

<b>Class: XI</b>	<b>Chapter 12</b>
<b>Subject: Chemistry</b>	<b>Organic Chemistry-Some Basic principles and Techniques</b>
	<b>Date-27/10/21</b>

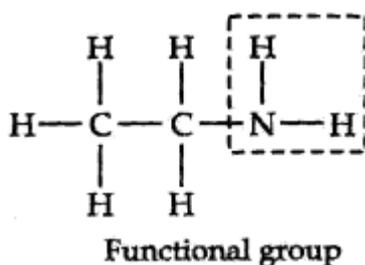
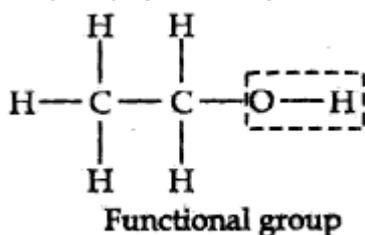
## Organic Chemistry

Organic chemistry is the branch of chemistry that deals with the study of hydrocarbons and their derivatives.

### The Shapes of Carbon Compounds:

In organic or carbon compounds, s and p orbitals are involved in hybridisation. This leads to three types of hybridisation which are  $sp^3$  (in alkanes) – Tetrahedral in shape  $sp^2$  (in alkenes) – Planar structure  $sp$  (in alkynes) – Linear molecule

**Functional Group:** The functional groups are atoms or groups of atoms joined in a specific manner which determines the chemical properties of the organic compound. The examples are hydroxyl group ( $-OH$ ), aldehyde group ( $-CHO$ ) and carboxylic acid group ( $-COOH$ ) etc.



### • Homologous Series

A homologous series may be defined as a family of organic compounds having the same functional group, similar chemical properties and the successive members differ from each other in molecular formula by  $-CH_2$  units.

The members of a homologous series can be represented by same general molecular formula.

### • Nomenclature of Organic Compounds

**Common name (Common system):** Before the IUPAC system of nomenclature, organic compounds were named after the sources of origin, for example, urea was so named because it was obtained from the urine of mammals. Formic acid was so named since it was extracted from red ants called formica.

Compound	Common name
CH <sub>4</sub>	Methane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>n</i> -Butane
(H <sub>3</sub> C) <sub>2</sub> CHCH <sub>3</sub>	Isobutane
(H <sub>3</sub> C) <sub>4</sub> C	Neopentane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> OH	<i>n</i> -Propyl alcohol
HCHO	Formaldehyde
(H <sub>3</sub> C) <sub>2</sub> CO	Acetone
CHCl <sub>3</sub>	Chloroform
CH <sub>3</sub> COOH	Acetic acid
C <sub>6</sub> H <sub>6</sub>	Benzene
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Anisole
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	Aniline
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	Acetophenone
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub>	Ethyl methyl ether

● **IUPAC (International Union of Pure and Applied Chemistry) System**

According to IUPAC system, the name of an organic compound contains three parts:

(i) word root, (ii) suffix, (iii) prefix.

**(i) Word root:** Word root represents the number of carbon atoms present in the principal chain, which is the longest possible chain of carbon atoms.

For special word roots

meth	—	C <sub>1</sub>
eth	—	C <sub>2</sub>
Prop	—	C <sub>3</sub>
but	—	C <sub>4</sub>

**(ii) Suffix:** Suffix are of two types, primary suffix, secondary suffix.

(a) Primary Suffix: It indicates the type of bond in the carbon atoms.

**For example:** Primary suffix

ane	for	C—C bond
ene	for	C=C bond
yne	for	C≡C bond

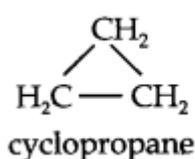
(b) Secondary Suffix: Secondary suffix is used to represent the functional group.

**(iii) Prefix:** Prefix is a part of IUPAC name which appears before the word root.

Prefix

are of two types:

(a) Primary prefix: For example, primary prefix cyclo is used to differentiate cyclic compounds.



