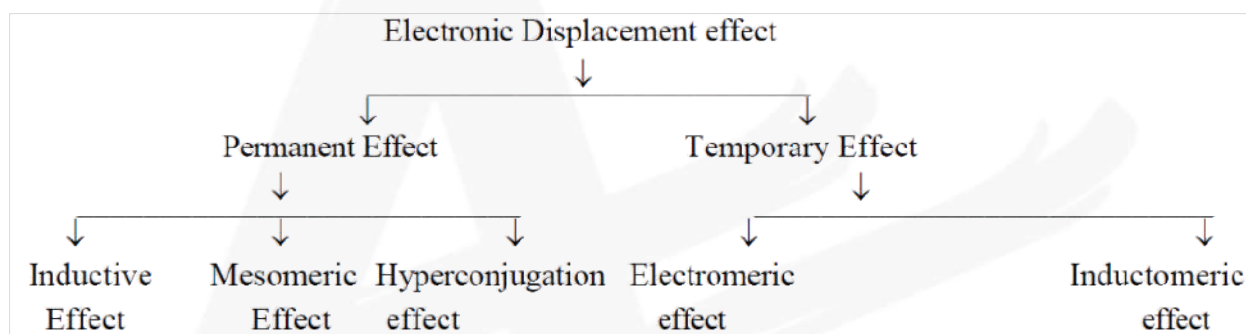
- It reacts with electrophiles.
- It stabilize by presence of electron withdrawing group (EWG)

## (Organic Chemistry)

## 3. Carbon Free Radical

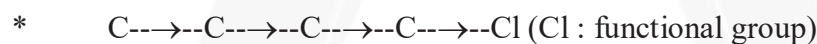
- (i) Carbon free radicals are odd electron species in which carbon atom bears the odd electron.
- (ii) Homolytic bond fission of a covalent single bond gives rise to free radicals.
- (iii) There are seven electrons in the outer most shell of carbon free radicals.
- (iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.
- (v) Carbon free radicals are normally  $sp^2$  hybridized
- (vi) Free radicals are neutral electrophiles.
- (vii) It stabilize by presence of electron donating group (EDG)

## ELECTRONIC DISPLACEMENT EFFECTS



## INDUCTIVE EFFECT (I-EFFECT)

The permanent partial displacement of sigma electrons due to electronegativity difference between groups towards more electronegative atom is known as inductive effect.

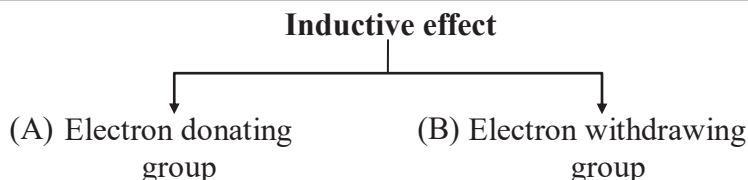


- This effect is transmitted through the chain of  $\sigma$  bonds and diminishes, with increasing chain length. Inductive effect is thus

## CHARACTERISTIC OF INDUCTIVE EFFECT

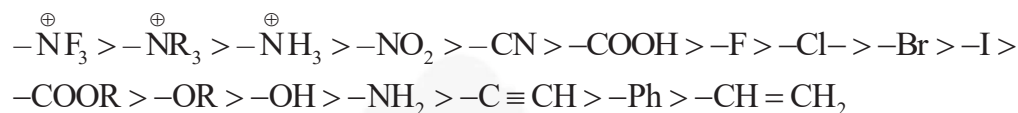
- (i) It is a permanent effect and distance dependent.
- (ii) After three carbon effect is decreases.
- (iii) Operates through  $\sigma$  bonds
- (iv) Polarisation of electrons is always in single direction.
- (v) It is generally observed in saturated compounds.
- (vi) Its magnitude (i.e., electron withdrawing or donating power) decreases with increase in distance. On the basis of electron releasing group (ERG) or elctron withdrawing group (EWG) inductive effect, can be of two types.

There are two types of inductive effect



1. **–I groups** : The group which withdraws electrons is known as –I group and its effect is known as – I effect.

**–I SERIES**



2. **+I group** : The group which donates or gives electron is known as + I group and effect is known as + I effect.

e.g., Alkyl groups,  $-\overset{\ominus}{\text{O}}, -\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$  are + I groups. (Generally negative charged atoms or groups)

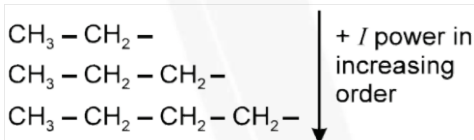
- (a) **+I power of different type groups and anions** :

\*  $-\text{CH}_2^- > -\text{NH}^- > -\text{O}^- > -\text{COO}^- > \text{tertiary alkyl} > \text{secondary alkyl} > \text{primary-alkyl} > -\text{CH}_3 > -\text{H}$   
+ I power in decreasing order with reference to H-atom

- (b) **+ I power of same type of alkyl groups** :

+ I power  $\propto$  number of C's in same type of alkyl group

For example:



**APPLICATIONS OF INDUCTIVE EFFECT**

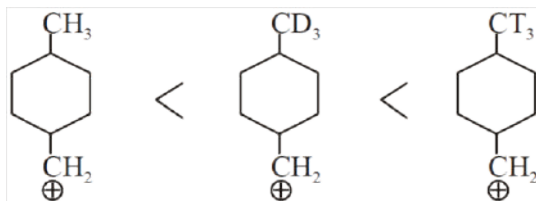
- (A) **Stability of reaction intermediates**

(i) Stability of carbocation    (ii) Stability of free Radical    (iii) Stability of carbanion

- (i) **Stability of carbocation**

Stability of carbocation  $\propto$  Presence of electron releasing group

$$\propto + \text{I group} \propto \frac{\text{I}}{-\text{I group}}$$

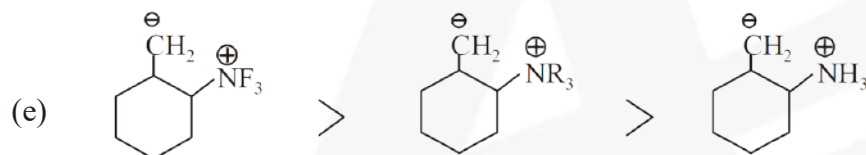
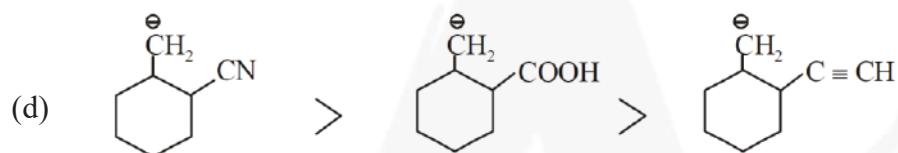
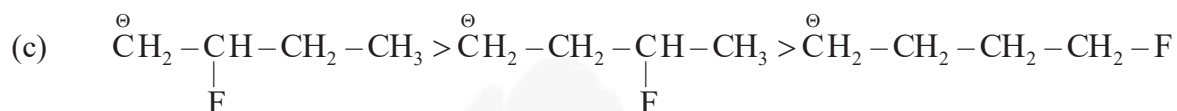
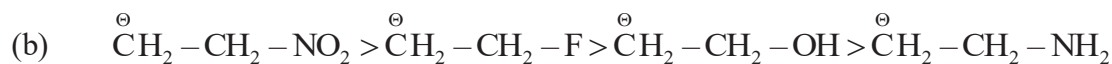
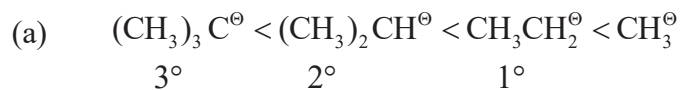




(Organic Chemistry)

## (iii) Stability of carbanion

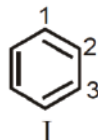
Stability of carbanion  $\propto$  Presence of electron withdrawing group  $\propto$  -I group  $\propto \frac{1}{+I \text{ group}}$ .



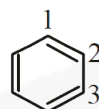
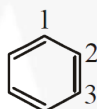
## RESONANCE

When a molecule or ion cannot be represented by single Lewis dot structure and more than one structure are needed to represent all properties of the molecule these structures are known as resonating structure and combined structure of all resonating structure are known as resonance hybrid and this phenomenon is known as resonance.

Consider structures of benzene :

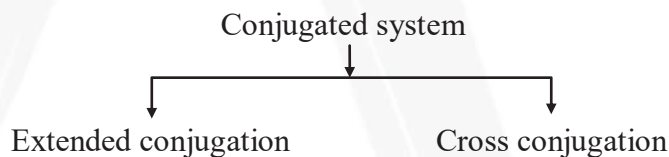


According to the given structure  $C_1-C_2$  bond length should be smaller than  $C_2-C_3$  bond length but  $C_1-C_2$  and  $C_2-C_3$  bond length must be equal. So this bond length data is not explained by single structure so we need two structures of benzene which is following

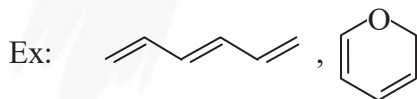


I and II are resonating structures of  $C_6H_6$ .

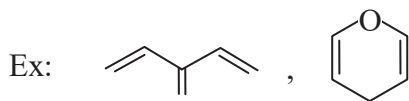
- Resonating structure are hypothetical and actual structure is a resonance hybrid.
- Resonance generally occurs when there is a conjugation of  $\pi$ -bonds (alternate double - single - double bond arrangement)



- (1) **Extended Conjugation:** Conjugated system having at least 3 segments, also which has unidirectional flow of electrons are known as extended conjugation.



- (2) **Cross Conjugation:** Conjugated system having at least 3 segment and also having opposite direction of flow of electrons with no interaction between terminal segment is known as cross conjugation.



**NOTE:** Extended conjugated system more stable than cross conjugated system if number of segment are equal.

## (Organic Chemistry)

**Condition for Resonance :**

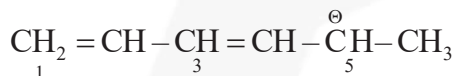
- (i) Compound must be planar  $sp^2$  or  $sp$ -hybridised not  $sp^3$  hybridised.
- (ii) Conjugation – System in which p-orbitals are arranged parallel and continuous to each other is considered as conjugated system.
- (1) Negative charge electron alternate to  $\pi$  electron conjugation
- (2) Lone pair electron alternate to  $\pi$  electron conjugation
- (3)  $\pi$  electron alternate to  $\pi$  electron conjugation
- (4)  $\pi$  electron alternate to vacant orbital (Positive charge) conjugation
- (5)  $\pi$  electron alternate to odd electron (free radical) conjugation
- (6) Lone pair electron alternate to vacant orbital (Positive charge) conjugation

**Conjugate positions of the molecule :**

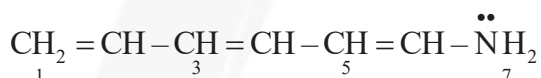
Alternate positions of the molecule having  $\pi$  bond, positive charge, negative charge, odd electron or lone pair of electrons are known as conjugative positions.



1, 3, 5 are alternate positions having  $\pi$  bonds. Hence these positions are known as conjugate positions.



1, 3 and 5 are conjugate positions.

