

I N D E X

IIT JAM ORGANIC – THEORY BOOK

CHAPTER NO.	CHAPTER NAME	PAGE NO.
1	IUPAC NOMENCLATURE	1
2	GOC & ACID – BASE CHEMISTRY	9
3	AROMATICITY	37
4	STEREOCHEMISTRY	49
5	REACTIVE INTERMEDIATE	91
6	REACTION MECHANISM	141
7	REAGENTS	186
8	PERICYCLIC CHEMISTRY	232
9	AROMATIC & HETEROCYCLIC CHEMISTRY	265
10	ORGANIC SPECTROSCOPY	337
11	NATURAL PRODUCT CHEMISTRY	397

CHAPTER 1

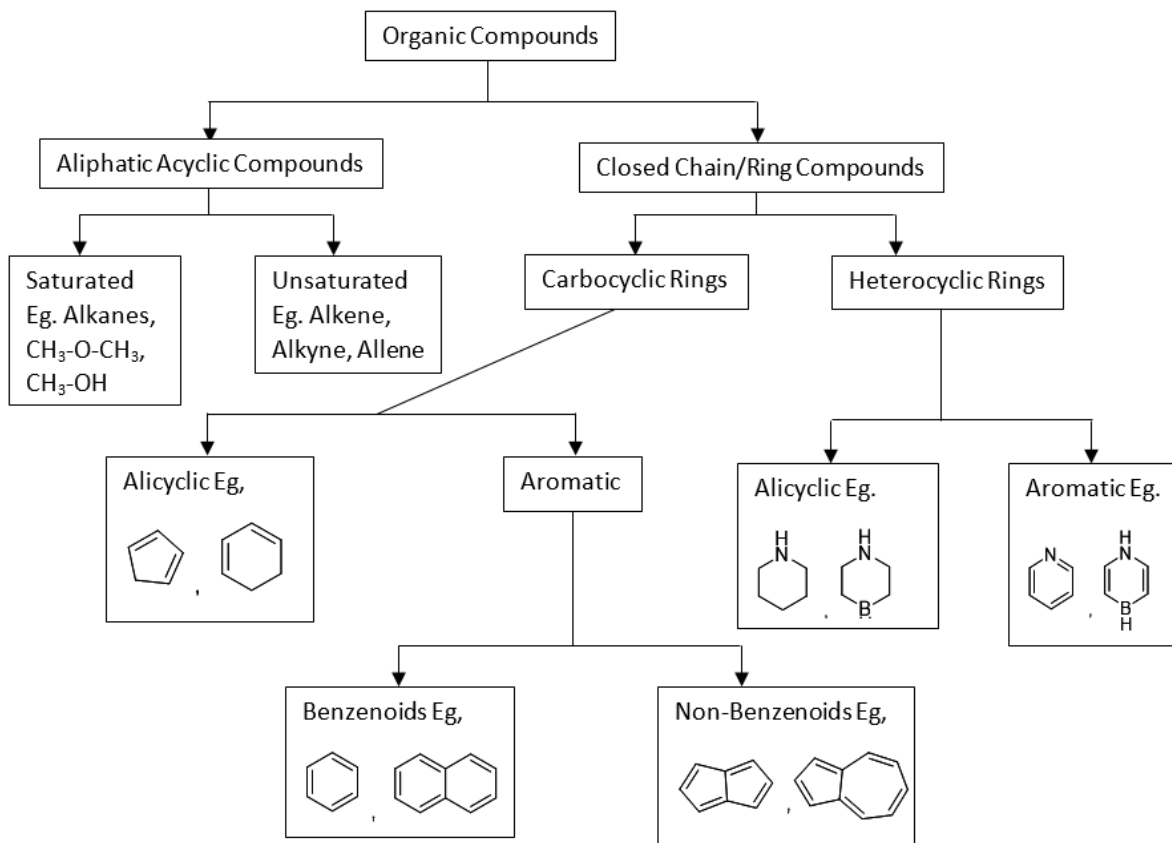
IUPAC NOMENCLATURE

Introduction:

So far, we have talked a lot about compounds by name. Many of the names we've used (polytoxin, muscone, brevetoxin) are simple names given to complicated molecules without regard for the actual structure or function of the molecule—these three names, for example, are all derived from the name of the organism from which the compound was first extracted. They are known as trivial names, not because they are unimportant, but because they are used in everyday scientific conversation.

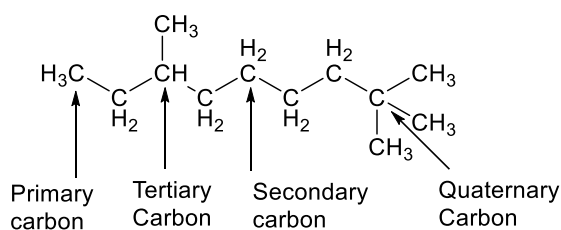
Names like this are fine for familiar compounds that are widely used and referred to by chemists, biologists, doctors, nurses, and perfumers alike. But there are over 16 million known organic compounds. They can't all have simple names, and no-one would remember them if they did. For this reason, the International Union of Pure and Applied Chemistry (IUPAC) have developed systematic nomenclature, a set of rules that allows any compound to be given a unique name that can be deduced directly from its chemical structure. Conversely, a chemical structure can be deduced from its systematic name.

Classification of Organic Compounds:



Identification of Carbon: There are four types of carbons in the carbon chain.

- Primary carbon: A carbon atom attached to one other carbon atom is termed primary carbon or 1° carbon atom.
- Secondary carbon: A carbon atom attached to two other carbon atoms is termed secondary carbon or 2° carbon atom.
- Tertiary carbon: A carbon atom attached to three other carbon atoms is termed tertiary carbon or 3° carbon atom.
- Quaternary carbon: A carbon atom attached to four other carbon atoms is termed quaternary carbon or 4° carbon atom.



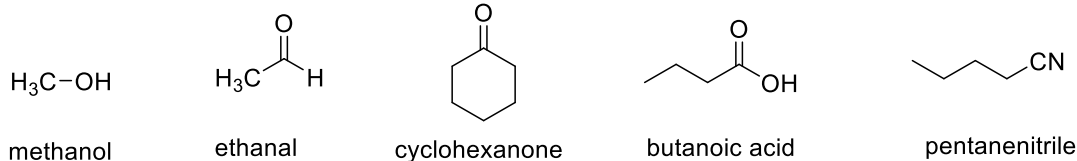
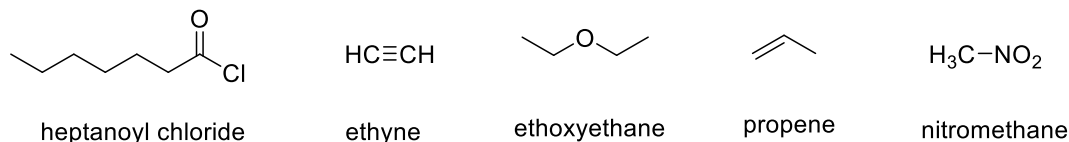
Systematic Names: Systematic names can be divided into three parts: one describes the hydrocarbon framework,

one describes the functional groups and one indicates where the functional groups are attached to the skeleton.