(b) Secondary prefix: Some functional groups are considered as substituents and

denoted by secondary prefixes.

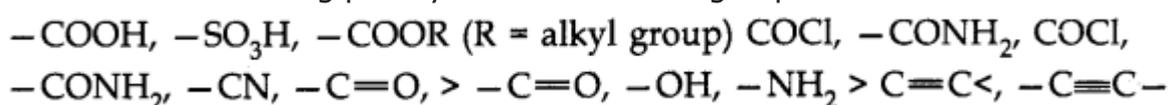
For example:

Substituted Group	Secondary prefix.
— F	Flupro
— Cl	Chloro
— Br	Bromo
— NO	Nitroso
— NO <sub>2</sub>	Nitro
— CH <sub>3</sub>	Methyl
— OCH <sub>3</sub>	Methoxy

**Naming of Compounds Containing Functional Groups:** The longest chain of carbon atoms containing the functional group is numbered in such a manner that the functional group is attached at the carbon atoms possessing lowest possible number in the chain.

In case of polyfunctional compounds, one of the functional group is selected as principal functional group and the compound is named on that basis. The choice of principal functional group is made on the basis of order of preference.

The order of decreasing priority for the functional group is



### Isomerism

When there are two or more compounds possessing the same molecular formula but different structural formula and different physical and chemical properties, the phenomenon is called isomerism. Such compounds are called isomers.

It is of two types:

- (1) Structural Isomerism
- (2) Stereoisomerism

**(1) Structural Isomerism:** Structural isomerism is shown by compounds having the same molecular formula but different structural formulae differing in the arrangement of atoms.

#### The structural isomerism type:

- Chain
- Position
- Functional
- Meta-merism
- Tauto-merism

#### The different types of stereoisomerism are:

- Geometrical
- Optical

- o conformational

Let us study first structural isomerism types :

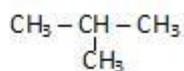
1 . **Chain isomerism**– The compounds that have same molecular formula ,but different arrangement of atoms within the chain.

Example:  $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$

Propane will not show chain isomerism



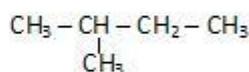
normal – Butane



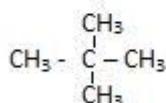
iso-butane



Normal pentane

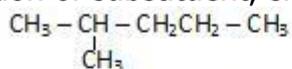


iso – pentane (2methyl butane)

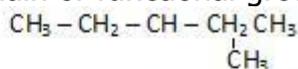


(neo -pentane)

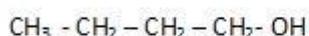
**2.Position isomerism:** The compounds with same molecular formula, but differ in position of substituent, side chain or functional groups.



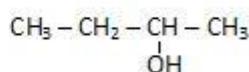
(2-methyl pentane)



(3-methyl pentane)



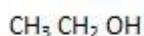
(Butanol)



2- Butanol

3. **Functional isomerism:** The compounds with same molecular formula but differ in type of functional group and also in physical and chemical properties.

Example:



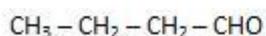
Ethanol

(Alcohol)

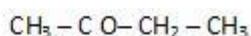


methoxy methane

(ether)



(Aldehyde)

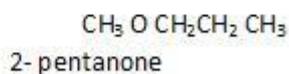
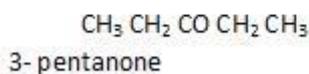
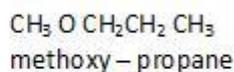
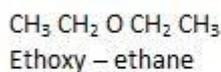


(Ketone)

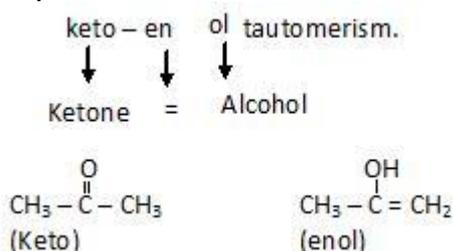
3. **Metamerism:** The compounds that have same molecular formula ,but differ in number of carbon atoms around functional group.