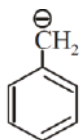


1, 3, 5, 7 are Conjugate positions

**Note :** Compound having at least two conjugate positions is known as conjugated compound.

**TYPES OF CONJUGATIONS**

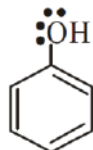
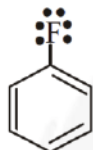
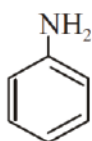
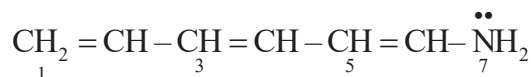
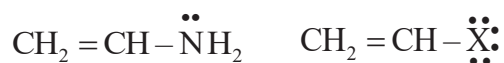
- (1) **Negative charge electron alternate to  $\pi$  electron conjugation :** If in a conjugated system  $\pi$  bond and  $\ominus$  charge at alternate position so conjugation is known as negative charge electron alternate to  $\pi$  electron conjugation



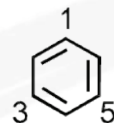
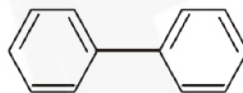
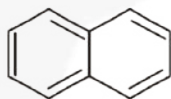
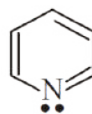
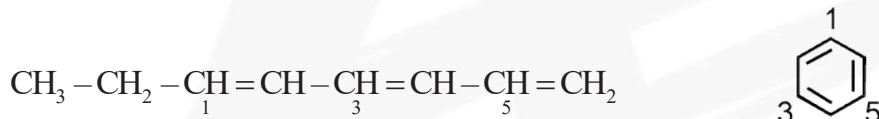


(Organic Chemistry)

- (2) **Lone pair electron alternate to  $\pi$  electron conjugation** : If in a conjugated system  $\pi$  bond and lone pair at alternate position so conjugation is known as lp electron alternate to  $\pi$  electron conjugation.

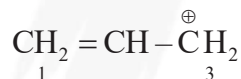


- (3)  **$\pi$  electron alternate to  $\pi$  electron conjugation** : If  $\pi$  bond alternate with  $\pi$  bond so conjugation is known as  $\pi$  electron alternate to  $\pi$  electron conjugation

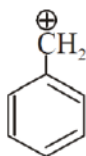


All of the above compounds have  $\pi$ ,  $\pi$  conjugation.

- (4)  **$\pi$  electron alternate to vacant orbital (Positive charge) conjugation** : If  $\pi$  bond alternate with vacant orbital so conjugation is known as positive charge alternate to  $\pi$  electron conjugation.



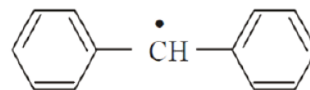
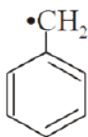
It has positive charge,  $\pi$  conjugation.



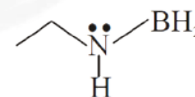
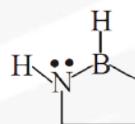
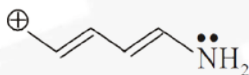
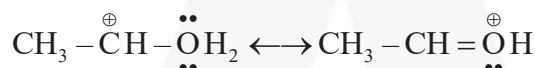
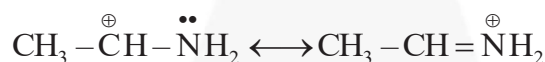
These species has two type of conjugation  $\pi$  electron alternate to  $\pi$  electron conjugation and positive charge alternate to  $\pi$  electron conjugation.

(Organic Chemistry)

- (5)  $\pi$  electron alternate to odd electron (free radical) conjugation : If  $\pi$  bond and odd  $e^-$  are in alternate position.

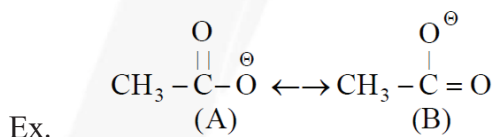


- (6) Lone pair electron alternate to vacant orbital (Positive charge) conjugation : If lone pair and vacant orbital are alternate position

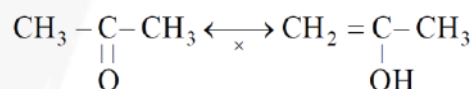


### Rules to draw valid resonating structures

1. Electron flow occurs from high electron density to low electron density. Negative charge  $\rightarrow$  Lone pair electron  $\rightarrow \pi$ -bond electron  $\rightarrow \delta^+ \rightarrow$  positive charge
2. Position of atom cannot be change, only the  $\pi$ -electrons are delocalised.

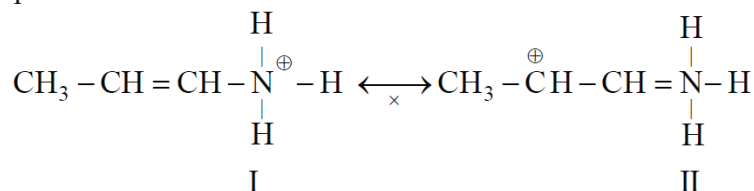


A & B are Resonance forms.



Above forms are not resonating forms because position of H is changed.

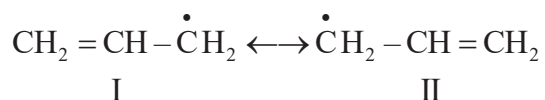
3. Second period elements should not violate the octet rule while drawing resonating structures



Above structures are not resonance form because in structure II, nitrogen has 10 valence electrons which violates octet rule.

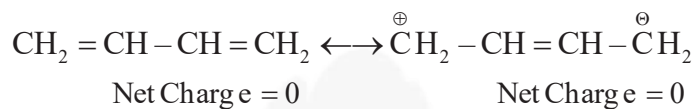
(Organic Chemistry)

4. Each Resonating structures must have the same number of unpaired and paired electrons.



I & II are resonating structure because both have 8 paired electrons and 1 unpaired electron

5. Net charge should be conserved in all resonating structures.



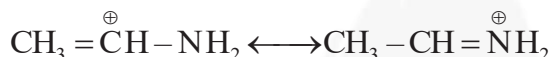
Both structures have same net charge so both are resonance forms.

## RULES FOR DETERMINING STABILITY ORDER OF RESONATING STRUCTURES

1. Among various resonating structure non polar resonating structure is more stable than polar resonating structure more number of covalent bonds is considered to be more contributing than others.

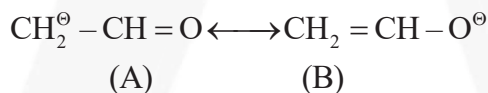


2. If two resonance structures have same number of bonds then that structure in which octate of every atom is complete is more contributing than structure having incomplete octate.



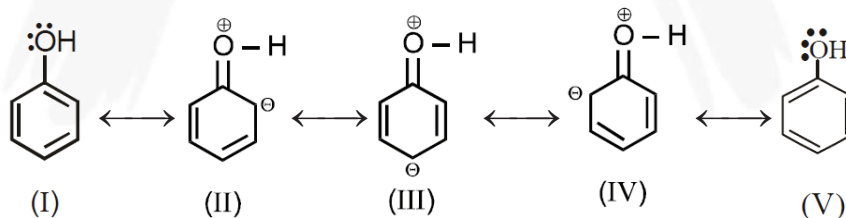
3. If resonating structures have same number of bonds then the neutral structure is more stable than charged structure and if both are charged Resonating structure then less charged resonating structure is more stable.

4. In case of charged resonating structures, the most stable one is that in which the positive and negative charge reside on the most electropositive and most electronegative atoms of the structure respectively.



stability of B > A

5. Resonating structure in which unlike charges are closer is more contributing than that structures in which unlike charges are far away.



6. Resonating structure in which like charges are farther away is more contributing as compared to structure in which like charges are closer.

## RESONANCE ENERGY

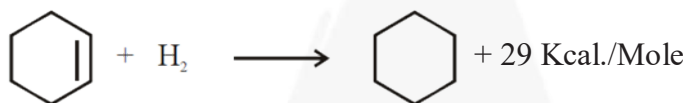
The energy difference between most stable resonating structure and resonance hybrid is known as resonance energy.

- It's the experimental value which is calculated by heat of hydrogenation (HOH)
- Higher the value of resonance energy, greater is the resonance stabilization.

## Resonance Energy of Benzene :



The resonance energy of benzene is calculated from the heat of hydrogenation as given below:



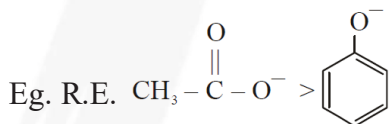
but experimental value for benzene is 51 Kcal./mole so,

$$\begin{aligned} \text{Resonance energy} &= \text{Calculated value} - \text{Experimental value} \\ &= 87 - 51 \\ &= 36 \text{ Kcal./mole} \end{aligned}$$

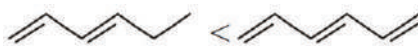
Resonance energy  $\propto$  extent of resonance  
 $\propto$  quality of resonance

## Resonance energy comparison

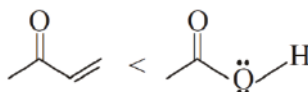
1. Consider better resonance or equivalent resonating structures, molecules having equivalent resonating structures must have more resonance energy, than non-equivalent resonating structures.



2. Aromatic compound have more resonance energy than non-aromatic compound.
3. In case of larger conjugation, more will be the Resonance energy.



4. Resonance energy will be more, when  $\pi$ -bond, lone pair conjugation is present than  $\pi$ ,  $\pi$ -conjugation



## COMPARISON OF BOND LENGTH, BOND STRENGTH AND BOND ROTATIONAL ENERGY BARRIER

Bond length  $\propto$  extent of resonance (if initially bond is double)

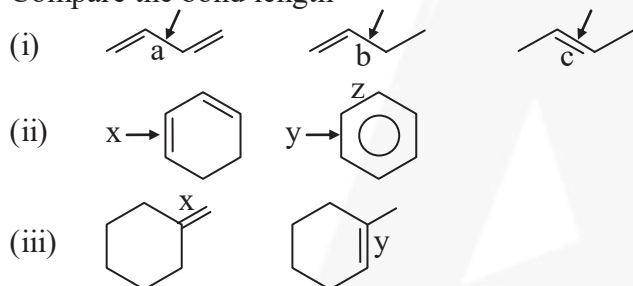
$$\propto \frac{1}{\text{Extent of resonance}} \quad (\text{if initially bond is single})$$

$$\propto \frac{1}{\text{bond strength}}$$

$$\propto \frac{1}{\text{bond rotational energy barrier}}$$

## DO YOURSELF – 2

Compare the bond length



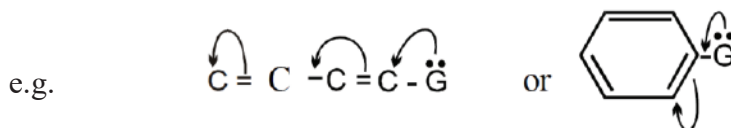
## MESOMERIC EFFECT OR RESONANCE EFFECT

**Definition:** Permanent displacement of  $\pi$  electrons cloud of a conjugated system due to p-orbital of directly attached atoms or groups is known as mesomeric effect/resonance effect.

- This is a permanent effect where the displacement of conjugational  $\pi$  electrons are influenced by the group attached to carbon chain.
- There is a push or pull of  $\pi$  electrons of the conjugated system of molecule.
- M effect operates only in the conjugated system.
- If the conjugation is not available, M effect does not propagate further.
- M-effect has no correlation with the electro negativity of the connecting atom of the group
- M-effect is two type; +M and -M

There are two types of mesomeric effect

- +M effect (+R) :** If the group pushes the electrons into the  $\pi$  electron system, the effect is said as +M effect and the group is called ERG (electron releasing group) or +M group.



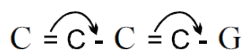
+ M Effect is shown by :  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ ,  $-\text{NHCOCH}_3$ ,  $-\text{OH}$ ,  $-\text{OR}$

**Condition :** Electron pair must be present at first atom of group.

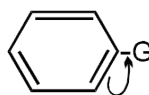
## (Organic Chemistry)

- (2) **–M effect (–R) :** If the  $\pi$  electrons are present system is pulled by the group then the effect is called –M effect and the group is called EWG group (electron withdrawing group) or –M group.

e.g.