1) Names for the Hydrocarbon Framework:

Number of Carbon Atoms	Systematic Name	Hydrogen Framework	Cyclic Structures
One	Methane	CH ₄	-
Two	Ethane	H ₃ C—CH ₃	-
Three	Propane	H ₃ C—CH ₂ —CH ₃	
Four	Butane	H ₃ C—CH ₂ —CH ₂ —CH ₃	
Five	Pentane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₃	
Six	Hexane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₃	
Seven	Heptane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₃	
Eight	Octane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₃	
Nine	Nonane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₃	
Ten	Decane	H ₃ C—CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₂ —CH ₃	

2) Functional Group: The name of a functional group can be added to the name of a hydrocarbon framework either as a suffix or as a prefix. Some examples follow. It is important to count all of the carbon atoms in the chain, even if one of them is part of a functional group: pentanenitrile is actually BuCN. Compounds with functional groups attached to a benzene ring are named in a similar way,

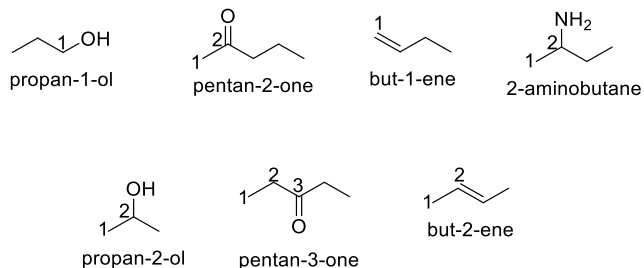


Common Names of Functional Group Having Carbons:

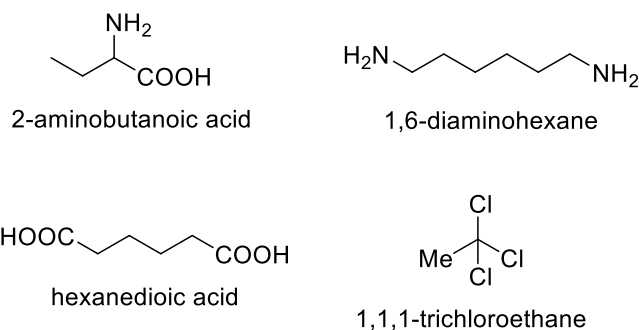
Sr. No	Functional group	Suffix
1.		-ic acid
2.		-ic anhydride
3.		-ate
4.		-amide
5.		-yl halide
6.		-aldehyde
7.	$\text{—C}\equiv\text{N}$	-o-nitrile
8.	$\text{—}\overset{+}{\text{N}}\equiv\text{C}^-$	-o-isonitrile

3) Position of Functional Group: Numbers are used to locate functional groups. Sometimes a number can be included in the name to indicate which carbon atom the functional group is attached to. When numbers are used, the carbon atoms are counted from one end. In most cases, either of two numbers could be used (depending on which end you count from); the one chosen is always the lower of the two. Notice

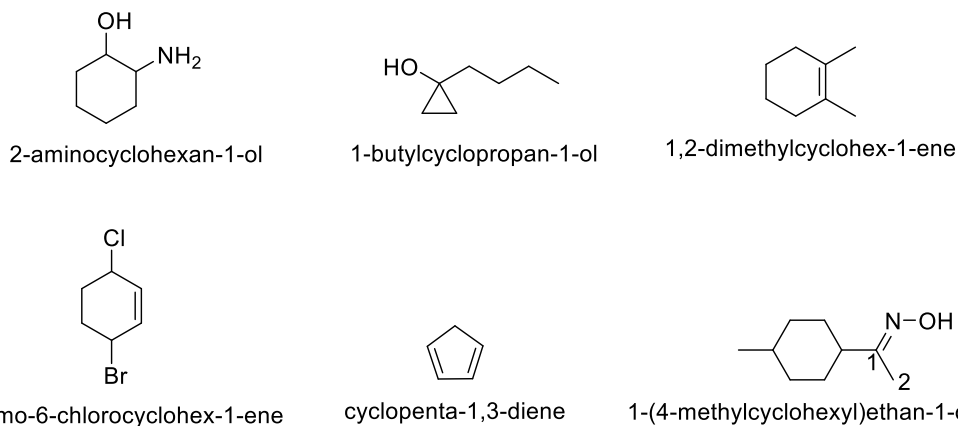
again that some functional groups are named by prefixes, some by suffixes, and that the number always goes directly before the functional group name.



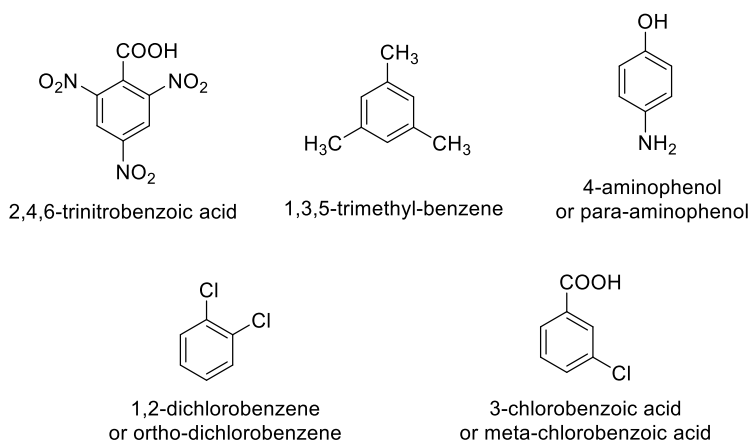
One carbon atom can have as many as four functional groups:



With cyclic compounds, there isn't an end to the chain, but we can use numbers to show the distance between the two groups—start from the carbon atom carrying one of the functional groups, then count round. These rules work for hydrocarbon frameworks that are chains or rings, but many skeletons are branched. We can name these by treating the branch as though it were a functional group



Ortho, meta, and para: With substituted benzene rings, an alternative way of identifying the positions of the substituents is to use the terms ortho, meta, and para. Ortho compounds are 1,2-disubstituted, meta compounds are 1,3-disubstituted, and para compounds are 1,4-disubstituted.

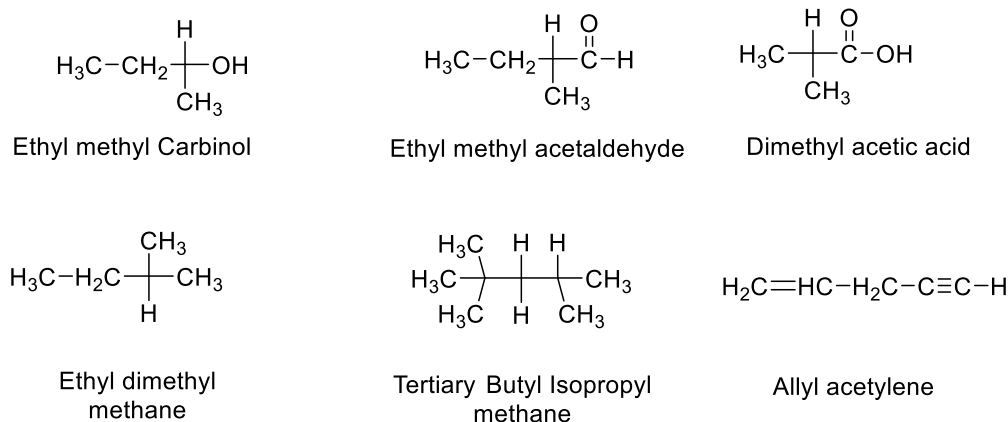


The terms ortho, meta, and para are used by chemists because they're easier to remember than numbers, and the words carry with them chemical meaning. Ortho shows that two groups are next to each other on the ring even though the atoms may not happen to be numbered 1 and 2. They are one example of the way in which chemists don't always use systematic nomenclature but revert to more convenient 'trivial' terms.