It is shown by functional groups like ether, esters, ketones.

Example:



4. **Tautomerism:** In this simultaneous movement of  $n$  electron cloud and Hydrogen take place. Most common tautomerism is keto – enol tautomerism.



**(2) Stereoisomerism:** When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called stereoisomerism. The stereoisomers have same structural formula but differ in arrangement of atoms in space. Stereoisomerism is of two types:

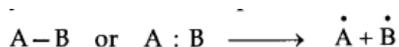
- Geometrical or Cis-Trans Isomerism
- Optical Isomerism

• **Fundamental Concepts in Organic Reaction Mechanism**

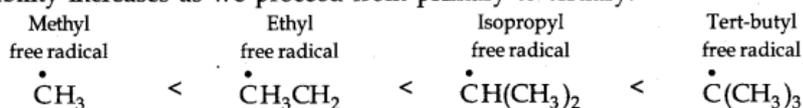
Fission of a covalent bond: A covalent bond can undergo Fission in two ways:

- By Homolytic Fission or Homolysis
- By Heterolytic Fission or Heterolysis

**Homolytic Fission:** In this process each of the atoms acquires one of the bonding electrons.

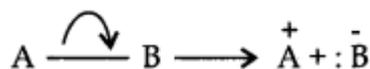


The products  $\dot{\text{A}}$  and  $\dot{\text{B}}$  are called free radicals. They are electrically neutral and have one unpaired electron associated with them. Homolytic fission is the most common mode of fission in vapour phase. Alkyl radicals are classified as primary, secondary or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary.



**Heterolytic Fission:** In this process one of atoms acquires both of the bonding electrons when the bond is broken.

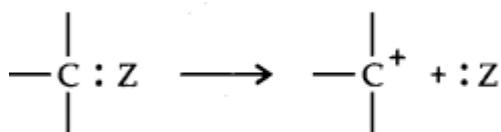
If B is more electronegative than A which thereby acquires both the bonding electrons and becomes negatively charged.



The products of heterolytic fission are ions.

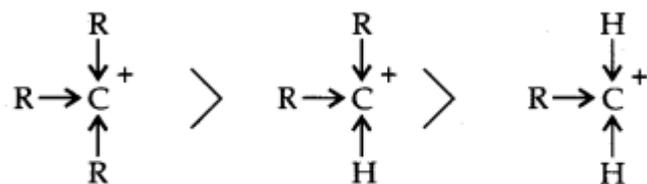
**Reaction Intermediates:** Heterolytic and homolytic bond fission results in the formation of short-lived fragments called reaction intermediates. Among the important reaction intermediates are carbonium ions, carbanions, carbon free radicals and carbenes.

**Carbonium Ions (carbocations):** Organic ions which contain a positively charged carbon atom are called carbonium ions or carbocations. They are formed by heterolytic bond fission.



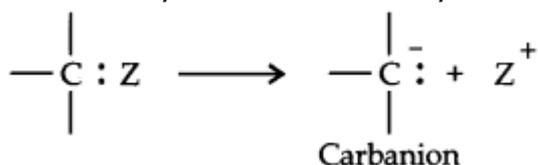
where Z is more electronegative than carbon.

Tertiary carbonium ion is more stable than a secondary, which in turn is more stable than a primary because of +I effect associated with alkyl group.

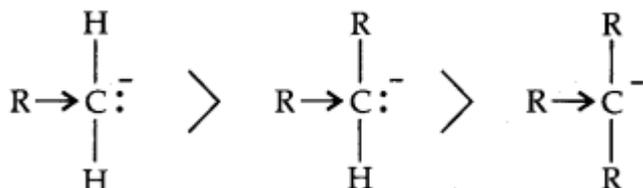


3° TERTIARY    2° SECONDARY    1° PRIMARY

**Carbanion:** Organic ion which contains a negatively charged carbon atom are called carbanions. They are also formed by heterolytic bond fission.