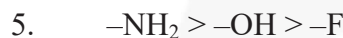
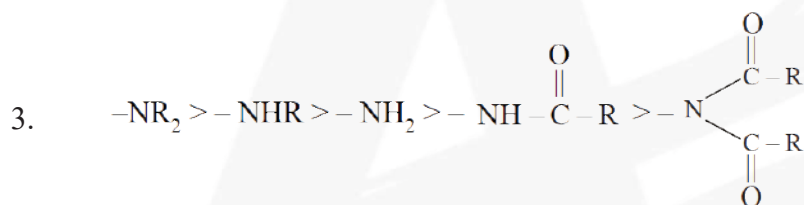
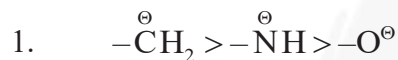
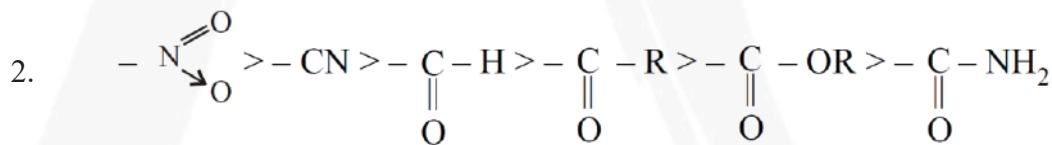
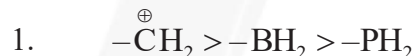
or



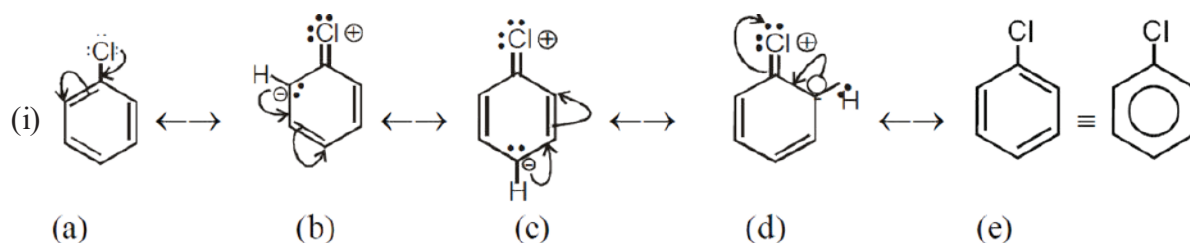
–M effect is shown by :

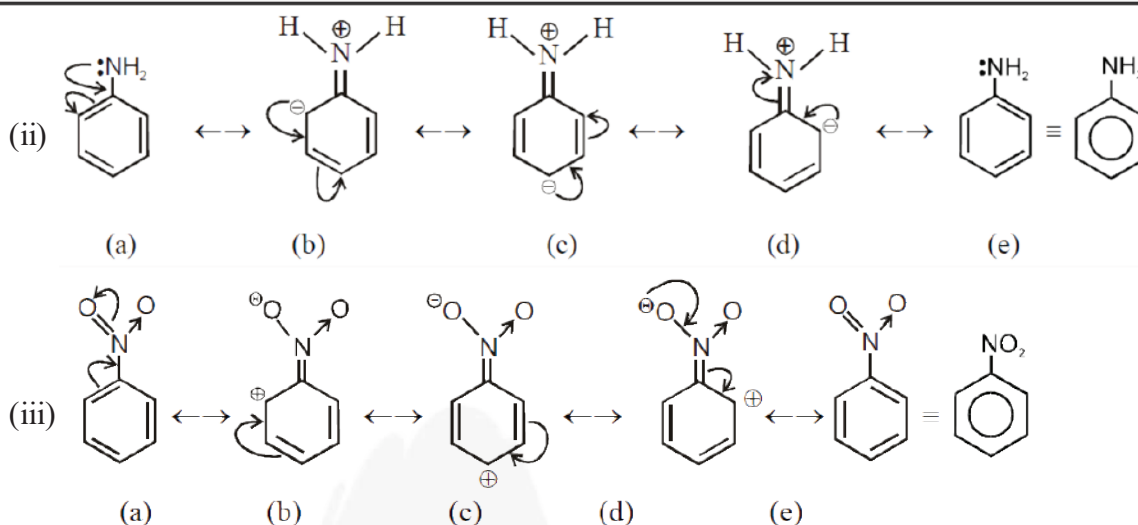
–CHO, C = O, –COOH, –NO<sub>2</sub>, –CN, –SO<sub>3</sub>H, –SO<sub>2</sub>Cl

- Condition :** (i) Vacant orbital must be present  
(ii) Multiple bond with more electron negative second atom.

**+ M effect order****–M effect order**

The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams. Note that –Cl and –NH<sub>2</sub> show + M effect and –NO<sub>2</sub> show –M effect.



**Note :**

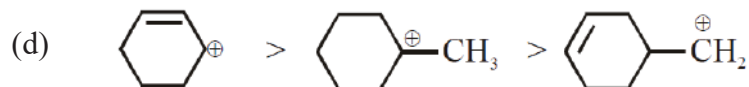
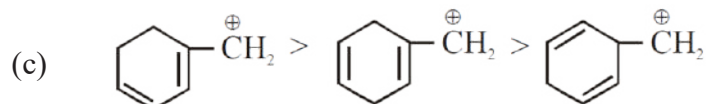
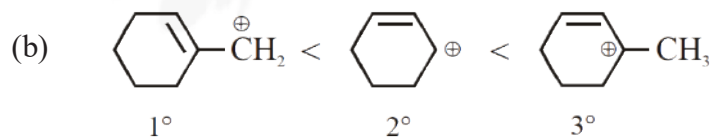
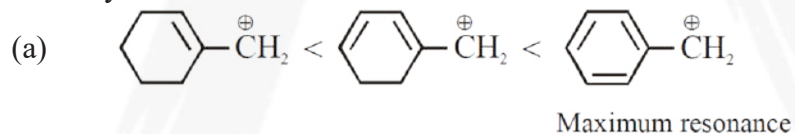
- (i) Thus, mesomeric effect works at only ortho & para position, it is absent on meta position, while inductive effect works at all three position o, m, p however intensity of effect decreases as the distance increases.
- (ii) Mesomeric effect always dominates on inductive effect except halogen (Cl, Br, I, only).

**APPLICATION OF MESOMERIC EFFECT****Stability of reaction intermediates****(i) Stability of carbocation**

- More resonance in carbocation, more stability of carbocation.
- Aromatic cations are more stable than non aromatic cations.

**Example:**

Stability order :



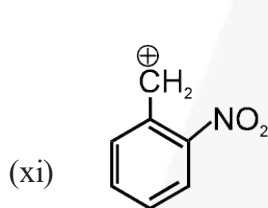


## DO YOURSELF – 3

Compare stability of following carbocations

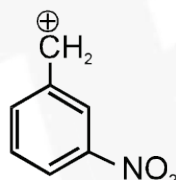
- (i)  $\text{CH}_3 - \overset{\oplus}{\underset{\text{CH}_3}{\text{C}}} - \text{CH} = \text{CH}_2, \text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CH} = \text{CH}_2, \overset{\oplus}{\text{CH}_2} - \text{CH} = \text{CH}_2$
- (ii)  $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{CH}_2}, \text{CH}_3 \rightarrow \text{CH}_2 - \overset{\oplus}{\text{CH}_2}, \text{CH}_2 = \text{CH} - \text{CH}_2 \leftarrow \overset{\oplus}{\text{CH}_2}$
- (iii)  $(\text{C}_6\text{H}_5)_3\overset{\oplus}{\text{C}}, (\text{C}_6\text{H}_5)_2\overset{\oplus}{\text{CH}}, \text{C}_6\text{H}_5\overset{\oplus}{\text{CH}_2}, \text{CH}_2 = \text{CH} - \overset{\oplus}{\text{CH}_2}, (\text{CH}_3)_3\overset{\oplus}{\text{C}}, (\text{CH}_3)_2\overset{\oplus}{\text{CH}},$   
 $\text{CH}_3 - \overset{\oplus}{\text{CH}_2}, \overset{\oplus}{\text{CH}_3}, \text{CH}_2 = \overset{\oplus}{\text{CH}}, \text{CH} \equiv \overset{\oplus}{\text{C}}$
- (vi)  $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{CH}_2}$                        $\text{C}_6\text{H}_5 - \overset{\oplus}{\text{CH}_2}$   
 allyl carbocation                      benzyl carbocation  
 Number of resonating  
 Structures = 2                      Number of resonating  
 Structures = 5

Hence the benzyl carbocation is more stable than the allyl carbocation.



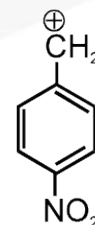
(I)

Increase in  
positive charge by  
-I and -R effect  
stability order II > III > I



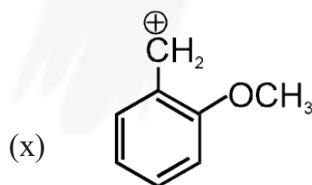
(II)

Increase in  
positive charge  
only by -I effect -



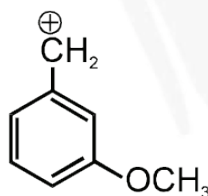
(III)

Increase in  
Positive charge by  
-I and -R effect



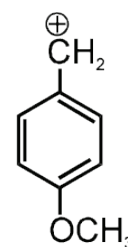
(I)

Stabilised by + R effect  
destabilised by -I effect  
-I power is maximum  
(due to distance)  
stability order III > I > II



(II)

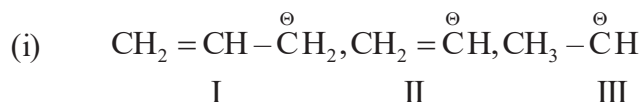
destabilised by  
-I effect only



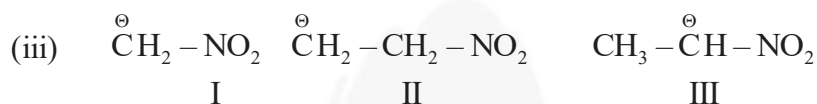
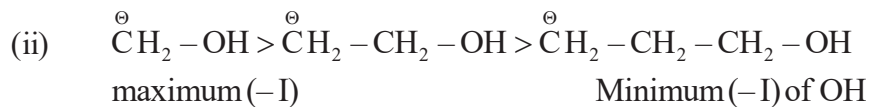
(III)

Stabilised by + R effect  
destabilised by -I effect  
-I power is minimum  
(due to distance)

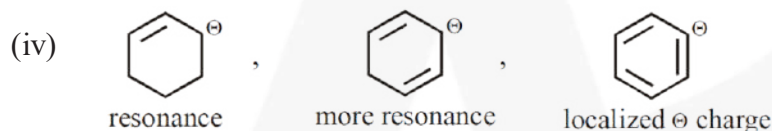
**Example:** stability order for following



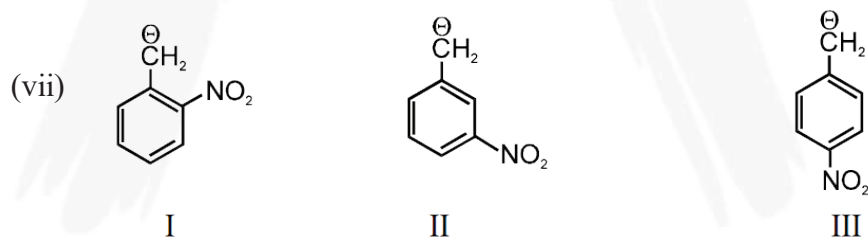
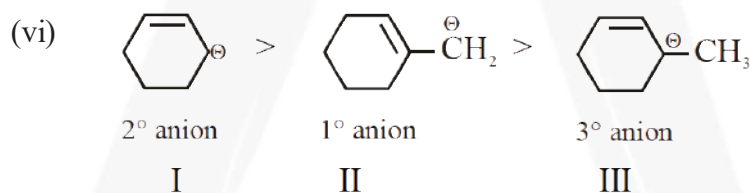
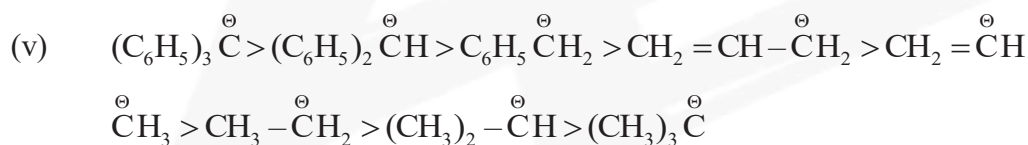
stability order  $I > II > III$