Derived System: According to this system name to any compound is given according to the parent name of the homologous series. This system is reserved for the following homologous series,

Sr.No	Homologous Series	Derived Name	Structure
1.	Alkane	Methane	$\begin{array}{c} \\ -C- \\ \end{array}$
2.	Alkene	Ethylene	$\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array}$
3.	Alkyne	Acetylene	$-C \equiv C-$
4.	Alkanol	Carbinol	$\begin{array}{c} \\ -C-OH \\ \end{array}$
5.	Alkanal	Acetaldehyde	$\begin{array}{c} \\ -C-CHO \\ \end{array}$
6.	Alkanoic acid	Acetic Acid	$\begin{array}{c} \\ -C-COOH \\ \end{array}$
7.	Alkanoyl halide	Acetyl halide	$\begin{array}{c} \\ -C-COX \\ \end{array}$
8.	Alkanamide	Acetamide	$\begin{array}{c} \\ -C-CONH_2 \\ \end{array}$
9.	Alkanone	Acetone	$\begin{array}{c} \quad \quad \\ -C-C-C- \\ \quad \quad \\ \quad O \quad \end{array}$

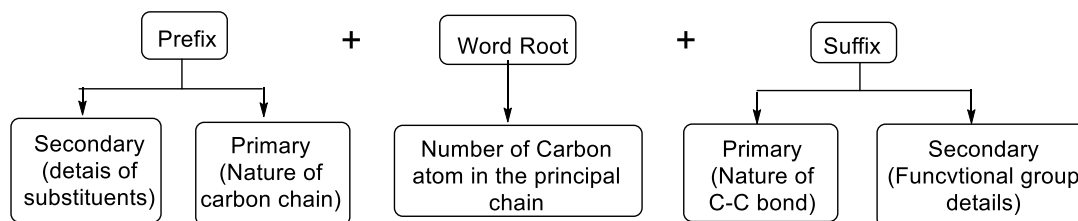
Derived Names of some organic compounds:



IUPAC NOMENCLATURE: Features of IUPAC nomenclature system is given as,

- A given compound can be assigned only one name.
- A given name can clearly direct in writing of one and only one molecular structure.
- The system can be applied in naming complex organic compounds.
- The system can be applied in naming multifunctional organic compounds.
- This is a simple, systematic and scientific method for nomenclature of organic compound.

IUPAC Nomenclature of Aliphatic Compounds: The name of an organic compound consists of three parts:



1) Prefix:

A. Primary Prefixes:

Sr. No.	Functional Group	Prefix
1.	Cyclic	cyclo-
2.	Bicyclic	bicycle-
3.	Tricyclic	tricycle-
4.	Spiro	spiro-

B. Secondary Prefixes:

Sr. No.	Functional Group	Prefix
1.	-X	Halo
2.	-OR	Alkoxy
3.	-NO ₂	Nitro
4.	-N=O	Nitroso
5.	-N=N-	Azo
6.	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{O} \end{array}$	Epoxy

2) Word Root: It represents number of carbon atom in parent chain.

No. Of Carbons	1	2	3	4	5	6	7	8	9	10	11	12	20
Word root	meth	eth	prop	but	pent	hex	hept	oct	non	dec	undec	dodec	eicos

3) Suffix:

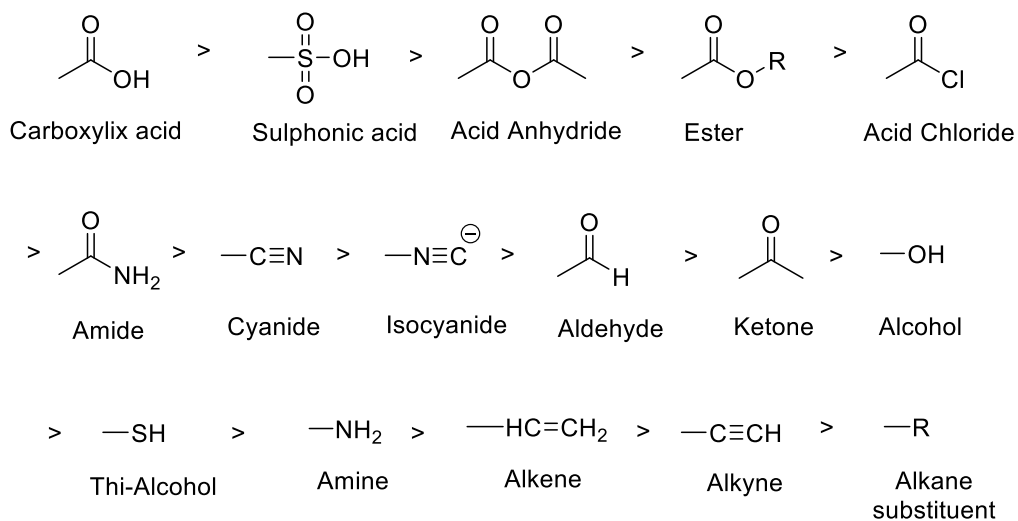
A. Primary Suffix: It represents the bonding nature between C–C in selected parent chain.

Sr. No	Nature of bond	Suffix
1.	C-C	ane
2.	C=C	ene
3.	2 C=C	diene
4.	C≡C	yne
5.	2 C≡C	diyne
6.	C=C + C≡C	enyne

B. Secondary Suffix: It is given on the basis of principal functional group present in parent chain. 2° Suffix always written after 1° Suffix. Last letter of primary suffix 'e' is cancelled only when 1st alphabet of 2° suffix is vowel (a,i,e,o,u).

Sr. No.	Functional group	Secondary Suffix
1.	-OH	-ol
2.	-SH	-thiol
3.	-NH ₂	-amine
4.	—C≡N	-nitrile
5.	—N≡C [⊖]	-isocarbonitrile
6.		-al
7.		-one
8.		-oyl chloride
9.		-oate
10.		amide
11.		-oic anhydride
12.		-oic acid
13.	—SO ₃ H	Sulphonic acid

Priority Order of Functional Groups for Nomenclature:

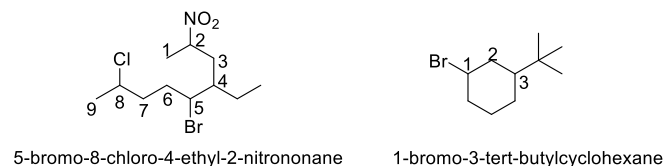


Naming Substituted Alkanes and Cycloalkanes with SECONDARY SUFFIXES:

Organic compounds containing substituents are named following this sequence of steps:

- A. Step 1:** Find the longest continuous carbon chain. Determine the root name for this parent chain. In cyclic compounds, the ring is usually considered the parent chain, unless it is attached to a longer chain of carbons; indicate a ring with the prefix “cyclo” before the root name. When there are two longest chains of equal length, use the chain with the greater number of substituents.
- B. Step 2:** Number the chain in the direction such that the position number of the first substituent is the smaller number. If the first substituents from either end have the same number, then number so that the second substituent has the smaller number, etc.
- C. Step 3:** Determine the name and position number of each substituent. A substituent on a nitrogen is designated with an “N” instead of a number.
- D. Step 4:** Indicate the number of identical groups by the prefixes di, tri, tetra, etc.
- E. Step 5:** Place the position numbers and names of the substituent groups, in alphabetical order, before the root name. In alphabetizing, ignore prefixes like sec-, tert-, di, tri, etc., but include iso and cyclo. Always include a position number for each substituent, regardless of redundancies.

Examples:



Naming Substituted Alkanes and Cycloalkanes with PRIMARY SUFFIXES:

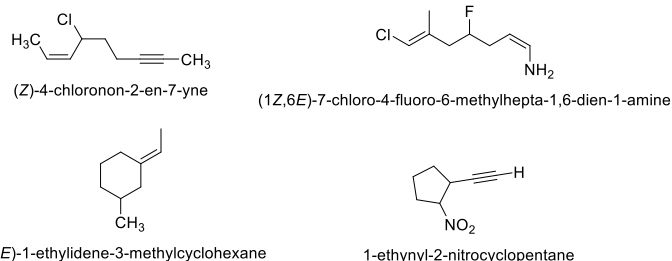
- 1) Alkenes:** Follow the same steps as for alkanes, except:
 - a. Number the chain of carbons that includes the C=C so that the C=C has the lower position number, since it has a higher priority than any substituents;
 - b. Change “ane” to “ene” and assign a position number to the first carbon of the C=C.

- c. Designate geometrical isomers with a cis,trans or E,Z prefix.