Where Z is less electronegative than carbon. A primary carbanion is more stable than a secondary, which in turn is more stable than a tertiary, because of +I effect associated with alkyl group.



**Electrophile:** It is positively charged or neutral species which is electron deficient, e.g.,

$He^+$ ,  $H_2O^+$ ,  $CH_3^+$ ,  $NH_4^+$ ,  $AlCl_3$ ,  $SO_3$ ,  $CHCl_2$ ,  $CCl_3$ .

**Nucleophile:** It is negatively charged or neutral species with lone pair of electrons e.g.,  $(HO^-)$ , Cyanide  $(C \equiv N^-)$ ,  $H_2O$ :  $R_3N$ ,  $R_2NH$  etc.

**Electron Displacement Effects in Covalent Bonds:** Electronic displacements in covalent bonds occurs due to the presence of an atom or group of different electronegativity or under the influence of some outside attaching group.

These lead to a number of effects which are as follows:

- (i) Inductive effect (ii) Electromeric effect
- (iii) Resonance or Mesomeric effect (iv) Hyperconjugation effect.

**Inductive Effect:** It involves  $\sigma$  electron. The  $\sigma$  electrons which form a covalent bond are seldom shared equally between the two atoms. Due to different electronegativity electrons are displaced towards the more electronegative atom. This introduces a certain degree of polarity in the bond.

The more electronegative atom acquires a small negative charge ( $\delta^-$ ). The less electronegative atom acquires a small positive charge ( $\delta^+$ ).

Consider the carbon-chlorine bond

As chlorine is more electronegative, it will become negatively charged with respect to the carbon atom.



Structure I- indicates the relative charges on the two atoms.

Structure II- indicates the direction in which the electrons are drawn.

Atoms or groups which lose electrons towards a carbon atom are said to have a +I effect. Those atoms or groups which draw electrons away from a carbon atom are said to have a -I Effect.

Some common atoms or groups which cause +I or -I effects are shown below:

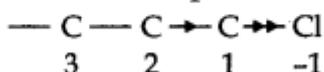
- (i) -I Effect Groups (Electrons-attracting)

$\text{NO}_2$ , F, Cl, Br, I, OH,  $\text{C}_6\text{H}_5-$

- (ii) +I Effect Groups (Electron -releasing)

$(\text{CH}_3)_3\text{C}-$ ,  $(\text{CH}_3)_2\text{CH}-$ ,  $\text{CH}_3\text{CH}_2-$ ,  $\text{CH}_3-$

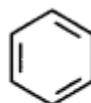
An inductive effect is not confined to the polarization of one bond.



The inductive effect of  $\text{C}_3$  upon  $\text{C}_2$  is significantly less than the effect of the chlorine atom on  $\text{C}_1$ .

**Resonance Structure:** A number of organic compounds cannot be accurately represented by one structure.

For example, benzene is ordinarily represented as



Benzene

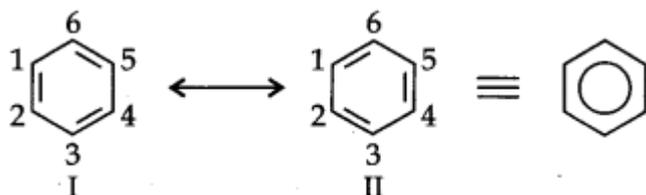
This structure has three  $\text{C}-\text{C}$  bonds and three  $\text{C}=\text{C}$  bonds.

