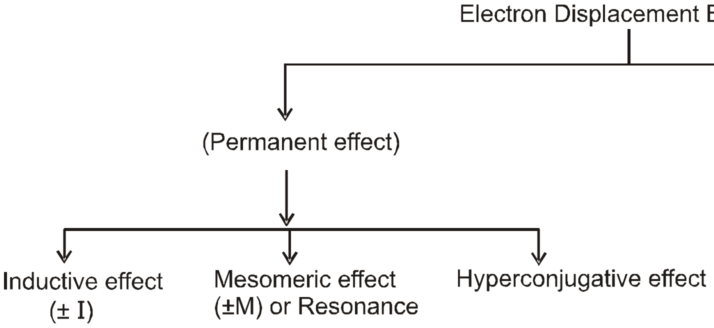
General Organic Chemistry (GOC)-I

Electronic effect:

Introduction

The effect which appears due to electronic distribution is called electronic effect.

Classification:



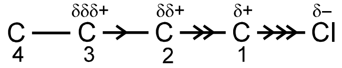
Section (A): Inductive effect

Th1: Inductive effect

The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative (δ–) charge over Cl atom and partial positive (δ+) charge over C_1 atom.

Now since C_1 is slightly positive, it will also cause shifting of C_1–C_2 bond pair electrons towards itself causing C_2 to acquire small positive charge. Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

Diagram showing I effect.



$$\underset{4}{C} - \underset{3}{\overset{\delta\delta\delta+}{C}} \rightarrow \underset{2}{\overset{\delta\delta+}{C}} \twoheadrightarrow \underset{1}{\overset{\delta+}{C}} \ggg \overset{\delta-}{Cl}$$

The arrow shows electron withdrawing nature of –Cl group.

D1: Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

(a) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.
(b) It is also called transmission effect.
(c) It causes permanent polarisation in molecule, hence it is a permanent effect.
(d) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.
(e) The electrons never leave their original atomic orbital.
(f) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.
(g) The inductive effect is always operative through σ bond, does not involve π bond electron.

1.1 Types of inductive effects:

D2: **(a) –I Effect:** The group which withdraws electron cloud is known as –I group and its effect is called –I effect. Various groups are listed in their decreasing –I strength as follows.

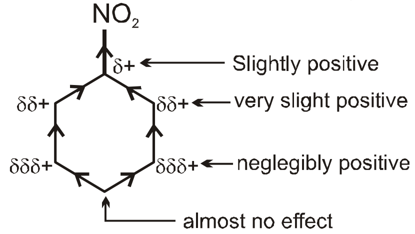
$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -SO_2Ar > -COOH > -F > -Cl >$$
$$-Br > -I > -OAr > -OR > -SR > -OH > -C{\equiv}CR > Ar > -CH{=}CR_2$$

D3: **(b) +I effect:** The group which release electron cloud is known as +I group and effect is +I effect.

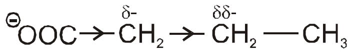
$$-\overset{\ominus}{O} > -CO\overset{\ominus}{O} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2{-}CH_3 > -CH_3 > -D > -H$$

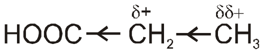
The hydrogen atom is reference for +I and –I series. The inductive effect of hydrogen is assumed to be zero.

Ex. Since – NO_2 is –I group it pulls or withdraws electron from cyclohexane ring making it electron deficient



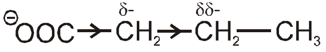
Ex. Let us consider effect of COOH & – COO^- in carbon chain

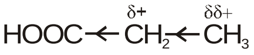
(a) 
$${}^{\ominus}OOC \rightarrow \overset{\delta-}{CH_2} \rightarrow \overset{\delta\delta-}{CH_2} - CH_3$$

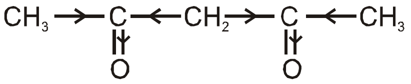
(b) 
$$HOOC \leftarrow \overset{\delta+}{CH_2} \leftarrow \overset{\delta\delta+}{CH_3}$$

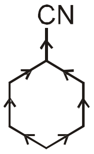
Due to e^- donating nature of $-COO^{\ominus}$ carbon chain has become partially negative but –COOH is –I group therefore carbon chain has become partially positive.