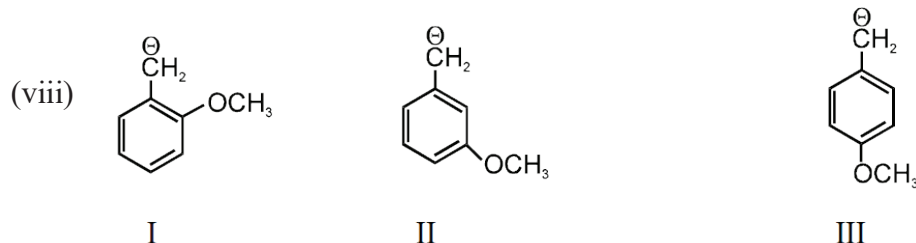
stability order  $I > III > II$



stability order  $II > I > III$



stability order  $I > III > II$

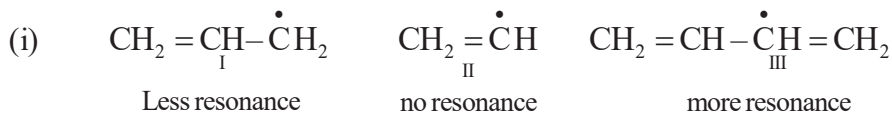
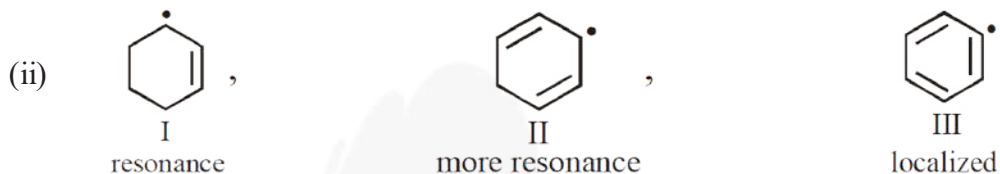
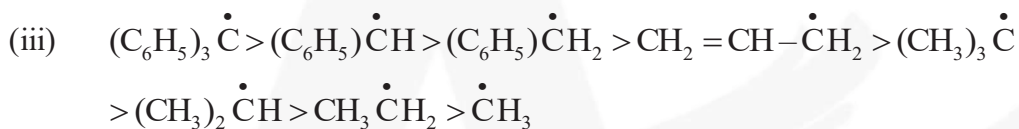


stability order  $\text{II} > \text{I} > \text{III}$

## (Organic Chemistry)

## (iii) Stability of free radicals.

- More resonance, more stability of free radical.

**Example:** Stability orderstability order  $\text{III} > \text{I} > \text{II}$ stability order  $\text{II} > \text{I} > \text{III}$ 

## AROMATICITY

**Definition :** Compound which are obtained from fractional distillation of coal tar and having characteristic aroma are known as aromatic compound.

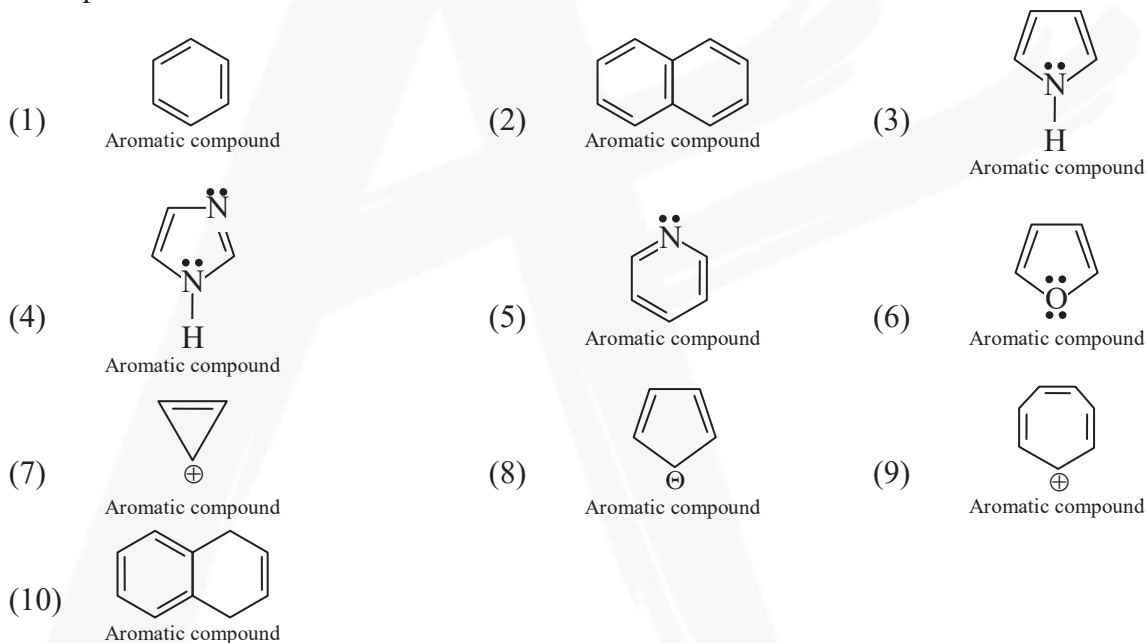
**Rules for compound to be aromatic:**

- Compound must be cyclic
- Compound must be planar or nearly planar.
- Compound must be conjugated throughout ring
- Compound must have  $(4n + 2) \pi$  conjugated or delocalised electrons where  $n$  is a whole number

$$n = 0, 1, 2, 3, 4, 5, 6, \dots$$

$n =$	0,	1,	2,	3,	4,	5.....
$(4n + 2)\pi$ electron	= 2	6	10	14	18	22....

Examples :



**(b) Anti aromatic Compounds :** According to Huckel rule, compound will be anti aromatic if it fulfills the following four conditions :

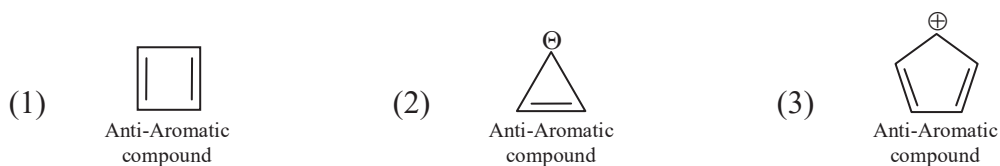
- Compound must be cyclic
- Compound must be planar.
- Compound must be conjugated through out ring and
- Compound must have  $(4n)\pi$  conjugated or delocalised electrons where  $n$  is a whole number

$$n = 1, 2, 3, 4, 5, 6$$

$n =$	1,	2,	3,	4,	5.....
$(4n) \pi$ electron	= 4	8	12	16	20.....

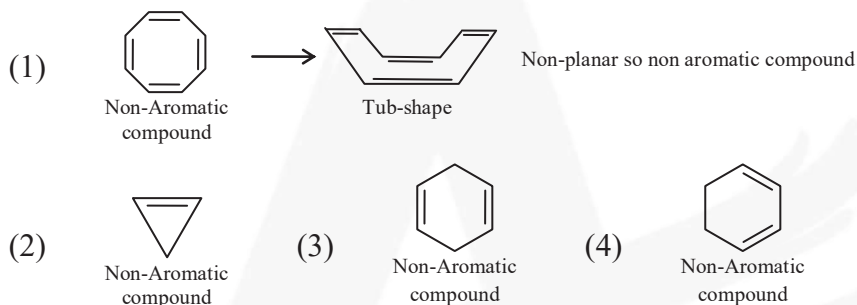
## (Organic Chemistry)

Example:



- (c) **Non aromatic compounds :** The compounds having  $sp^3$  hybridised atom is known as none aromatic compound.

Example:



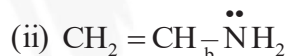
Although cyclooctatetraene has  $(4n)\pi$  electrons but even then it is not an anti aromatic. Geometry of this compound is non planar. Thus it is non aromatic. II<sup>nd</sup>, III<sup>rd</sup> & IV<sup>th</sup> compounds are not completely conjugated.

**Note :** Due to Aromaticity extra stability is achieved by aromatic molecule, than non-aromatic or anti aromatic molecule.

**Example :** Give the correct order of bond length of following mentioned compounds.



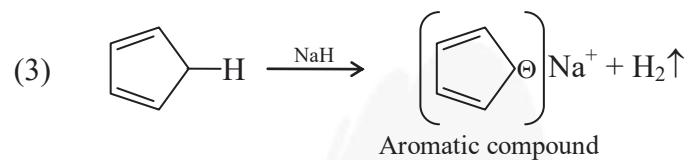
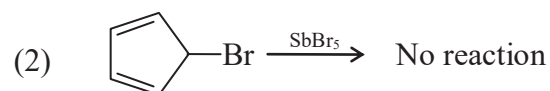
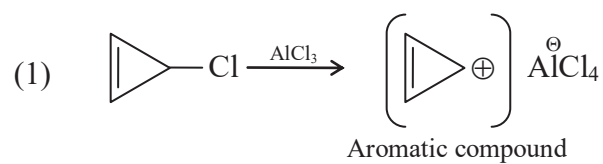
no resonance (only single bond characters)  
bond length order  $a > b$



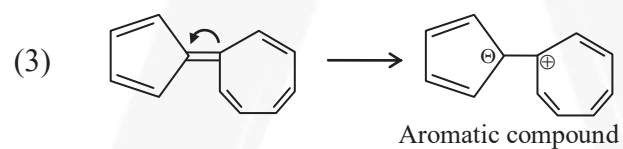
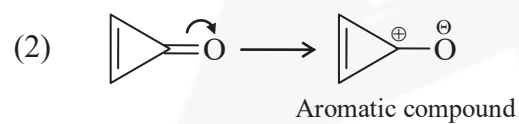
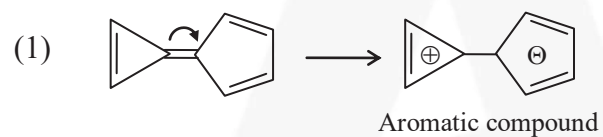
resonance (partial double bond characters)

(Organic Chemistry)

SOME REACTIONS:



DIRECTION OF DIPOLE MOMENT



## STERIC INHIBITION OF RESONANCE (SIR EFFECT)

(1) A steric inhibition of resonance occurs due to a steric repulsion of group/atom present at ortho position in known as **SIR EFFECT**.

(2) On following atoms/groups SIR EFFECT is not observed.

Atoms	Linear groups	Non planar groups
-I	-C≡N	-SO <sub>3</sub> H
-Cl	-C≡C-H	
-Br	-NH <sub>2</sub>	
-F	-OH	

(3) On following atoms/groups SIR EFFECT is observed.