- 2) Alkynes:** Follow the same steps as for alkanes, except:

- a. Number the chain of carbons that includes the C≡C so that the functional group has the lower position number;
- b. Change “ane” to “yne” and assign a position number to the first carbon of the C≡C.

Example:



Nomenclature of Alicyclic Compounds: Rule of nomenclature for substituted alicyclic system are given as follows,

Rule 1: The names of acyclic compounds are obtained by adding the prefix cyclo to the name of the corresponding straight chain hydrocarbons.

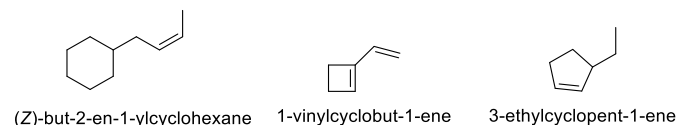
Rule 2: If number of carbon atom in cyclic chain are more in number than that of number of carbon in substituted aliphatic chain then cyclic chain is parent molecule.



Rule 3: If number of carbon in substituted aliphatic chain are more in number than that of number of carbon atom in cyclic chain then aliphatic chain is parent molecule.



Rule 4: Cyclic ring with functional group is considered as parent chain.



Rule 5: Chain containing multiple bond is considered as parent molecule.

Nomenclature of Bicyclo Compounds: Three modes of ring junction are possible for a bicyclic compound:

- In spirocyclic compounds, the two rings share only one single atom, the spiro atom, which is usually a quaternary carbon.
- In fused/condensed bicyclic compounds, two rings share two adjacent atoms. In other words, the rings share one covalent bond, *i.e.* the so-called bridgehead atoms are directly connected. e.g. decalin.
- In bridged bicyclic compounds, the two rings share three or more atoms, separating the two bridgehead atoms by a bridge containing at least one atom. For example, norbornane, also known as bicyclo[2.2.1] heptane.

Rules for Naming Bicyclo Compounds:

Rule 1: For unsubstituted bicyclo compounds name arrange in following order,

Prefix (Bicyclo) + Numbering of carbon atom in each bridge in decreasing order + Suffix

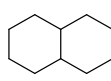
For E.g.



bicyclo[4.1.0]heptane

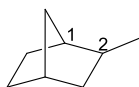


bicyclo[1.1.1]pentane

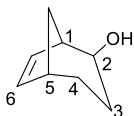


bicyclo[4.4.0]decane

Rule 2: For substituted bicycle compounds, numbering starts from bridge head carbon atom and proceeds towards longest bridge then smaller bridge and then smallest bridge.



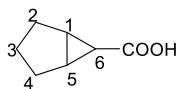
2-methylbicyclo[2.2.1]heptane



bicyclo[3.2.1]oct-6-en-2-ol



3-bromobicyclo[3.1.1]heptan-6-one



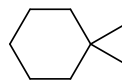
bicyclo[3.1.0]hexane-6-carboxylic acid

Rules for naming Spiro Compounds:

Rule 1: For unsubstituted spiro compounds name arrange in following order,

Prefix (Spiro) + Numbering of carbon atom in each bridge in increasing order + Suffix

For Eg.

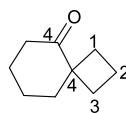


spiro[2.5]octane

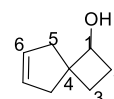


spiro[3.4]octane

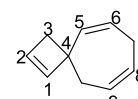
Rule 2: For substituted spiro compounds, numbering starts from carbon atom of small ring which is next to spiro atom proceeds toward other carbon atom of smaller ring then towards larger ring via spiro carbon atom.



spiro[3.5]nonan-5-one



spiro[3.4]oct-6-en-1-ol



spiro[3.6]deca-1,5,8-triene

CHAPTER - 2

GOC & ACID – BASE CHEMISTRY

Delocalization:

If in the system the π electrons are not localized in alternating double bonds but are actually spread out over the whole system in a molecular orbital shaped like a ring. The electrons are therefore said to be delocalized. We shall describe the π electrons in benzene as delocalized that is, no longer localized in specific double bonds between two particular carbon atoms but spread out or delocalized over all six atoms in the ring. Delocalization focuses on the molecular orbitals covering the whole system.

Delocalized electrons in a ring structure are represented by a circle rather than single and double bonds. This means that the electrons could be anywhere along with the chemical bond.

If the double bonds were localized then these two compound given below would be chemically different i.e. double bonds are drawn shorter than the single bonds.



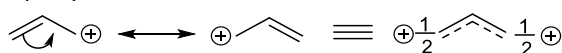
If the double bonds were localized
(Double and Single bond of different length)



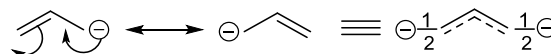
When double bonds were delocalized
(Double and Single bond of same length)

Conjugation: Conjugation focuses on the sequence of alternating double and single bonds. Conjugation to describe bonds and delocalization to describe electrons. When two double bonds are separated by just one single bond, the two double bonds are said to be conjugated. Conjugated double bonds have different properties from isolated double bonds, both physically and chemically. In the conjugated system, the electrons in the π system are spread out over all carbon atoms with most electron density on the central carbon. There are no localized double and single bonds i.e. all conjugated C–C bonds are identical. Both end carbons of system are equivalent.

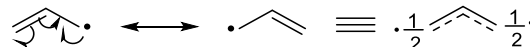
- Allylic cation conjugation:** In allyl cation conjugated system the positive charge is shared equally over the two end carbons.



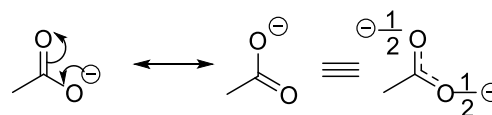
- Allylic anion conjugation:** In allyl anion conjugated system the negative charge is shared equally over the two end carbons.



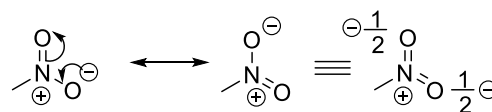
- Allylic radical conjugation:** In allyl radical conjugated system the radical (unpaired electron) is shared equally over the two end carbons.



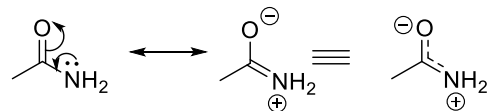
- Other allyl-like systems :**



Carboxylate anion

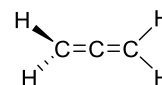


Nitro group



Amide group

If an atom has two double bonds directly attached to it, that is, there are no single bonds separating them, again no conjugation is possible. The simplest compound with such an arrangement is allene.



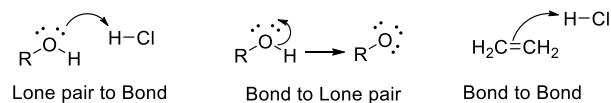
Allene

Electronic Movement in Organic Reaction:

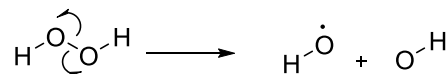
- A curly arrow ($\curvearrowright$, $\curvearrowleft$) represents the actual movement of a pair of electrons from a filled orbital into an empty orbital. Overall charge is always conserved in a reaction.
- The arrow always starts with its tail on the source of the moving electrons, representing the filled orbital involved in the reaction. The head of the arrow indicates the final destination of the pair of electrons.

- The tail of the arrow shows the source of the electron pair, which will be a filled orbital (HOMO) and can be represented by: a lone pair, a negative charge, a π bond or a σ bond.
- The head of the arrow indicates the destination of the electron pair, which will be: an empty atomic orbital where a new bond will be formed, a π^* or σ^* antibonding orbital where a new bond will be formed and an old bond will break or an electronegative atom that can support a negative charge.
- There are three moves we can do with curved arrows. These three moves are for depiction of a pair of electrons moving from:

- lone pair $\rightarrow$ bond
- bond $\rightarrow$ lone pair
- bond $\rightarrow$ bond



- Movement of single electron is indicated by single barbed 'fish hook' i.e. half headed curved arrow ($\curvearrowright$).