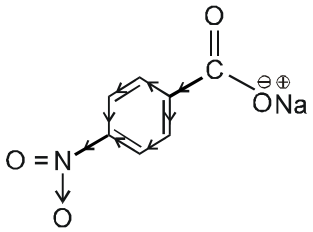
Ex. Direction of electron displacements

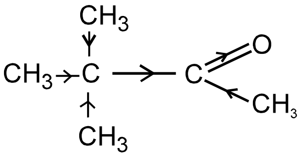
1. 
$${}^{\ominus}OOC \rightarrow \overset{\delta-}{CH_2} \rightarrow \overset{\delta\delta-}{CH_2} - CH_3$$

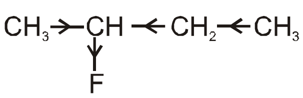
2. 
$$HOOC \leftarrow \overset{\delta+}{CH_2} \leftarrow \overset{\delta\delta+}{CH_3}$$

3. 
$$CH_3 \rightarrow \underset{\underset{O}{\Downarrow}}{C} \leftarrow CH_2 \rightarrow \underset{\underset{O}{\Downarrow}}{C} \leftarrow CH_3$$

4. 

5. 

6. 

7. 
$$CH_3 \rightarrow \underset{\underset{F}{\downarrow}}{CH} \leftarrow CH_2 \leftarrow CH_3$$

8. $CH_2 \Rightarrow C \Rightarrow O$

9. 
$$CH_3 \rightarrow \overset{+\delta\delta}{CH} \Rightarrow \overset{+\delta}{CH} \rightarrow\rightarrow\rightarrow \overset{-\delta}{NO_2}$$

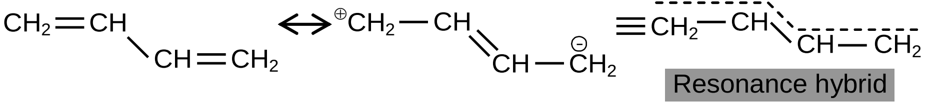
Section (B) : Resonance Concepts, Conditions, Resonating Structures & Conjugation

Th2: Resonance

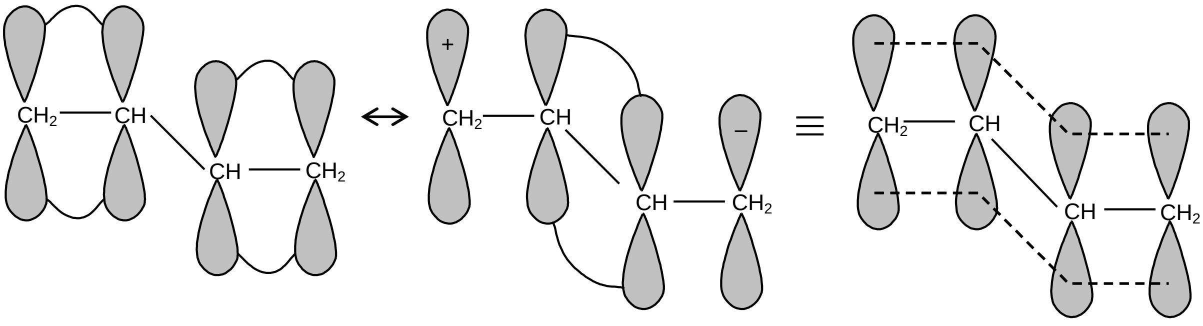
When two or more structures that differ only in the distribution of electrons can be written for a molecule, no single Lewis structure is sufficient to describe it's true electron distribution. The true structure is said to be a resonance hybride of the various Lewis formulas.

The various Lewis formulas called resonating structure/contributing structure/canonical structure, that can be written for a molecule.

D4: Resonating structures are hypothetical but contribute to the real structure, which is called resonance hybrid. The resonance hybrid is more stable than any other resonating structures.

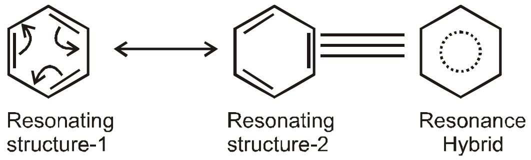
Ex. 

Resonance hybrid



Resonance hybrid

Ex.



The most stable resonating structure contribute maximum to the resonance hybrid and less stable resonating structure contribute minimum to resonance hybrid.

2.1 Conjugation:

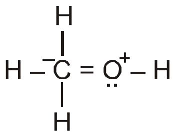
A given atom or group is said to be in conjugation with an unsaturated system if:-
(i) It is directly linked to one of the atoms of the multiple bond through a single bond.
(ii) It has bond, positive charge, negative charge, odd electron or lone pair electrons.