(i) -NMe<sub>2</sub>

(ii) -NHMe

(iii) -COOH

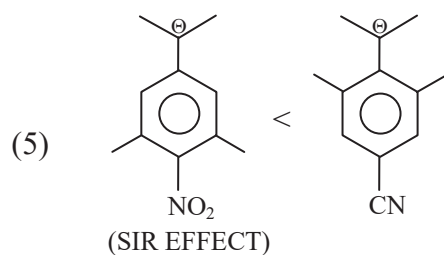
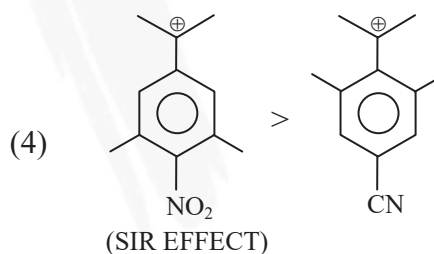
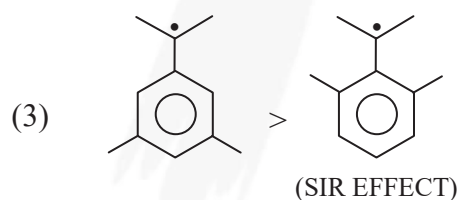
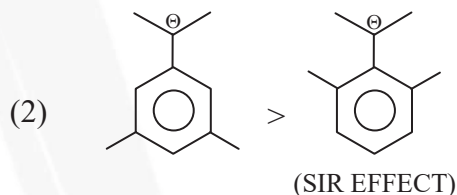
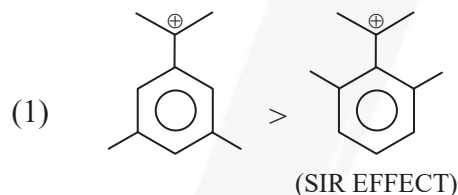
(iv) -NO<sub>2</sub>

(v) -C<sup>⊕</sup>Me<sub>2</sub>

(vi) -C<sup>⊖</sup>Me<sub>2</sub>

(vii) -C<sup>•</sup>Me<sub>2</sub>

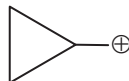
Example: Stability order of following compound:



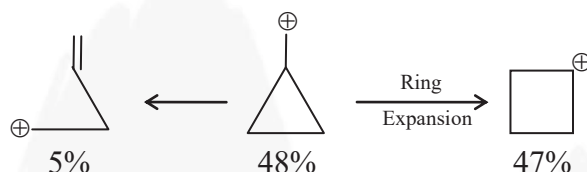
(Organic Chemistry)

**SIGMA BOND RESONANCE (DANCING RESONANCE)**

Sigma bond resonance is observed in cyclopropyl methyl carbocation.



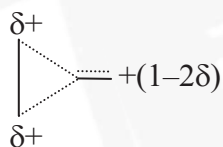
The Sigma bond of ring of cyclopropane (three carbon atoms) are very weak due to excess of angle strain.



The overlapping area between orbitals is so small that the C–C bond is extremely weak. The C–C bond is weaker than  $\pi$ -bond in ethene.

Due to this close overlapping the electrons are delocalized to the p-orbital of  $\text{CH}_2^+$ .

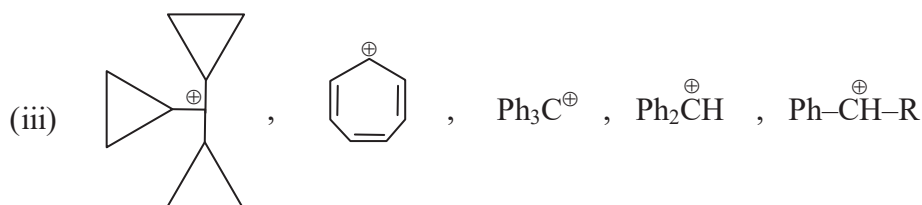
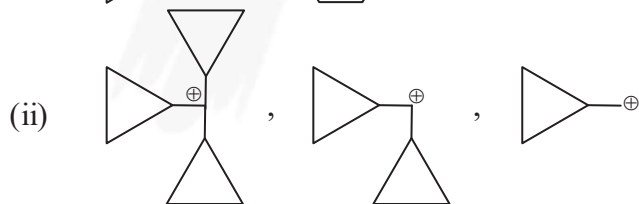
The effect is observed to be very strong and is even stronger than hyper conjugation due to weakness of delocalized bond.



Resonance hybrid

**Example: Stability order:****DO YOURSELF – 4**

Compare stability of following carbocations





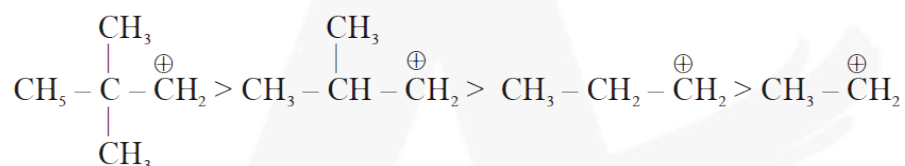
## HYPER CONJUGATION

**Definition :-** Delocalization of conjugated (C–H) sigma electrons with  $\pi$ -bond or positive charge or free radical is called hyperconjugation or H-effect.

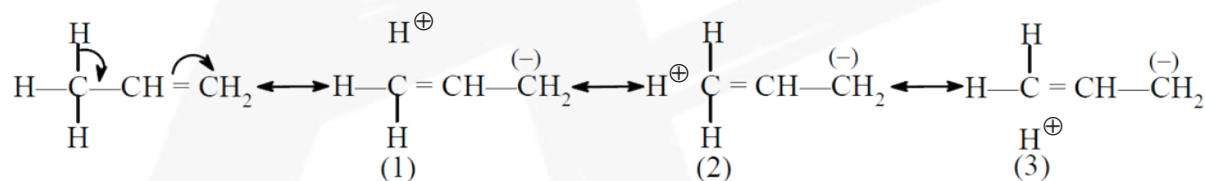
- (i) Hyperconjugating structures may be written involving "no bond" between the alpha carbon and hydrogen atoms so known as **"no bond resonance."**
- (ii) Nathan baker observed this effect so known as "Nathan baker effect"
- (iii) It is also permanent effect

## Introduction

According to inductive effect order of stability of cations should be



But actually order should be reversed which is explained on the basis of hyper conjugation.

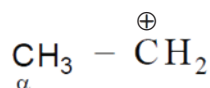
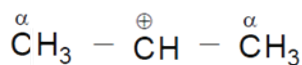
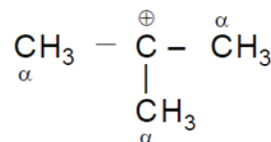


Condition for hyperconjugation:

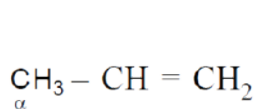
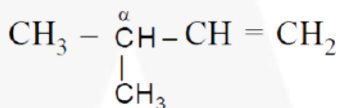
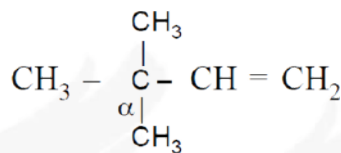
- (i) Compound should have at least one  $\text{sp}^2$ -hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.
- (ii)  $\alpha$ -carbon with respect to  $\text{sp}^2$  hybrid carbon should have at least one hydrogen. If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

## TYPES OF HYPER CONJUGATION

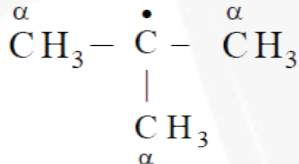
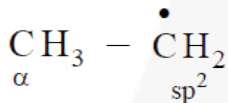
- (i)  $\sigma$  (C–H), vacant orbital (positive charge) hyperconjugation : This type of conjugation occurs in alkyl carbocation.

no. of  $\alpha$  H = 3no. of  $\alpha$  H = 6no. of  $\alpha$  H = 9

- (ii)  $\sigma$  (C–H),  $\pi$  hyperconjugation : This type of conjugation occurs in alkenes.

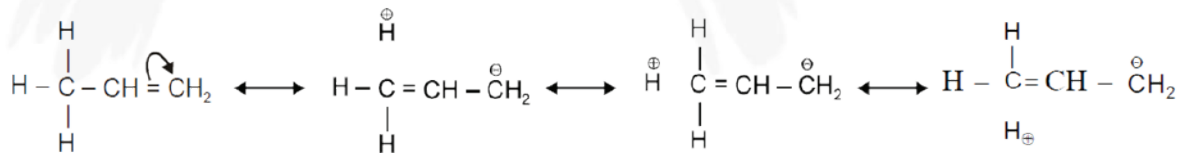
no. of  $\alpha$  H = 3no. of  $\alpha$  H = 1no. of  $\alpha$  H = 0

- (iii)  $\sigma$  (C–H), odd electron hyperconjugation : This type of conjugation occurs in alkyl free radicals –



**Note:** Carbanion never shows hyperconjugation, if there is one –C–H sigma bond alternate with negative charge then there will be no H-effect

Hyper conjugating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.



In the above hyper conjugating structures there is no covalent bond between carbon and hydrogen.

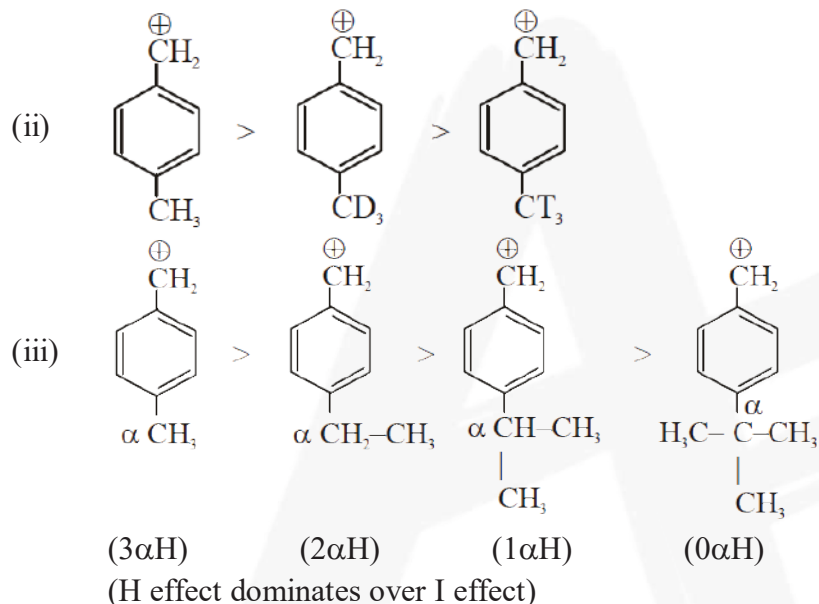
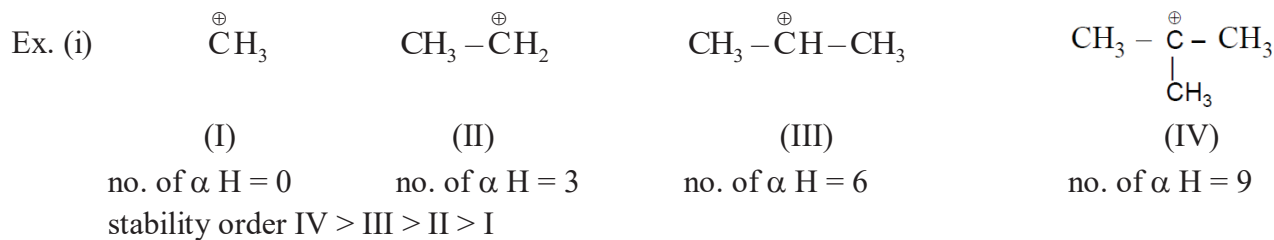
From this point of view, hyperconjugation may be regarded as "**no bond resonance**". Order of effectiveness of hyperconjugation :  $\alpha$  C–H bond >  $\alpha$  C–D bond >  $\alpha$  C–T bond



## (Organic Chemistry)

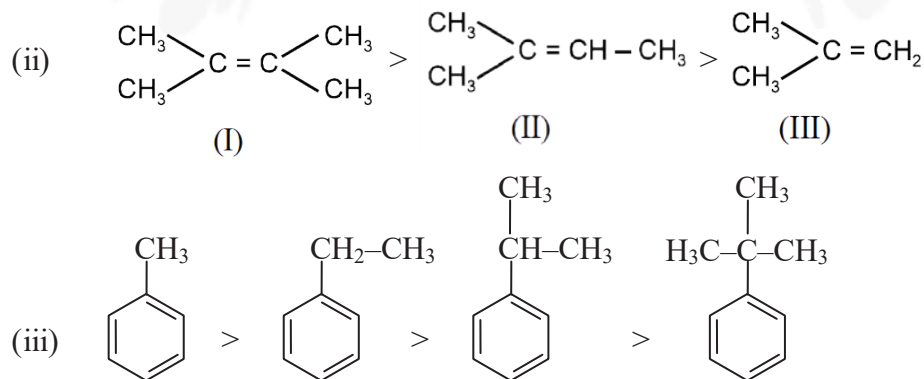
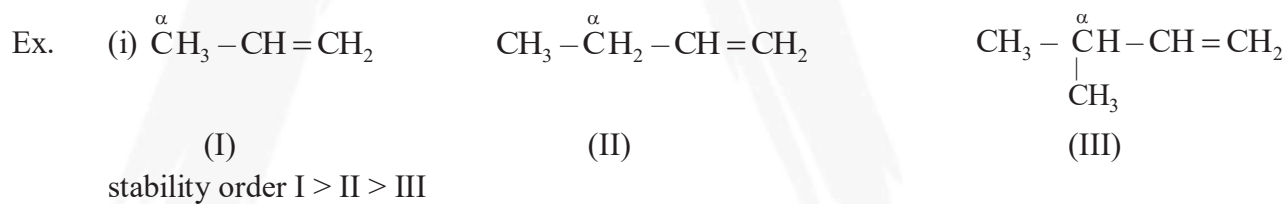
## APPLICATION OF HYPERCONJUGATION

(A) **Stability of Alkyl Carbocations** : Stability of alkyl carbocations  $\propto$  number of hyperconjugating structures  $\propto$  number of  $\alpha$ -hydrogens.