Bond Fission: Breaking of the covalent bond in the organic molecule occur in two ways;

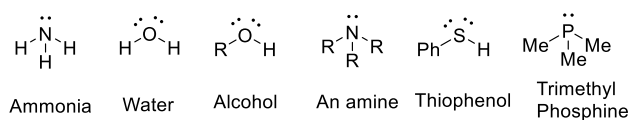
HOMOLYTIC FISSION (HOMOLYSIS)		HETEROLYTIC FISSION (HETEROLYSIS)	
(1)	Homolytic fission is a type of bond fission which involves the symmetric dissociation of a covalent bond.	(1)	Heterolytic fission is a type of bond fission which involves the asymmetric dissociation of a covalent bond.
(2)	In homolytic fission one electron is retained by each of the original fragments of the molecule.	(2)	In heterolytic fission one group retain negative charge i.e. both electron while other group get positive charge i.e empty orbital.
(3)	When a covalently bonded neutrally charged molecule is subjected to homolytic fission, two <u>free radicals</u> are obtained as the product	(3)	When a covalent bond is subjected to heterolytic fission, the bonded species with the greater <u>electronegativity</u> is the one that usually retains the bond pair of electrons and obtains a negative charge. On the other hand, the more electropositive species usually does not retain any electrons and obtains a positive charge.
(4)	In homolytic fission movement of electron is shown by single headed arrow (fish hook arrow).	(4)	In heterolytic fission movement of electrons is shown by double headed arrow.
(5)	Reaction : $\text{R}-\text{X} \longrightarrow \dot{\text{R}} + \dot{\text{X}}$	(5)	Reaction : $\text{R}-\text{X} \longrightarrow \text{R}^{\oplus} + \text{X}^{\ominus}$

Concept of Nucleophile and Electrophile:

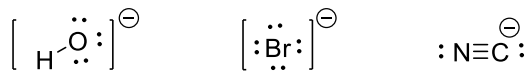
A) Nucleophile: Nucleophile is a chemical species with a pair of electrons (usually a non-bonding, or lone pair) that can be shared. The best nucleophiles have high-energy occupied molecular orbitals (HOMOs).

There are mainly four type of Nucleophiles:

1. Nucleophiles with a lone pair: Typical neutral nucleophiles with lone pairs are ammonia, amines, water, phosphines, thiols, and sulphides and alcohols.

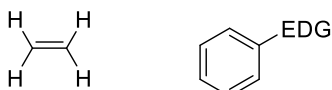


- 2. Nucleophiles with a negative charge:** In the nucleophile with negative charge the anionic centre is usually O, S, or halogen, each of which can have several identical lone pairs. For example, hydroxide has three lone pair. Carbon nucleophile with a lone pair of electrons is the cyanide ion.



Hydroxide ion Bromide ion Cyanide ion

- 3. Nucleophile with a C=C double bond:** The only common π nucleophiles are alkenes and aromatic rings. Simple alkenes are weakly nucleophilic.



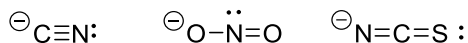
Ethylene Aromatic Nucleophile

- 4. Nucleophiles with a σ bond:** In this type, σ bond of a nucleophile is used to donate electrons, provided that a σ bond associated with electropositive atoms such as B, Si, or the metals, along with C or H. Example of that type of nucleophiles are, Borohydride anion BH_4^- , Organometallics.



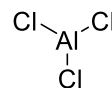
Borohydride ion Methyl Lithium

- 5. Ambident Nucleophile:** These are the Species having two nucleophilic centres, one is neutral while other is charged. They basically have two nucleophilic sites / atoms. For e.g.



- B) Electrophile:** Electrophiles are neutral or positively charged species with an empty atomic orbital (such as the empty p orbital) or a low-energy antibonding orbital that can easily accept electrons. The best electrophiles have low-energy unoccupied molecular orbitals (LUMOs).

- 1. Electrophiles with an empty atomic orbital:** The simplest electrophile is the hydrogen cation (proton) H^+ . Other electrophiles with empty atomic orbitals include boron trifluoride, aluminium trichloride, FeCl_3 , ZnCl_2 , etc.

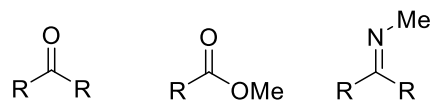


Aluminium trichloride



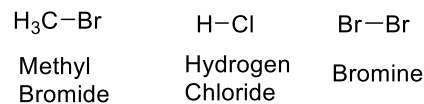
Boron trifluoride

- 2. Electrophiles with a double-bonded electronegative atom:** The most important molecules with a double bond to an electronegative atom are carbonyl compounds.



Ketone Ester imine

- 3. Electrophiles with a single bond to an electronegative atom:** Molecules with a single bond to electronegative atoms can also act as good electrophiles. Example, such as HCl or CH_3Br . Some σ bonds are electrophilic even though they have no dipole at all. The bonds in the halogens I_2 , Br_2 , and Cl_2 are a case in point. For example, Bromine is strongly electrophilic because it has a weak $\text{Br}-\text{Br}$ bond with a low energy σ^* orbital.



Polarity of the Molecules:

Electronegativity of an atom is a measure of its power to attract electrons that it is sharing in a covalent bond.

Nonpolar bond: When two identical atoms are joined by a sigma bond, both attract the sigma electrons equally towards each other. For example in C-C, H-H and F-F bonds, the electrons involved in the sigma bond are attracted equally by each atom, i.e. There is no development of charge on any of the two atoms. Such a bond is known as nonpolar bond.

Polar bond: When two atoms of different electronegativities are bonded by a sigma bond, the electrons involved are not shared equally between two atoms. The more electronegative atom attracts the bonded electrons more closely than the less electronegative atom. As a result more electronegative atom will acquire a small negative charge (δ^-) and less electronegative atom a small positive charge (δ^+). Such a bond which appears to have a positive and a negative end is called as a polar bond. The bonds such as C-Cl, C-Br, C-N, C-O, etc., are polar in nature.

The polarity of bonds can lead to polarity of molecules and affect melting point, boiling point and solubility. Molecule is said to be polar if it contains one or more polar bonds and the polar bonds are so directed that there are separate centres of positive and negative charges in the molecule. A symmetrical molecule is nonpolar even though it contains polar bonds. For example, molecules like carbon dioxide and carbon tetrachloride possess polar bonds but these are nonpolar molecules as they have symmetrical structures, i.e., the centre of the positive and negative charges is the same in the molecule.

Dipole Moments: The molecules such as H-F, H₂O, NH₃, CH₃Cl, CHCl₃, etc., are polar molecules. Polar molecules behave as small dipoles and possess a dipole moment. The dipole moment (μ) of a bond X-Y is the product of the magnitude of the charges and the distance between the charges. It is roughly equal to the difference in the electronegativities of X and Y in debye.

$$\mu = e \times d$$

Where,

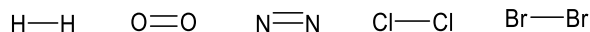
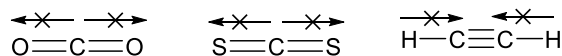
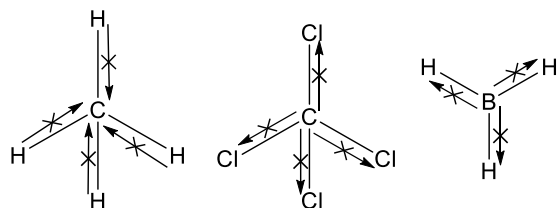
μ = dipole moment (in debye unit)

e = magnitude of separated charges (in esu)

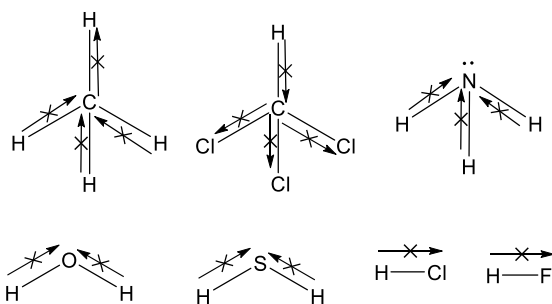
d = distance between the centre of charges (in cm).