2.2 Types of Conjugation:

1. Conjugation between C=C and C=C $(CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2)$
2. Conjugation between +ve charge and C=C $(CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2)$
3. Conjugation between lone pair and C=C $(:\ddot{C}l - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}l = CH - \overset{\ominus}{C}H_2)$
4. Conjugation between odd electron and C=C $(CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2)$
5. Conjugation between negative charge and C=C $(CH_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2)$

2.3 The Rules of Resonance:

(a) All the canonical forms (resonating structure) must have proper lewis structure. For instance none of them may have a carbon atom with five bonds.



$$H - \overset{-}{\underset{H}{\overset{H}{C}}} = \ddot{O}^{+} - H$$

This is not a proper resonating structure for methanol because carbon has five bonds.
Elements of the 2nd period (first major row) of the periodic table cannot have more than eight electrons in their valence shell

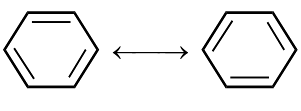
(b) The positions of the nuclei of the atoms must remain the same in all of the structures. Structures 3 is not a resonance structure of 1 or 2, for example, because in order to form it we would have to move a hydrogen atoms and this is not permitted:

$$\underbrace{\underset{1}{CH_3 - \overset{+}{C}H - CH = CH_2} \longleftrightarrow \underset{2}{CH_3 - CH = CH - \overset{+}{C}H_2}} \qquad \underbrace{\underset{3}{\overset{+}{C}H_2 - CH_2 - CH = CH_2}}$$

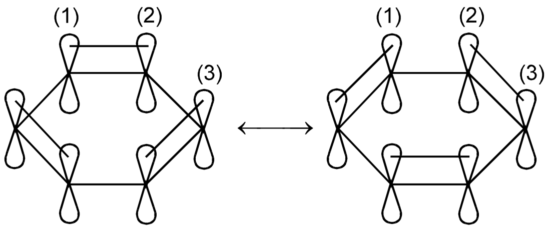
These are resonance structures

This is not a proper resonance structure of 1 or 2 because a hydrogen atom has been moved.

(c) All atoms taking part in the delocalisation must lie in a plane so that orbitals overlaping become parallel to each other.



i.e.



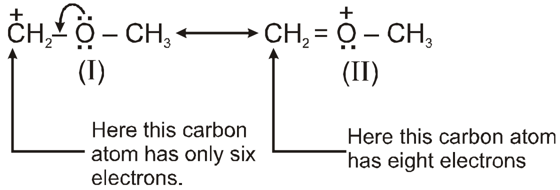
(d) All canonical forms must have the same number of unpaired electron.
(e) The energy of actual molecule is lower than of any form. Therefore delocalisation is a stabilizing phenomenon.
(f) All canonical forms do not contribute equally to the true molecule. The more stable structure is the greater contributor to its resonance hybrid.

Section (C) : Stability of Resonating Structures and different species

2.4 How to compare stability of resonating structure:

(a) Structures in which all of the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are especially stable and make large contributions to the hybrid.

Ex.



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

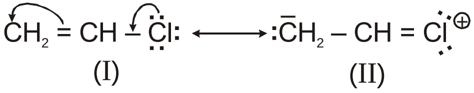
(I) (II)

(II is more stable than I)

Here this carbon atom has only six electrons.

Here this carbon atom has eight electrons

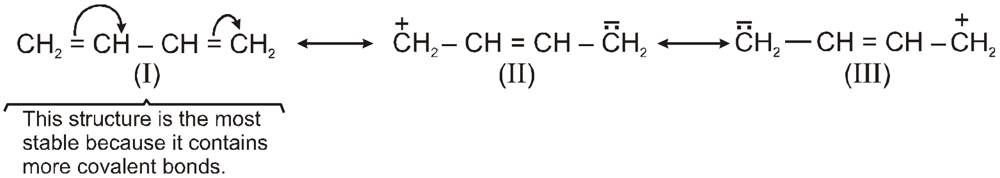
(b) Nonpolar (uncharged) structure are most stable. Charge separation decreases stability. Separating opposite charges requires energy. Therefore, structures in which opposite charges are separated have greater energy (lower stability) than those that have no charge separation.



$CH_2=CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow :\overset{-}{C}H_2-CH=\overset{\oplus}{Cl}$

(I) (II)

(c) Structures with more covalent bonds are more stable than other structures



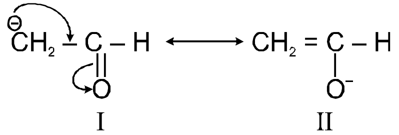
$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH-\overset{-}{\ddot{C}}H_2 \longleftrightarrow \overset{-}{\ddot{C}}H_2-CH=CH-\overset{+}{C}H_2$

(I) (II) (III)

This structure is the most stable because it contains more covalent bonds.