Carbon-carbon double bond length = 1.34 Å

Carbon-carbon single bond length = 1.54 Å. But it has been determined

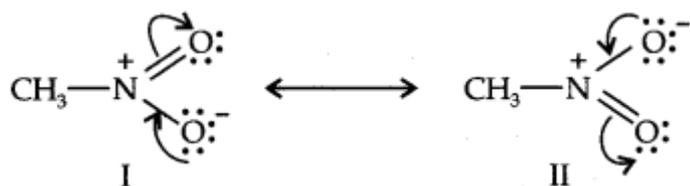
experimentally that all carbon-carbon bonds in benzene are identical and have same bond length (1.39Å).

Thus the structure of benzene cannot be represented by single structure. It can be represented equally well by the energetically similar structures I and II. The two structures are called resonance structures.



Actual structure of benzene is resonance hybrid of structures I and II.

Another example of resonance is provided by nitromethane ( $\text{CH}_3\text{NO}_2$ ) which can be represented by two Lewis structures.



The actual structure of nitromethane is a resonance hybrid of the two canonical forms I and II. Resonance energy: The difference in the energy between the most stable contributing structure for a compound and its resonance hybrid is called as resonance energy or resonance stabilisation energy.

**Resonance Effect:** The polarity produced in the molecule by the interaction of two  $\pi$ -bonds or between a  $\pi$ -bond and a lone pair of electrons present on an adjacent atom. There are two types of resonance or mesomeric effects designated as R or M effect.

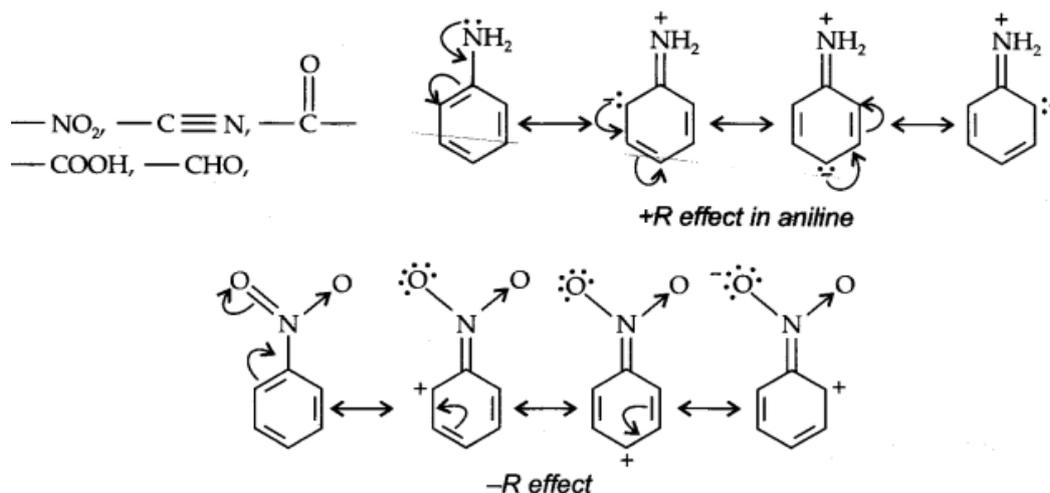
Positive Resonance Effect (+R effect):

Those atoms which lose electrons towards a carbon atom are said to have a +M effect or +R effect. For example:

$-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $-\text{NH}_2$ ,  $-\text{NR}_2$ ,  $-\text{OH}$ ,  $-\text{OCH}_3$

**Negative Resonance Effect (-R effect):** Those atoms or groups which draw electrons away from a carbon atom are said to have a -M effect or -R effect.