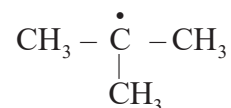
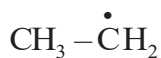


(B) **Stability of Alkenes** : Hyperconjugation explains the stability of certain alkenes over other alkenes:

Stability of alkenes  $\propto$  Number of alpha hydrogens  $\propto$  Number of hyperconjugating structures



(Organic Chemistry)

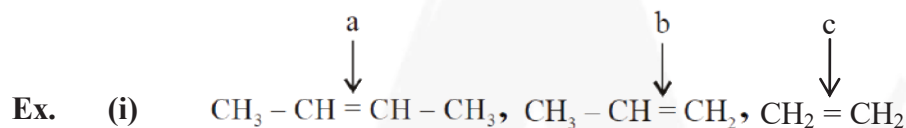
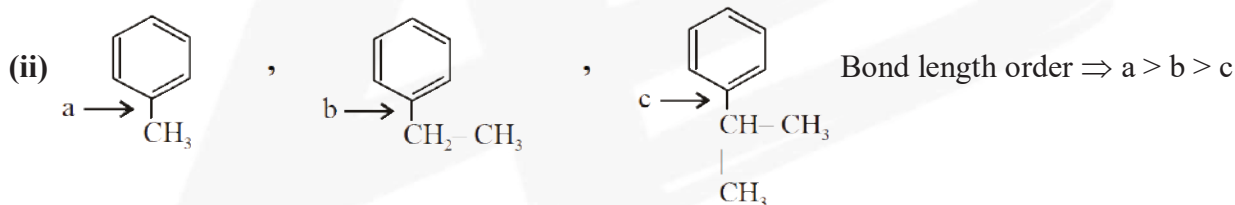
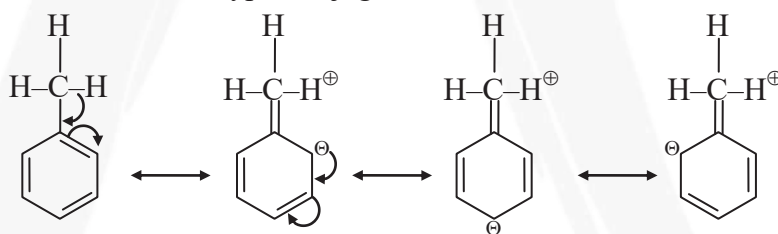
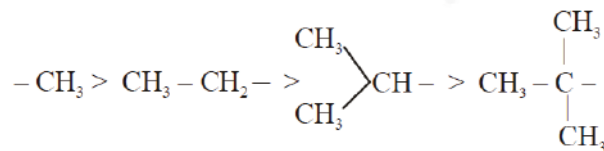
(C) Stability of Alkyl free radicals :  $\propto +I, +R, -R$  effect

(I)

(II)

(III)

(IV)

(i) Stability is in increasing order  $\text{IV} > \text{III} > \text{II} > \text{I}$ (D) **Bond length in alkenes:** More is the number of hyperconjugating structures, the more will be single bond character in carbon-carbon double bond.**The bond length between carbon-carbon double bond  $\propto$  number of hyperconjugating structures.**Bond length order  $\Rightarrow a > b > c$ (E) **Electron releasing (or donating) power in alkyl benzene :**  $\text{CH}_3 -$  (or alkyl group) is +H group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.The electron donating power of alkyl group will depend on the number of hydrogens present on  $\alpha$ -carbon. The electron releasing power of some groups are as follows –

$\xrightarrow{\hspace{10em}}$   
 Electron donating power in decreasing order due to the hyperconjugation

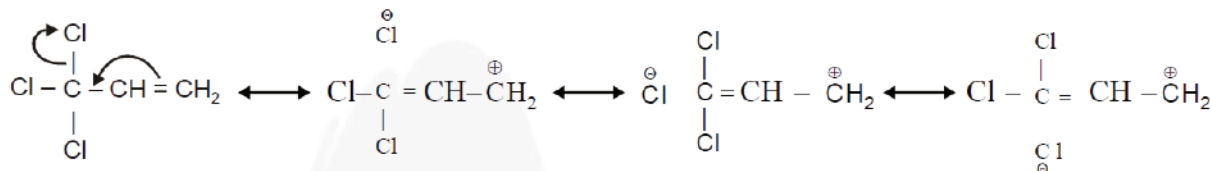
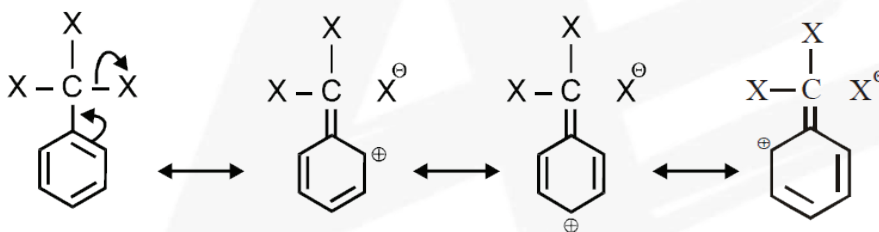
(Organic Chemistry)

**Note : Reverse Hyperconjugation (–H effect) :**

The phenomenon of hyperconjugation is also observed in the system given below :



In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.

The meta directing influence and deactivating effect of  $-\text{CX}_3$  group for electrophilic aromatic substitution reaction can be explained by this effect.

## HEAT OF HYDROGENATION (HOH)



- (a) heat evolved when 1 mole of any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation ( $\Delta H$ ) If alkene is more reactive towards hydrogen then it will evolve more  $\Delta H$ .

So,  $HOH \propto \text{Number of } \pi - \text{bond}$

$$HOH \propto \frac{1}{\text{Stability of Alkene}}$$


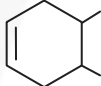
- (b)  $\Delta H \propto \text{number of } \pi \text{ bonds}$
- (c) It is exothermic process (energy release)

### Examples of HOH order

#### DO YOURSELF – 5

Compare HOH of following

- (i)  $CH_2 = CH-CH_2-CH_3$  ,  $CH_3-CH = CH-CH_3$
- (ii)  $CH_2 = CH-CH_2-CH_3$ ,  $CH_2 = CH-\underset{\substack{| \\ CH_3}}{CH}-CH_3$

- (iii)  , 

## HEAT OF COMBUSTION (HOC)

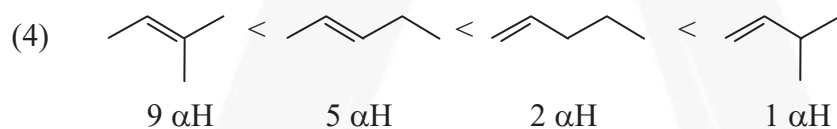
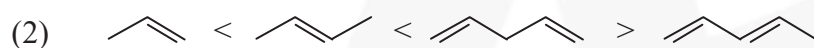
- (i) Enthalpy change when one mole of a compound is completely burnt (oxidation).  
 (ii) It is the energy liberated during complete combustion of organic compound.

HOC  $\propto$  Number of carbon atoms

$\propto \frac{1}{\text{Stability of hydrocarbon}}$

$\propto$  Strain

Examples:



$d > c > b > a$

## ACIDIC STRENGTH

For an acid  $\text{HA}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{A}^-_{(\text{aq})}$

From law of mass action,  $K_a = \frac{[\text{H}^+_{(\text{aq})}][\text{A}^-_{(\text{aq})}]}{[\text{HA}_{(\text{aq})}]}$

where,  $K_a \rightarrow$  Acidity constant, or dissociation constant of acid

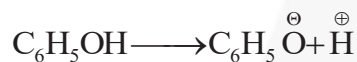
$K_a \rightarrow$  Explain the strength of acid

$\text{p}K_a = -\log K_a$ ,  $K_a \propto \text{Acidic strength} \propto 1/\text{p}K_a$

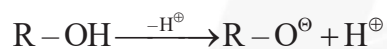
$\text{pH} = -\log [\text{H}^+]$

$$\text{Acidic strength} \propto \text{stability of conjugate base} \propto -M \text{ effect} \propto \frac{1}{+M} \propto -I \propto \frac{1}{+I}$$

Acidity of Phenol v/s alcohol



Phenol stabilized by resonance

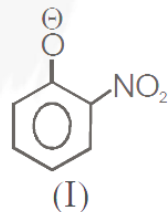
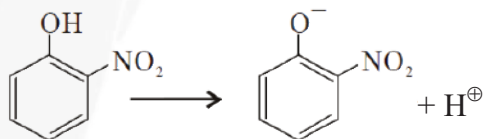


Alcohol no resonance

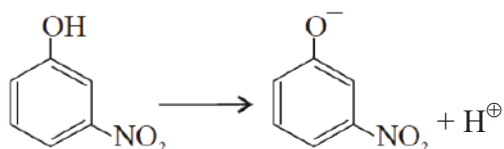
thus acidic strength of phenol > alcohol

more is the stability of phenoxide ion more will be the acidity of phenol

**Acidity of Substituted Phenols :** Acidity of substituted phenols depend on the stability of the phenoxide ion because acidity is the function of conjugate base.