(d) Structure that carry negative charge on a more electronegative atom and positive charge on less electronegative atom are comparatively more stable.

Ex.



$\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-H \longleftrightarrow CH_2=\underset{\underset{O^-}{|}}{C}-H$

I II

(II is more stable than I)

2.5 Resonance Energy:

D5: The P.E. difference between the most stable resonating structure and resonance hybride is called resonace energy. The stability of molecule is directly proportional to resonance energy.

The difference in energy between the hybrid and the most stable canonical structure is referred as the resonance energy. (as shown in Fig.2)

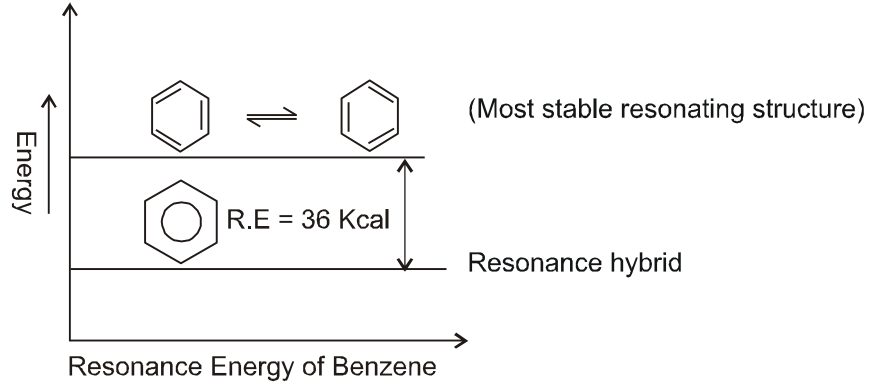


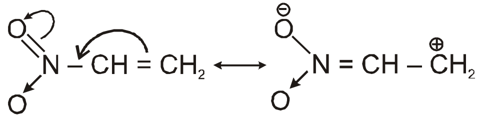
Fig.2

Section (D) : Mesomeric Effect

Th3: Mesomeric effect (or Resonance effect)

D6: Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond. This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

Ex.



$O=\overset{\overset{O}{\swarrow}}{N}-CH=CH_2 \longleftrightarrow \overset{\ominus}{O}-\overset{\overset{O}{\swarrow}}{N}=CH-\overset{\oplus}{C}H_2$

Types of Mesomeric effects :

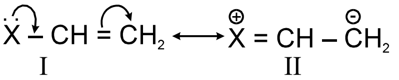
D7: (a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect.

Relative order of +M groups (usually followed) :

$-\overset{\ominus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I$

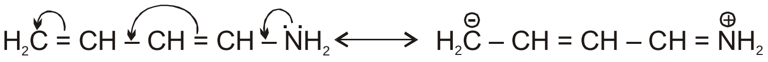
Ex. (I)



$\ddot{X}-CH=CH_2 \longleftrightarrow \overset{\oplus}{X}=CH-\overset{\ominus}{C}H_2$

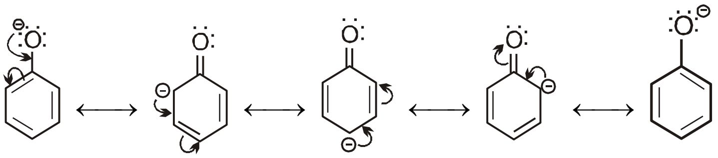
I II

(II)

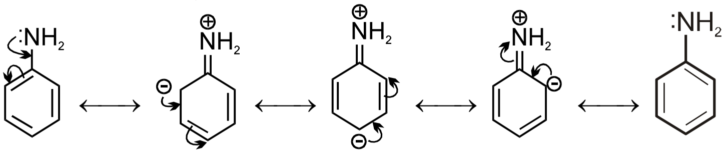


$H_2C=CH-CH=CH-\ddot{N}H_2 \longleftrightarrow H_2\overset{\ominus}{C}-CH=CH-CH=\overset{\oplus}{N}H_2$

(III)



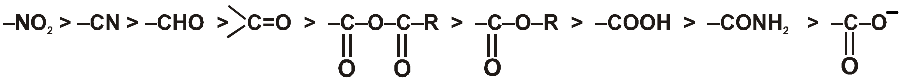
(IV)



D8: (b) Negative Mesomeric effect (–M effect) :