For example:



### Electromeric Effect (E Effect):

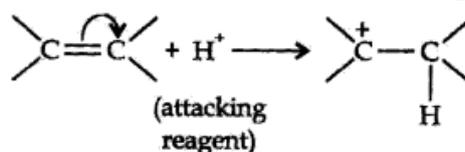
The electromeric effect refers to the polarity produced in a multiple bonded compound when it is attacked by a reagent when a double or a triple bond is exposed to an attack by an electrophile  $\text{E}^+$  (a reagent) the two  $\pi$  electrons which from the  $\pi$  bond are completely transferred to one atom or the other. The electromeric effect is represented as:



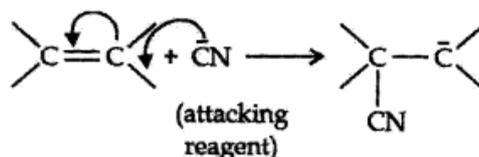
The curved arrow shows the displacement of the electron pair. The atom A has lost its share in the electron pair and B has gained this share. Therefore A acquires a positive charge and B a negative charge.

It is represented by E and the shifting of the electrons is shown by a curved arrow ( $\curvearrowright$ ). There are two distinct types of electromeric effect.

- (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.



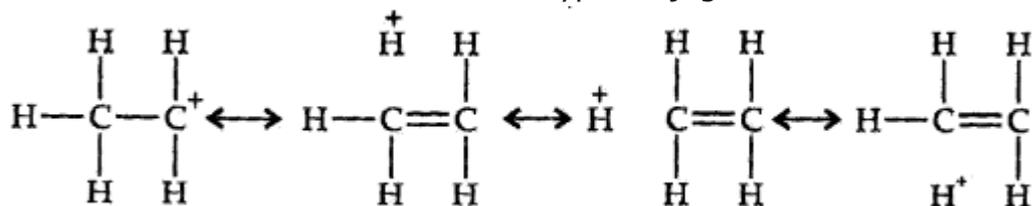
- (ii) **Negative Electromeric Effect (-E effect):** In this effect the  $\pi$  electrons of the multiple bond are shifted to that atom to which the attacking reagent does not get attached.



**Hyperconjugation or No Bond Resonance:** When the alkyl group is attached to an unsaturated system such as  $-\text{CH}=\text{CH}_2$  group the order of inductive effect gets reversed. The behaviour can be explained by hyperconjugation effect.

Such structures are arrived at by shifting the bonding electrons from an adjacent C—H bond to the electron deficient carbon. In this way, the positive charge originally on carbon is dispersed to the hydrogen.

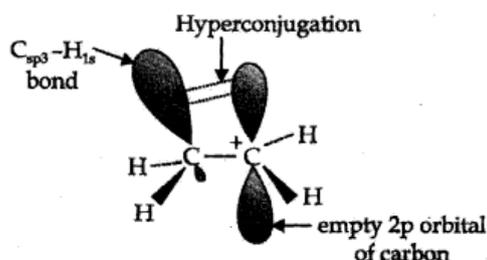
This way of electron release by assuming no bond character in the adjacent C—H bond is called No-Bond Resonance or Hyperconjugation.



### Orbital Concept of Hyperconjugation

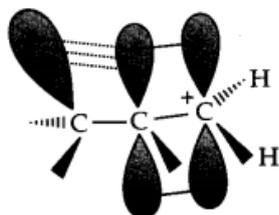
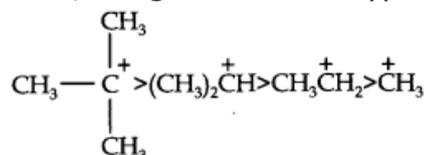
It involves delocalisation of  $\sigma$  electrons of C—H bond of an alkyl group which is attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital.

Let us consider  $\text{CH}_3\text{CH}_2^+$  (ethyl cation) in which the positively charged carbon atom has an empty p-orbital. One of the C—H bonds of the methyl group can align in the plane of this empty p-orbital and electron constituting the C—H bond in plane with this p-orbital can then be delocalised into the empty p-orbital as in Fig.



Orbital diagram showing hyperconjugation in ethyl cation

In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation.



Orbital diagram showing hyperconjugation in propene

**Note-**The above content has been absolutely prepared from home