Dipole moment of a molecule does not depend only on the polarity of the bond but also depends on the directions of the bond, i.e., the shape of the molecule.

- (i) Dipole moment of symmetrical compound is always zero ($\mu = 0$). For example H₂, O₂, N₂, Cl₂, Br₂, CH₄, CCl₄, BH₃, BF₃, CO₂, CS₂, H₂C=CH₂ and HC≡CH, etc.



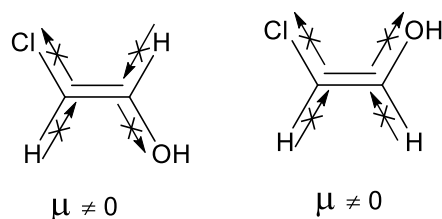
- (ii) Dipole moment of unsymmetrical compound is always greater than zero. For example H₂O, H₂S, HCl, CHCl₃, CH₃Cl, NH₃ and HF, etc.



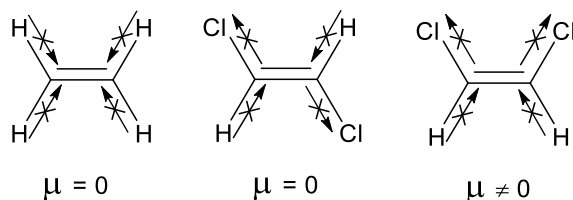
- (iii) Dipole moment increases with increase of electronegativity. Thus, the dipole moment of



- (iv) Dipole moment of cis isomer is greater than trans isomer in geometrical isomers. For example,



- (v) Dipole moment of trans isomer is zero if trans group are identical. For example



Electronic Substituent Effects on Reaction Intermediates:

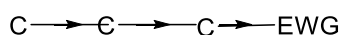
A) Inductive effect: The polarization of σ bond due to electron donating or withdrawing nature of adjacent group or atom is called as inductive effect.

- Inductive effect arises due to electronegativity difference between atoms at the either end of the bond.
- It is a permeant effect which is transmitted along the carbon-carbon chain.
- This effect is insignificant beyond the third carbon atom as it is distance dependent effect.
- This effect only operates through σ bond.
- This effect is weak effect.
- Induced charges appear as partial charges (δ^+ or δ^-).

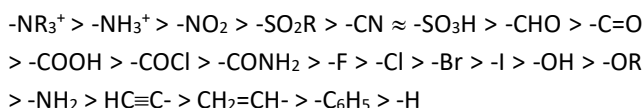
Type of Inductive Effects:

- Negative inductive effect or -I effect
- Positive inductive effect or +I effect

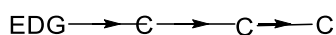
Electron withdrawing Inductive Effect / Negative inductive effect (-I): When an electronegative atom is inserted to a chain of carbon atoms, the resulting unequal sharing of electrons generates a positive charge which is transmitted through the chain. This causes a permanent dipole to arise in the molecule wherein the electronegative atom holds a negative charge and the corresponding effect is called the electron-withdrawing inductive effect or the -I effect.



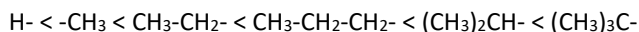
Increasing order of -I effect of groups is given as,



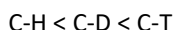
Electron donating Inductive Effect / Positive inductive effect (+I): When a chemical species which has tendency to release or donate electrons is introduced to a carbon chain, the charge is transferred through the chain and this effect is called the Positive Inductive Effect or the +I Effect.



Increasing order of +I effect of alkyl groups is given as,



Increasing order of +I effect after isotopic substitution is given as,

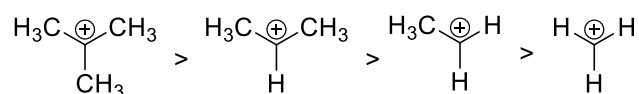


where, H is Hydrogen, D is Deuterium and T is Tritium. All are isotopes of hydrogen.

Application of Inductive Effect:

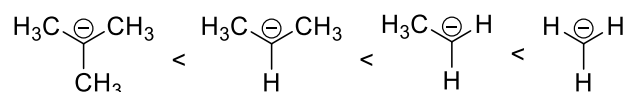
(1) Stability of Carbocation:

The stability of carbocation's increase when +I groups like alkyl groups are present adjacent to positively charged carbon. The electron donating group reduce the positive charge on the carbon by donating electron density through electron donating inductive effect (+I). This results in greater stability of carbocation. Whereas, the electron withdrawing groups destabilize the carbocation as they increase the positive charge by withdrawing electron density. The tertiary carbocation containing three alkyl groups is more stable as it give more (+I) effect than the secondary carbocation with two alkyl groups and which in turn is more stable than the primary carbocation. Methyl carbocation is the least stable among the given.



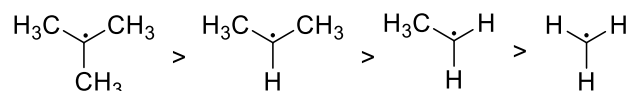
(2) Stability of Carbanion:

The stability of carbanion increase when -I groups are present adjacent to negatively charged carbon. The electron withdrawing group reduce the negative charge on the carbon by withdrawing electron density through electron withdrawing inductive effect (-I). This results in greater stability of carbanion. Whereas, the electron donating groups destabilize the carbanion as they increase the negative charge by donating electron density.



(3) Stability of Free Radical:

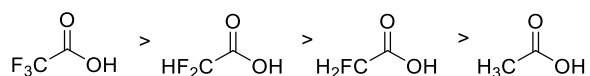
In the same way as the carbocation the stability of free radicals increases with increase in the number of alkyl groups.



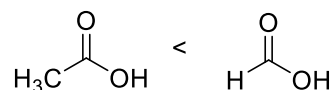
(4) Acidic Strength of Carboxylic Acid and Phenols:

A protonic acid is always in equilibrium with its conjugate base that is formed by loss of a proton. Any factor that stabilizes the negatively charged conjugate base favours greater ionization of acid. i.e. increases the acidic strength.

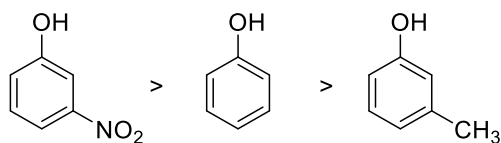
- The acidic strength increases with increase in the number of electron withdrawing Fluorine atoms as shown below.



- Formic acid is stronger acid than acetic acid since the $-\text{CH}_3$ group destabilizes the carboxylate ion.

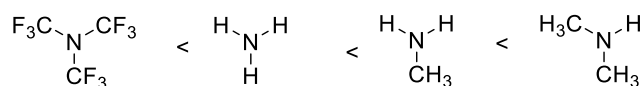


- The acidic strength of phenols increases when -I groups are present on the ring. E.g. the m-nitrophenol is stronger acid than phenol since the $-\text{NO}_2$ group is a -I group that withdraws electron density. Whereas, the meta-cresol is weaker acid than phenol, since the $-\text{CH}_3$ group shows positive inductive effect (+I).



(5) Basic Strength of Amines:

The electron donating groups increase the electron density on nitrogen which result in increasing the basic strength of amines whereas the electron withdrawing groups decrease the basic nature by decreasing electron density. Therefore alkyl amines are stronger Lewis bases than ammonia, whereas aryl amines are weaker than ammonia. Thus the order of basic strength of alkyl amines with respect to ammonia is:



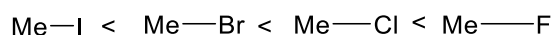
(6) Dipole Moment:

As Inductive effect arises due to electronegativity difference between atoms at the either end of the bond. As the formation of partial charges on both end take place which result in the formation of dipole. More the inductive effect of groups more will be polarity and dipole moment of the compound.