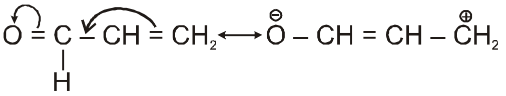
When the group withdraws electron from the conjugated system, it shows – M effect

Relative order of –M groups (usually followed) :



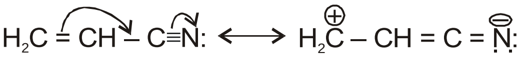
$-NO_2 > -CN > -CHO > \;>C=O > -\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-O-R > -COOH > -CONH_2 > -\underset{\underset{O}{\|}}{C}-O^{-}$

Ex. (I)



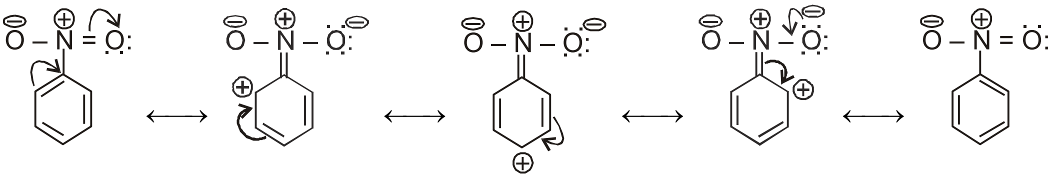
$O=\underset{\underset{H}{|}}{C}-CH=CH_2 \longleftrightarrow \overset{\ominus}{O}-CH=CH-\overset{\oplus}{C}H_2$

(II)



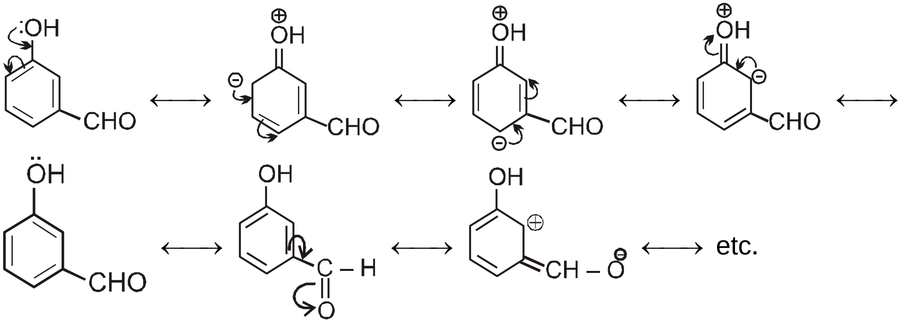
$H_2C=CH-C\equiv N: \longleftrightarrow H_2\overset{\oplus}{C}-CH=C=\overset{\ominus}{\ddot{N}}:$

(III)



Note :

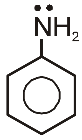
1. When a +M group and –M group are at meta-positions with respect to each other then they are not in conjugation with each other, but conjugation with benzene ring exists.



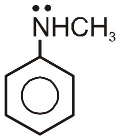
2. +M group increases electron density in benzene ring, called activating group while –M group decreases electron density in the benzene ring, called deactivating group.

Ex. Write electron density order in the following compound.

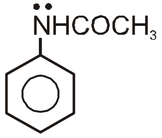
(a)



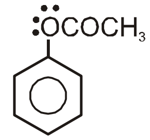
I



II

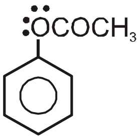


III

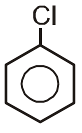


IV

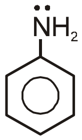
(b)



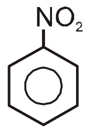
I



II



III



IV

Ans. (a) I > II > III > IV (b) III > I > II > IV

Section (E) : Steric Inhibition of Resonance (SIR Effect)

Th4: SIR (Steric Inhibition of Resonance):

Restriction in exhibition of resonance due to steric hindrance is known as SIR effect.

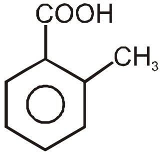
In case of 1,2-Disubstituted benzene if the substitutents are bulky then due to steric repulsion (vander wall repulsion) the group go out of plane with respect to benzene ring.

Due to this change in planarity the conjugation between the substituents on benzene is silightly diminished.

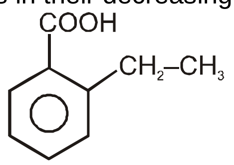
SIR effect $\propto$ Size of group.

Ex. Arange the following compounds in their decreasing SIR effect order.