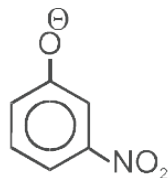


Stabilised by -R and -I



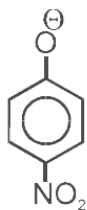
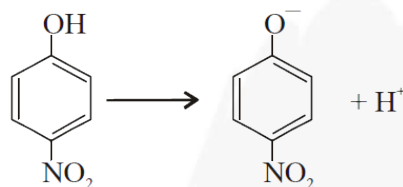


(Organic Chemistry)



(II)

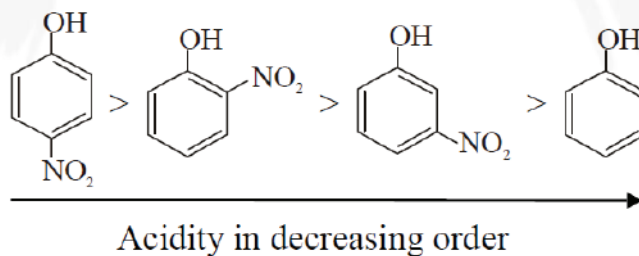
Stabilised by -I  
effect only



(III)

Stabilised by -R and -I  
stability order should be I > III > II

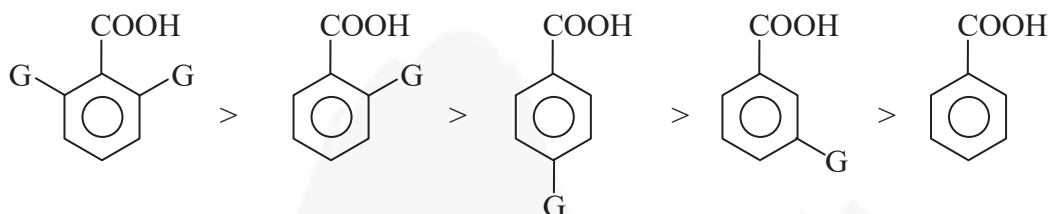
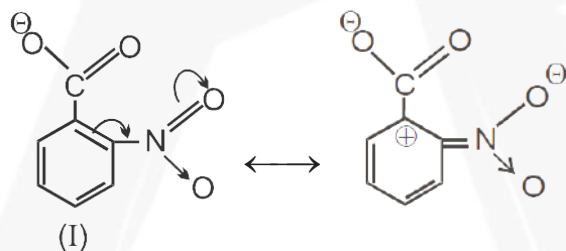
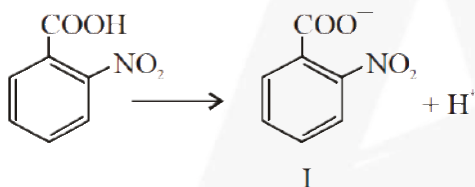
Thus according to stability of anions o-derivative will be more acidic than p-derivative which will be more acidic than m-derivative. But result is as follows in case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative, there is intramolecular hydrogen bonding which decrease acidity. Thus order of acidity is as follows :



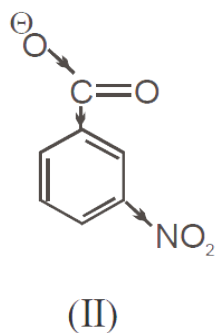
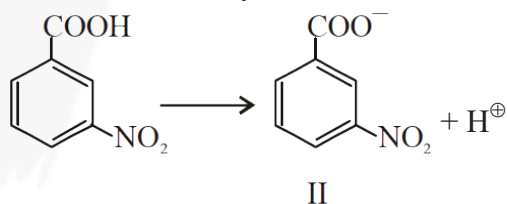
(Organic Chemistry)

**ACIDITY OF SUBSTITUTED BENZOIC ACIDS (ORTHO POSITION EFFECT)**

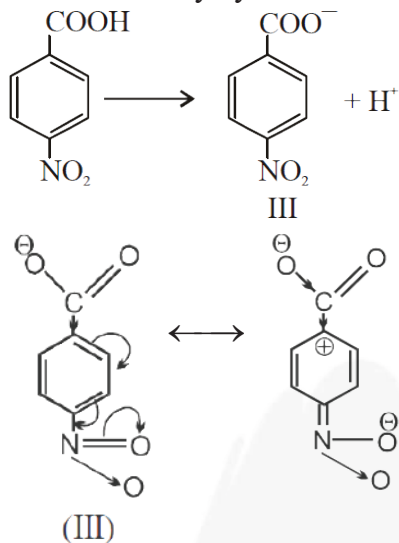
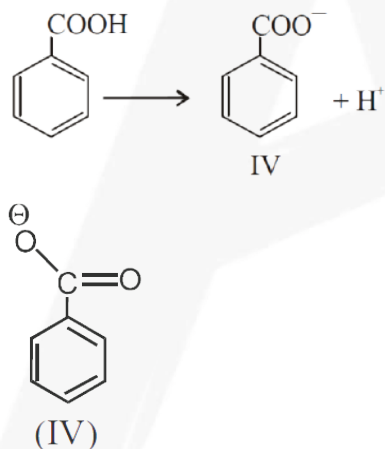
- (i) Ortho substituted benzoic acid is always a stronger acid than m- and p-derivative. This is known as ortho effect.
- (ii) A large group brings the COOH group out of plane and resist resonance through benzene ring.
- (iii) This is the SIR EFFECT caused by the groups.
- (iv) This occurs only when the groups are at ortho position.

**Acidity order of substituted benzoic acids****NOTE : G = EWG**

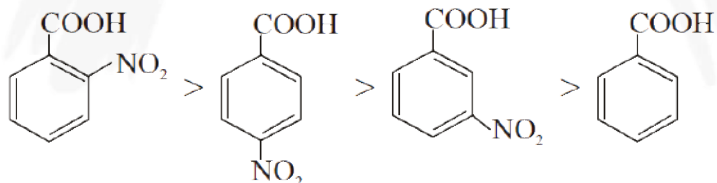
Thus, anion is stabilised by -R and -I effect and -I power is maximum.



(Organic Chemistry)

Anion is stabilised only by  $-I$  effect of  $\text{NO}_2$  groupAnion is stabilised by  $-R$  and  $-I$  effect of  $\text{NO}_2$  groupThus decreasing order of the stability of these anions is follows :  $\text{I} > \text{III} > \text{II} > \text{IV}$ 

We know that ortho derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :



→

Acidity in decreasing order

## BASIC STRENGTH

For an base,  $\text{BOH}_{(\text{aq})} \rightleftharpoons \text{B}_{(\text{aq})}^+ + \text{OH}_{(\text{aq})}^-$

From law of mass action,  $K_b = \frac{[\text{B}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-]}{[\text{BOH}]}$

where,  $K_b \rightarrow$  Basicity constant, or dissociation constant of base

$K_b \rightarrow$  Explains the strength of base

$K_b \propto \text{Basic strength} \propto 1/pK_b$

$$pK_b = -\log K_b$$

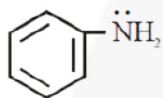
$$pOH = -\log [\text{OH}^-]$$

$$\text{basic strength} \propto +M \propto \frac{1}{-M} \propto +I \propto \frac{1}{-I}$$

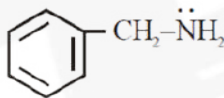
**Basicity of Aromatic Amines :** Basicity of nitrogen containing compounds  $\propto$  Electron density on nitrogen.

In aromatic amines, lone pair of electrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

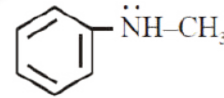
Ex.  $\text{C}_6\text{H}_5\text{NH}_2$  is less basic than  $\text{CH}_3\text{NH}_2$



lone pair is participating in resonance  
(I)



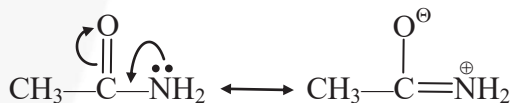
no resonance of lone pair  
so maximum basic  
(II)




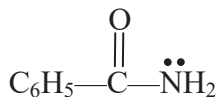
lone pair is participating in resonance  
and +I of  $\text{CH}_3$   
(III)

basic order  $\text{II} > \text{III} > \text{I}$

## Effect of conjugation on basicity :



Due to delocalisation and  $-I$  effect of  group, amides are less basic than amines.

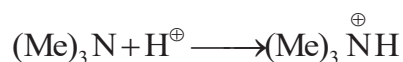
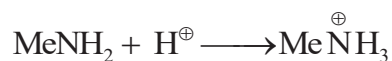
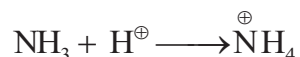


In this amide there is cross conjugation which increases basicity; thus  $\text{C}_6\text{H}_5\text{CONH}_2$  is more basic than  $\text{CH}_3\text{CONH}_2$ .  $\pi$  bond of  $\text{C}=\text{O}$  group is in conjugation to benzene ring as well as lone pair of  $\text{NH}_2$  group.

## (Organic Chemistry)

**Basic Strength of aqueous solutions**

Consider the following amines



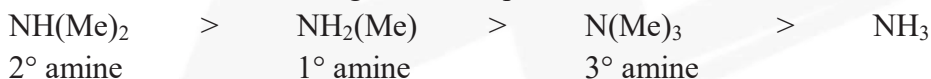
Consider the electron density only, we can clearly observed that  $(\text{Me})_3\text{N}$  has the highest electron density due to + I-effect of methyl group.

Now in aqueous solution, weak also need to consider solvation energy for the amines.

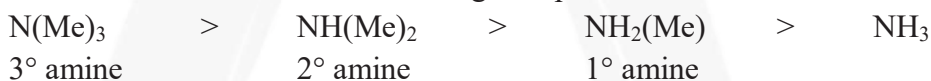
Thus, be consider the solvation energy and find the following analysis.

Amine	Electron density	Solvation energy
$\text{NH}_3$	$\times$	$\uparrow \uparrow \uparrow$
$\text{NH}_2(\text{Me})$	$\uparrow$	$\uparrow \uparrow$
$\text{NH}(\text{Me})_2$	$\uparrow \uparrow$	$\uparrow$
$\text{N}(\text{Me})_3$	$\uparrow \uparrow \uparrow$	$\times$

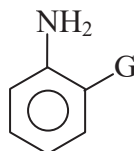
Thus, we find the following order in aqueous solution for the basic strength.

**For Gaseous phase**

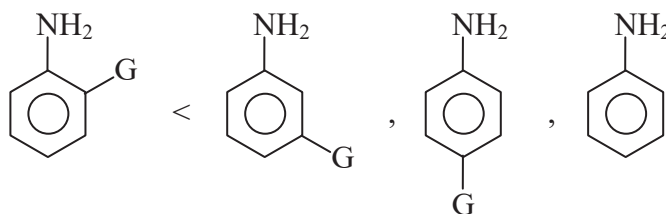
We obtained the order of basic strength as per the order of electron density.

**Solvation effect      Steric Inhibition to the Protonation (SIP)**

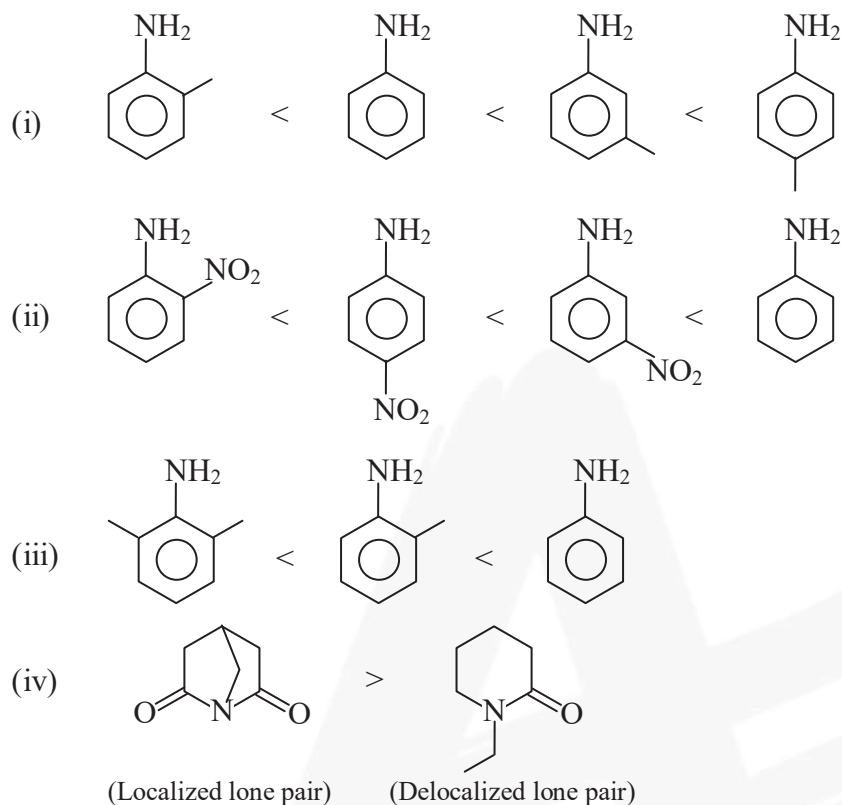
The presence of bulky group at the ortho position of an aromatic amine provides a steric hindrance and inability during solvation.