(7) Bond Length:

As the inductive effect leads to partial charge separation in compound that causes the partial ionic character to the bonds. As more the $-I$ effect of the group or atom more will be the ionic character and resultantly more be the bond length.

Bond length order of methyl halides is given as,



B) Resonance Effect:

- Resonance is the way of describing delocalisation of electrons within the certain molecule or ion.
- It also occurs by the interaction of two π bonds in the adjacent atoms.
- In resonance position of atom cannot be change but only transfer of electron density take place.
- Net charge and electron density is conserved in resonance.
- In resonance electron flow occurs from high electron density to low electron density.

- Most important condition for resonance is it requires adjacent and planar p-orbitals.
- Resonance structures or canonical structures are sets of Lewis structures that describe the delocalization of electrons in a polyatomic ion or a molecule.
- Resonance hybrid is the average of two or more structural formulas separated each from the next by a double-headed arrow in resonance.
- This effect is strong effect.
- Induced charges appear as partial charges ($\delta+$ or $\delta-$).
- This effect is distance independent effect i.e. intensity of effect remain same on all carbon atoms.

Type Of resonance Effects:

- Negative resonance effect or $-R$ effect
- Positive resonance effect or $+R$ effect

Positive Resonance Effect (+R): Positive resonance effect occurs when the groups release electrons to the other molecules by the process of delocalization.

Negative Resonance Effect (-R): Negative resonance effect occurs when the groups withdraw electrons from the other molecules by the process of delocalization.

Rules for writing resonance:

- Resonating structures are shown by double-headed arrows ($\leftrightarrow$), and we say that the real molecule or ion is a hybrid of all of the resonating structures.
- Electron flow movement occurs from high electron density region to low electron density region.

Negative charge $\rightarrow$ Lone pairs

$\rightarrow \pi$ bond electrons

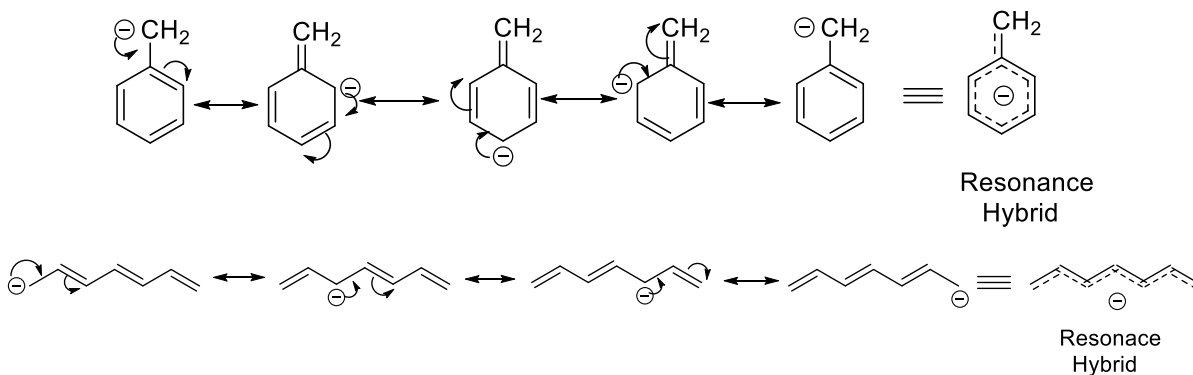
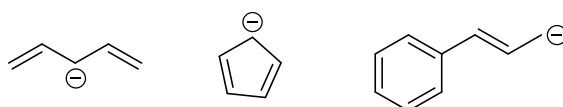
$\rightarrow \delta +$ charge

$\rightarrow$ positive charge

- σ -bond electrons never moves in resonance
- Position of atoms or molecules cannot be change only electrons are moves in resonance.
- All atoms that are part of the delocalized p-electron system must lie in a plane or be nearly planar.
- All of the structures must be proper Lewis structures. i.e octet rule must be followed by second period elements. For example, we should not write structures in which hydrogen has two bonds.

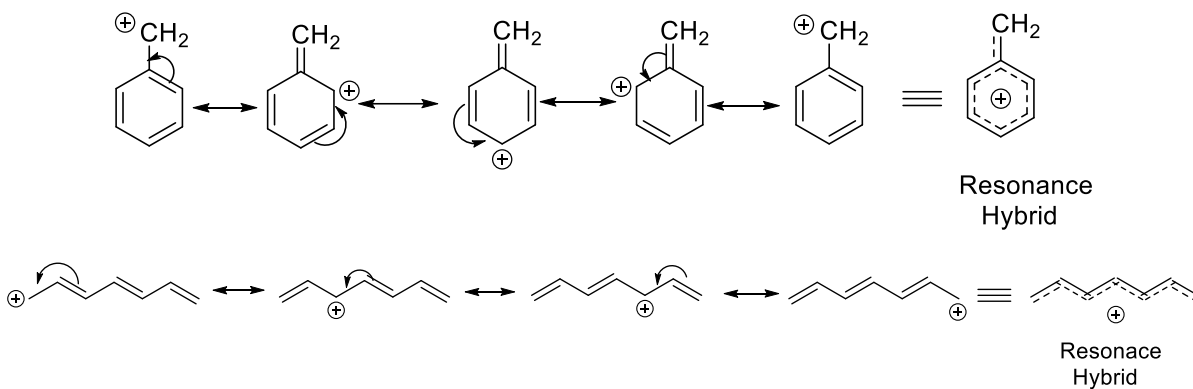
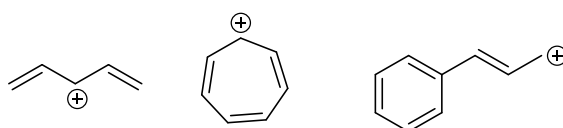
Types of Resonance:

- (1) **Negative charge and π electrons resonance:** In this type of the system stabilisation of negative charge by alternate π bonds take place.



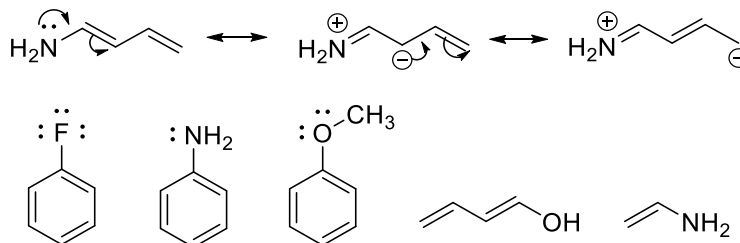
these compounds are stabilized by resonance.

- (2) **Positive charge and π electrons resonance:** In this type of the system stabilisation of positive charge by alternate π bonds take place.

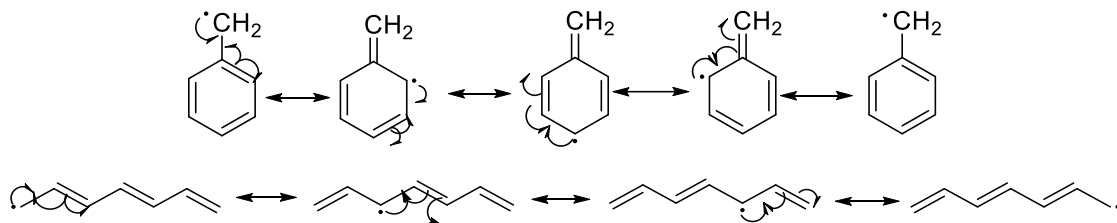


these compounds are stabilized by resonance.