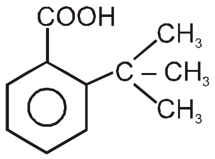
(a)



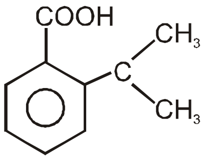
I



II



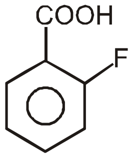
III



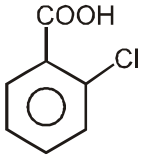
IV

SIR effect order = III > IV > II > I.

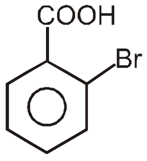
(b)



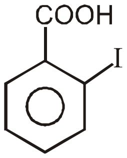
I



II



III



IV

SIR effect order = IV > III > II > I.

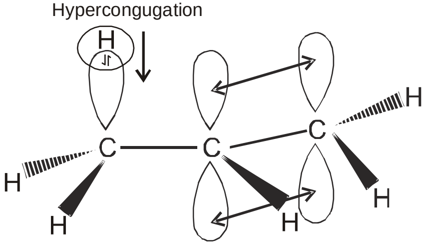
Section (F) : Th5: Hyperconjugation

D9: It is delocalisation of sigma electron with p-orbital. Also known as σ–π-conjugation or no bond resonance. It may take place in alkenes, alkynes, carbocations, free radicals and benzene nucleus.

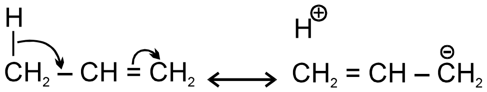
Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkenes, alkynes, carbocations, free radicals and benzene nucleus.

(i) Hyperconjugation in alkenes

Delocalisation of σ bond electrons in $\pi*$ orbital by hyperconjugation in the case of alkene can be depicted as in figure.

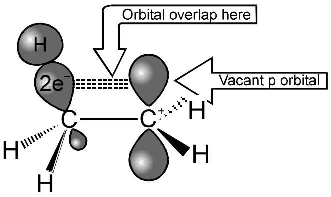


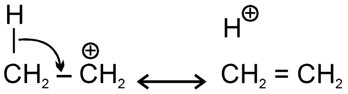
Orbital Diagram showing hyperconjugation in propene



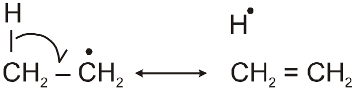
$H-CH_2-CH=CH_2 \longleftrightarrow \overset{\oplus}{H}\ CH_2=CH-\overset{\ominus}{C}H_2$

(ii) Hyperconjugation in carbocation

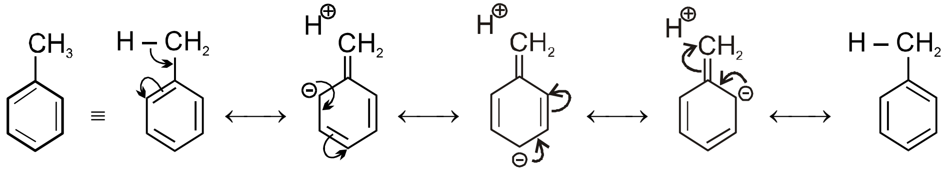




(iii) Hyperconjugation in radical



(iv) Hyperconjugation in toluene



(a) The effect of electron displacement due to this type of resonance is called hyperconjugative effect.

(b) Since canonical forms of this resonance may not contain any bond between H and C so hyperconjugation is also known as no bond resonance.

(c) These resonating structures only suggest that

- There is some ionic character between C–H bond.
- Carbon-carbon double bond acquires some single bond character.

(d) Number of no bond resonating structures due to hyperconjugation = Number of α-hydrogens (In aliphatic systems)

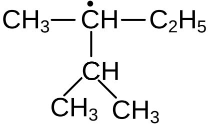
Number of α hydrogen in the following molecules/ion.

(i)

$CH_3-\overset{\oplus}{C}H-C_2H_5$

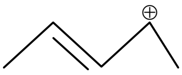
αH = 5

(ii)



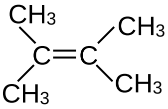
αH = 6

(iii)



αH=6

(iv)



αH = 12

Th6 Comparision between electronic effects :

Inductive effect	**Mesomeric effect**	**Hyperconjugative effect**
(1) It is found in saturated and unsaturated compounds.	(1) It is found in unsaturated compounds especially having conjugated system.	(1) It is found in carbocation, carbon free radical and unsaturated compounds.
(2) It involves partial shifting of sigma electrons.	(2) It involves complete shifting of pi-electrons of pi-bonds or lone pair of electrons.	(2) It involves partial shifting of sigma-electrons into adjacent p-orbital.
(3) The electron pair is slightly displaced from its position and thus partial charges are developed.	(3) The electron pair is completely transferred and thus full positive and negative charges are developed.	(3) The electron pair is partially transferred.
(4) It is transmitted over a quite short distance. The effect becomes negligible after third atom in the chain (distance dependent).	(4) It is transmitted from one end to other end of the chain provided conjugation is present. It is distance independent.	(4) It is transmitted from one end to other end of the chain provided conjugation is present. It is distance independent.