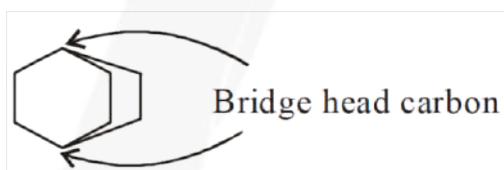
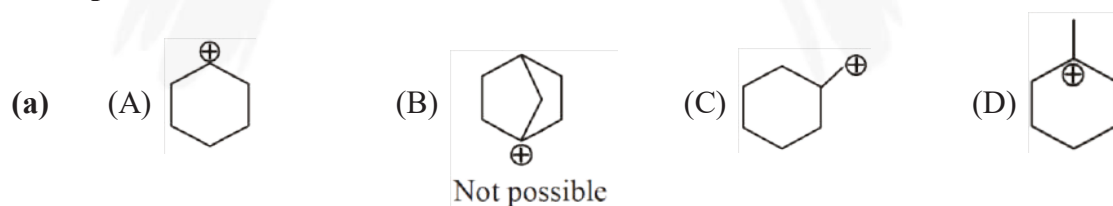
Thus, ortho substituted aromatic amine behaves as a poor base when compare to meta, para unsubstituted aromatic amines.



## (Organic Chemistry)

**Examples:** Basic strength order

**BRETT'S RULE :** Planarity can never be achieved on bridgehead centre of a bicyclic system containing 8 or less than 8 carbon atom is known as bredt's rule.

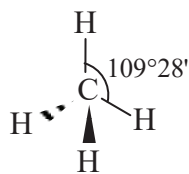
**Examples:-**

Stability order : d &gt; a &gt; c &gt; b



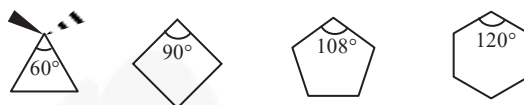
(Organic Chemistry)

## \* BAYER'S STRAIN ANGLE THEORY



For any  $sp^3$  atom angle must be  $109^\circ 28'$  or close to it for maximum stability.

For cycloalkanes



According to Bayer's cycloalkanes are strained.



$$\delta = \frac{1}{2} [109^\circ 28' - \alpha]$$

Hence for

3 carbon atoms  $\rightarrow \alpha = 60^\circ, \quad \delta = 24.5^\circ$

4 carbon atoms  $\rightarrow \alpha = 90^\circ, \quad \delta = 9.5^\circ$

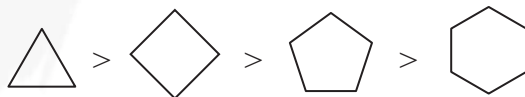
5 carbon atoms  $\rightarrow \alpha = 108^\circ, \quad \delta = 0.5^\circ$

6 carbon atoms  $\rightarrow \alpha = 120^\circ, \quad \delta = -5.5^\circ$

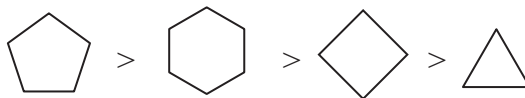
$$\text{Strain} \propto \frac{1}{\text{stability}}$$

**According to Bayer's**

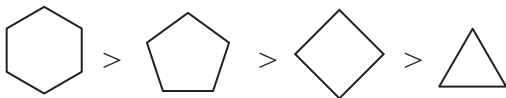
(i) Strain order:



(ii) Stability order:



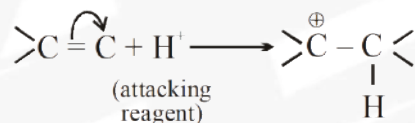
But, actual stability order:



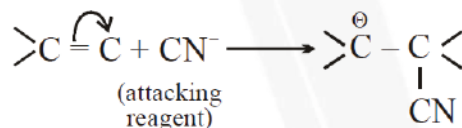
**ELECTROMERIC EFFECT : (E-EFFECT)**

- It is temporary effect.
- The organic compounds having a unsaturation (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.
- The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction.
- It is represented by E and the shifting of the electrons is shown by a curved arrow ( $\curvearrowright$ ).
- When inductive and electromeric effect operate in opposite directions, the electromeric effect predominates.

- (i) **Positive Electromeric Effect (+E effect)** : In this effect the  $\pi$ -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



- (ii) **Negative Electromeric Effect (–E effect)** : In this effect the  $\pi$ -electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example.





## ATTACKING REAGENTS

The species which attack on a substrate and form a product is called as attacking reagents.

**Substrate**-Reactant which is less reactive is generally taken in greater amount.

Attacking reagents are of two types

- (A) Electrophile                      (B) Nucleophile

**(A) Electrophiles or electrophilic reagents ( $E^{\oplus}$ ):**

- (a) They are electron deficient species.
- (b) They have a tendency to accept electron from another molecule
- (c) In a reaction, an electrophile attacks the substrate at the point of maximum electron density.
- (d) Neutral molecule having electron deficient centre,  $CCl_4, CO_2$

**Types of Electrophile :**

- (i) Positively charged electrophiles



**(ii) Neutral electrophiles**

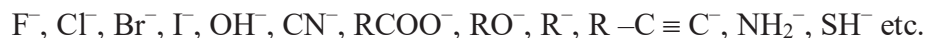
- (a) All Lewis acids as :  $BF_3, AlCl_3, SO_3, ZnCl_2, BeCl_2, FeCl_3, SnCl_4$
- (b) Free radicals, carbenes act as electrophiles.
- (c) Transition metal cations are electrophiles, e.g.  $Fe^{3+}, Fe^+, Ag^+, Cd^{2+}$  etc.]
- (d) Neutral molecule having electron deficient center, eg.  $CCl_4, CO_2$

**(B) Nucleophilic reagents or nucleophiles :**

- (a) They are electron rich species so they have a tendency to donate electron pair.
- (b) All nucleophiles are Lewis bases.
- (c) They attack the centre of minimum electron density in a molecule in a chemical reaction.

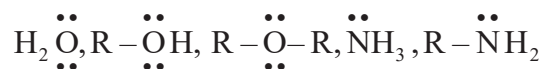
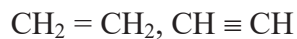
**Types of Nucleophile :**

- (i) Negatively Charged nucleophiles :



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(ii) Neutral nucleophile containing one pair :

(iii)  $\pi$ electron containing compounds(C) **Ambiphiles :**

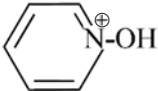

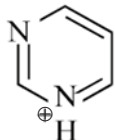
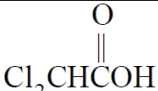


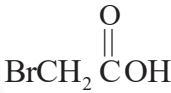


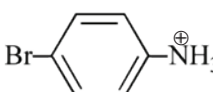
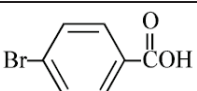
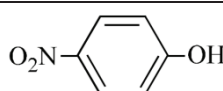
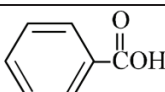
Ambiphiles are those which act as both electrophile and nucleophile.

Example :



S. No.	Electrophile	Nucleophile
1	Accept electron	Supplies the electron pair
2	Electron deficient (electron loving)	Electron rich
3	Usually positively charged species	Usually negatively charged species
4	Attacks the points of high electron density	Attacks the points of low electron density
5	e.g., $\text{H}^+, \text{CH}_3^+, \text{CO}_2^+, \text{NO}^+$	e.g., $\text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{H}_2\text{O}$

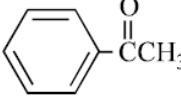
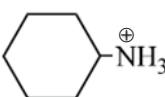
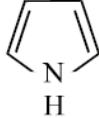
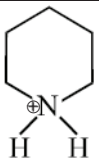

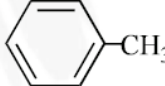
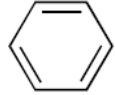

pK<sub>a</sub> values

Compound	pK <sub>a</sub>	Compound	pK <sub>a</sub>
$\text{CH}_3\text{C}\equiv\text{N}^\oplus\text{H}$	-10.1		0.79
HI	-10		1.0
HBr	-9		1.0
$\text{CH}_3\text{C}(\text{OH}^\oplus)=\text{CH}_2$	-8		1.3
HCl	-7	$\text{HSO}_4^-$	2.0
$\text{CH}_3\text{SH}_2^\oplus$	-6.8	$\text{H}_3\text{PO}_4$	2.1
$\text{H}_2\text{SO}_4$	-5		2.7
$\text{CH}_3\text{CH}_2\text{O}^+\text{CH}_2\text{CH}_3$	-3.6		2.8
$\text{CH}_3\text{CH}_2\text{OH}^\oplus$	-2.4		2.9
$\text{H}_3\text{O}^+$	-1.7		3.2
$\text{HNO}_3$	-1.3	HF	3.2
$\text{CH}_3\text{SO}_3\text{H}$	-1.2	$\text{HNO}_2$	3.4
$\text{CH}_2\text{CNH}_2^\oplus$	0.0		3.4
$\text{F}_3\text{CCOOH}$	0.2	$\text{HCOOH}$	3.8
$\text{Cl}_3\text{CCOOH}$	0.64		3.9
	4.0		7.1
	4.2	$\text{H}_2\text{PO}_4^\ominus$	7.2

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Compound	pK <sub>a</sub>	Compound	pK <sub>a</sub>
	4.3		7.8
	4.5		8.0
	4.6		8.1
	4.8		8.2
	4.9		8.6
	5.1		8.9
	5.2		9.1
	5.3		9.3
	5.5		9.4
	5.9		9.5
	6.4		9.8
	6.8		10.0
	7.0		10.2
	10.3		10.2
	10.5		10.2

(Organic Chemistry)

Compound	pK <sub>a</sub>	Compound	pK <sub>a</sub>
$\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OEt}$	10.7		16.0
	10.7		~17
$\text{CH}_3\text{CH}_2\text{NH}_3^+$	10.7	$\text{CH}_3\text{CHO}$	17
	11.1	$(\text{CH}_3)_3\text{COH}$	18
$\text{HPO}_4^{2-}$	12.3	$\text{CH}_3\text{C}(=\text{O})\text{CH}_3$	20
$\text{CF}_3\text{CH}_2\text{OH}$	12.4	$\text{CH}_3\text{C}(=\text{O})\text{OEt}$	24.5
$\text{EtOC}(=\text{O})\text{CH}_2\text{C}(=\text{O})\text{OEt}$	13.3	$\text{HC}\equiv\text{CH}$	25
$\text{HC}\equiv\text{CCH}_2\text{OH}$	13.5	$\text{CH}_3\text{C}\equiv\text{N}$	25
$\text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}_2$	13.7	$\text{CH}_3\text{C}(=\text{O})\text{N}(\text{CH}_3)_2$	30
$\text{CH}_3\text{N}^+(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OH}$	13.9	$\text{NH}_3$	36
	14.4	$\text{CH}_3\text{NH}_3$	40
$\text{CH}_3\text{OH}$	15.5		41
$\text{H}_2\text{O}$	15.7		43
$\text{CH}_3\text{CH}_2\text{OH}$	16.0	$\text{CH}_2=\text{CH}_2$	44
$\text{CH}_2\text{C}(=\text{O})\text{NH}_2$	16		46
		$\text{CH}_4$	50
		$\text{CH}_3\text{CH}_3$	50

(Organic Chemistry)

## ANSWER KEY

## DO YOURSELF – 1

- (i)  $1 > 2 > 3$       (ii)  $1 > 2 > 3$       (iii)  $3 > 2 > 1$       (iv)  $3 > 2 > 1$   
(v)  $3 > 2 > 1$

## DO YOURSELF – 2

- (i)  $b > a > c$       (ii)  $y = z > x$       (iii)  $y > x$

## DO YOURSELF – 3

- (i)  $1 > 2 > 3$       (ii)  $1 > 2 > 3$       (iii)  $1 > 2 > 3 > 4 > 5 > 6 > 7 > 8 > 9$   
(vi)  $2 > 1$

## DO YOURSELF – 4

- (i)  $1 > 2 > 3$       (ii)  $1 > 2 > 3$       (iii)  $1 > 2 > 3 > 4 > 5$   
(vi)  $1 > 2 > 3 > 4 > 5 > 6 > 7$

## DO YOURSELF – 5

- (i)  $1 > 2$       (ii)  $2 > 1$       (iii)  $2 > 1$