Th7 Important points :

(a) If any group has more than one π bond in conjugation, then only one π bond will take part in delocalisation.

$CH_2=CH-C\equiv CH$

↓

Out of two π bonds only one π bond will take part in delocalisation.

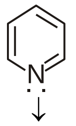
(b) If any conjugate position has more than one lone pair then only one lone pair will take part in the delocalisation.

$CH_2 = CH - \ddot{\underset{\cdot\cdot}{O}} - CH_3$

↓

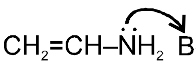
Out of the two lone pair's only one will take part in delocalisation.

(c) If any conjugate position has π bond and any of the positive charge, negative charge, odd electron, lone pair electrons then only π bond will take part in delocalisation on priority.

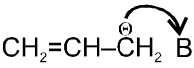


Nitrogen has π bond as well as lone pair, but only π bond of nitrogen will take part in delocalisation.

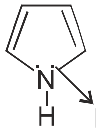
(d) Electrons of negative charge or lone pair behave as 2π electrons if it is in conjugation to π bond.



$CH_2=CH-\ddot{N}H_2$ Behaves as 2π e's;



$CH_2=CH-\overset{\ominus}{C}H_2$ Behaves as 2π e's;



behaves as 2π e′s

Section (G) : Concept of Aromaticity

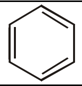
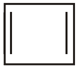
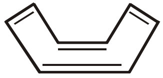
Th8: Aromatic character [The Huckel 4n + 2 rule]

D10 **Definition:** Aromatic compounds are characterized by a special stability and that they undergo substitution reactions more easily than addition reactions.

The following rules are useful in predicting whether a particular compound is aromatic or non–aromatic. Aromatic compounds are cyclic and planar. Each atom in an aromatic ring is sp^2 hybridised. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain (4n + 2) π electrons, i.e., 2, 6, 10, 14 .... π electrons. Where n = an integer 0, 1, 2, 3,..............

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Comparision between aromatic, anti aromatic and non-aromatic compounds.

	Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
	Example			
1	Structure	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic or acyclic planar,or non planar sp or sp^2 or sp^3
2	No. of πe^- in the ring	(4n + 2) πe^- (Huckle's rule)	(4n) πe^-	Any no. of πe^-
3	MOT	Unpaired e^- in B.M.O.	Some πe^- in non-bonding M.O.	B.M.O./Non-bonding M.O.
4	Overlapping	Favourable over lapping of p orbital	Unfavourable over lapping of p orbital	Simple overlaping like alkenes
5	Resonance energy (R.E.)	Very high R.E. > 20-25 kcal/mol	Zero	4-8 kcal/mol like alkenes
6	Stability	Have extra stability due to close conjugation of πe^-	Unstable not-exist at room temperature	Normal stability like a conjugated system
7	Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addtion reaction like alkenes

Stability of compounds: Aromatic > Non-Aromatic > Anti-Aromatic

(For compounds with same number of atoms and similar type of bonding)

Section (H) : Applications of electronic effect

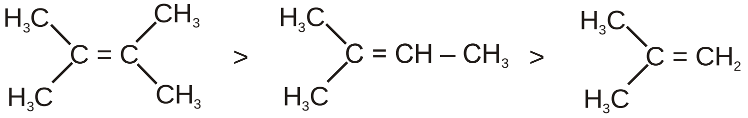
Th9 Applications of Electronic effects

(a) Stability of Alkenes: More is the number of hyperconjugative structures more stable is the alkene. "More alkylated alkenes are more stable".

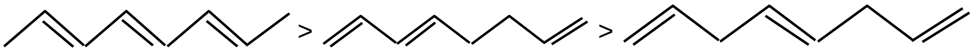
Stability of alkenes $\propto$ delocalisation of π electrons

$\propto$ no. of hyperconjugative structures

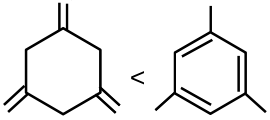
Ex.



Ex.



Ex.



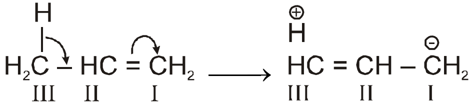
(b) Heat of hydrogenation : Greater the number of α hydrogen results greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation

Stability of alkenes $\propto$ no. of hyperconjugative structures $\propto \dfrac{1}{\Delta H_{\text{Hydrogenation}}}$

Ex. $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH = CH - CH_3$ $(\Delta H_{\text{Hydrogenation}})$

(c) Bond Length : Bond length is also affected by hyperconjugation

Ex.

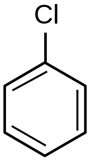


(i) Bond length of C(II) – C(III) bond is less than normal C–C bond.

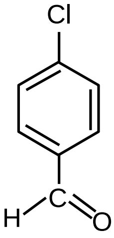
(ii) Bond length of C(II) – C(I) bond is more than normal C=C bond.

(iii) C–H bond is longer than normal C–H bond.

Ex.



(I)



(II)

C–Cl Bond length → I > II

(d) Stability of reaction intermediates:

(i) Stability of carbocation $\propto$ + M, +H, + I groups.

(ii) Stability of carbon free radical $\propto$ + I groups.

(iii) Stability of carbanion $\propto$ – M, – I groups.

Note: Resonance effect or delocalisation of electrons increases the stability of over all system.

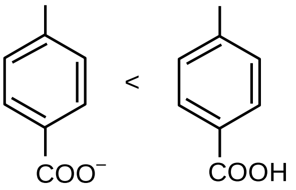
For example carbocation, carbon free radical, carbanion & Alkenes.

(e) Dipole moment: Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule.

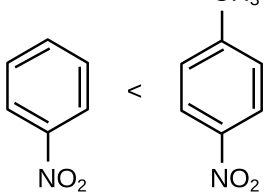
Ex. (i) $CH_2=CH_2 < CH_3-CH=CH_2$ (Dipole moment)

(ii) $H-CH=O < CH_3-CH=O < CH_3-CH=CH-CH=O$ (Dipole moment)

(iii)

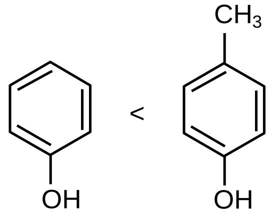


(iv)



μ=3.93D μ=4.93D

(iv)



μ=1.54D μ=1.57D

(f) Acidic & Basic strength of organic compounds :

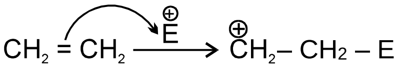
(i) Acidity (K_a) ∝ – M, –I groups.

(ii) Basicity (K_b) ∝ + M, +H, +I groups and solvation effect in aqueous solution.

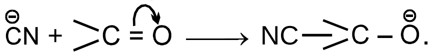
Th10: Electromeric effects

It is a temporary effect. The organic compound having a multiple bond (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 π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. It is represented by E and the shifting on the electrons is shown by a curved arrow. There are two types of eletromeric effect.

D11: **(i) +E effect:** In this effect π-electron of the multiple bond are transferred to that atom to which the reagent gets attached.



$$CH_2 = CH_2 \xrightarrow{\overset{\oplus}{E}} \overset{\oplus}{C}H_2 - CH_2 - E$$

D12: **(ii) –E effect:** In this effect the π-electron of the multiple bond are transferred to that atom to which the attacking reagent does not get attached  $\overset{\ominus}{C}N + {>}C = O \longrightarrow NC - {>}C - \overset{\ominus}{O}$.

Note : When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.

CHECK LIST

Definitions (D)

D1 Inductive Effect ☐
D2 – I Effect ☐
D3 + I Effect ☐
D4 Resonance ☐
D5 Resonacne Energy ☐
D6 Mesomeric Effect (or Resonance Effect) ☐
D7 +M Effect ☐
D8 –M Effect ☐
D9 Hyperconjugation ☐
D10 Aromaticity ☐
D11 +E Effect ☐
D12 –E Effect ☐

Theories (Th)

Th1: Inductive Effect ☐
Th2: Resonacne ☐
Th3: Mesomeric Effect (or Resonance Effect) ☐
Th4: SIR (Steric Inhibition of Resonance) ☐
Th5: Hyperconjugation ☐
Th6: Comparision between Electronic Effects ☐
Th7: Important Points ☐
Th8: Aromatic Character (The Huckel 4n+2 Rule) ☐
Th9: Applications of Electronic Effects ☐
Th10: Electromeric Effects ☐