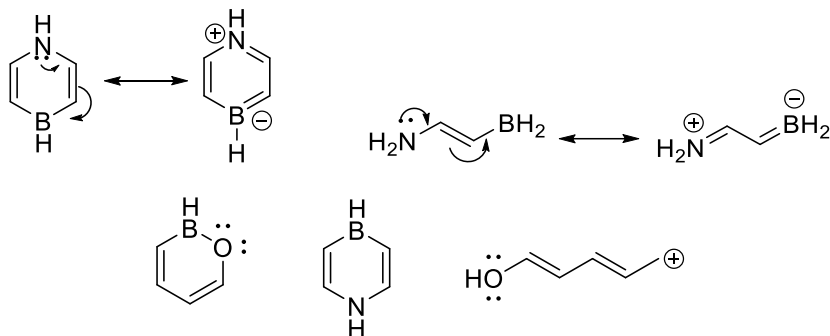
- (3) **Lone pair and π electrons resonance :** In this type of the system lone pair is in resonance with alternate π bonds.



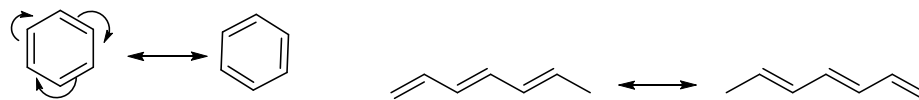
(4) **Radical and π electrons resonance:** In this type of the system stabilisation of Radical by alternate π bonds take place.



(5) **Lone pair and Vacant orbital/positive charge resonance:** In this type of the system stabilisation of positive charge by lone pair through alternate π bonds take place.

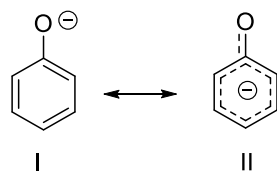


(6) **Alternate π bonds resonance:** In this type of the system π bond is in resonance with alternate π bonds.



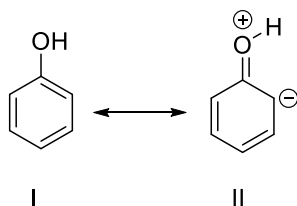
Stability of the Resonating Structures: To find which of the resonating structure among others is more stable following rules are made,

Rule 1: The resonance hybrid is more stable than any singular structure.



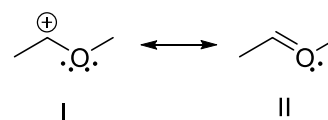
Stability : II > I

Rule 2: Molecules with minimum number of charged species are more stable. The structure with no charge is more stable than any structure with charges.



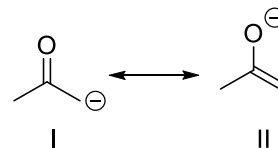
Stability : I > II

Rule 3: If rule 1 is not applicable, then compound containing maximum number of π bonds is more stable.



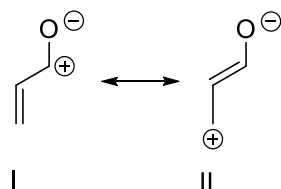
stability : II > I

Rule 4: The most stable structure will have the **negative charge** placed on the most **electronegative atom** also the most stable structure will have the **positive charge** placed on the least **electronegative atom**.



Stability : II > I

Rule 5: If all of the above rules fails then the structure with same charge at longer distance and opposite charges at shorter distance is more stable.



Stability : I > II

(C) Mesomeric Effect:

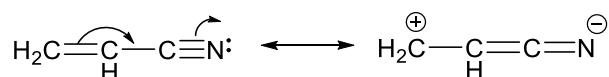
The mesomeric effect is the production of polarity in the organic molecule by the interaction of the two π bond or one π bond and lone pair of electrons present on the adjacent atom.

- Mesomeric effect is the permanent effect which transmitted through the chain.
- This effect is strong effect.
- Induced charges appear as partial charges ($\delta+$ or $\delta-$).
- This effect is distance independent effect i.e. intensity of effect remain same on all carbon atoms.

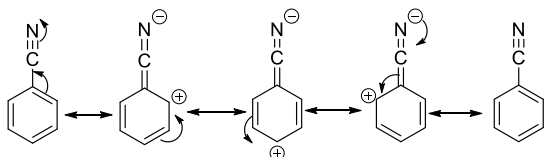
Type Of mesomeric Effects:

- Negative mesomeric effect or -M effect
- Positive mesomeric effect or +M effect

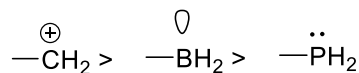
Electron withdrawing mesomeric Effect/ Negative mesomeric effect (-M) : In this effect the π -bond electrons density are transferred from the conjugate system to a particular electron withdrawing group thus the electron density of the conjugate system is decreased, therefore this phenomenon is known as Electron withdrawing mesomeric Effect (-M) effect.



- Condition : Empty orbital or very strong electron withdrawing group must be present as a withdrawing group (atom at which electronic movement is stop)
- -M effect order of the groups is given as,
 $-\text{NO}_2 > -\text{CN} > -\text{SO}_2\text{R} > -\text{SO}_3\text{H} > -\text{CHO} > -\text{C}=\text{O} > -\text{COOCOR} > -\text{COOR} > -\text{COOH} > -\text{CONH}_2$
- Electron withdrawing mesomeric Effect in benzonitrile is given below,



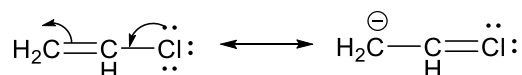
- As the electronegativity of atom increases then electron withdrawing ability of that atom is increases.
- Electron withdrawing mesomeric effect of positively charged species is much more than neutral species



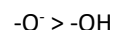
Charged species	vacant orbital present	vacant orbital and lone pair present
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- When withdrawing groups also connected with more electron donating groups then its withdrawing ability also decreases.
- When withdrawing groups also connected with more electron withdrawing groups then its withdrawing ability also increases.

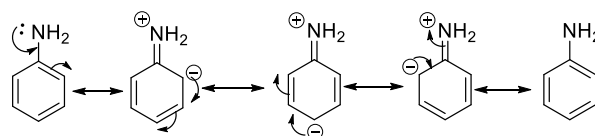
Electron donating mesomeric Effect/ Positive mesomeric effect (+M) : In this effect the π -bond electrons density are transferred from the particular electron donating group to conjugated system thus the electron density of the conjugate system is increased, therefore this phenomenon is known as Electron donating mesomeric Effect (+M) effect.



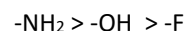
- Condition : Electron pair must be present at the donating atom (atom from which electronic movement is started)
- Electron donating mesomeric effect of negatively charged species is much more than neutral species.



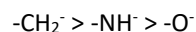
- +M effect order of the groups is given as,
 $-\text{O}^- > -\text{NH}_2 > -\text{NHR} > -\text{NR}_2 > -\text{OH} > -\text{OR} > -\text{NHCOR} > -\text{COOR} > -\text{Ph} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I}$
- Electron donating mesomeric Effect in aniline is given below,



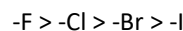
- As the electronegativity of atom carrying negative charge/lone pair increases then electron donating ability of that atom is decreases.



- +M effect order of negatively charged atoms/groups given below

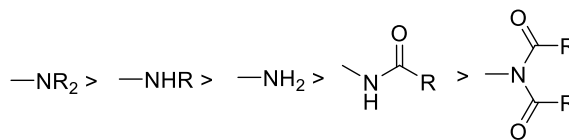


- In halogen group as we move down the group size of the halogen atom increases. In case of C-F bond more effective overlapping of 2p-2p orbital take place but as the size of -X group increases overlapping of C-X bond is not too much effective to transfer electron density, resultantly +M effect decreases.



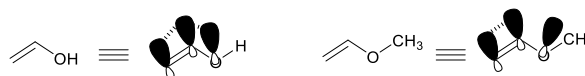
- When lone pair/negative charged containing groups also connected with electron donating groups then its donating ability also increases. When lone pair/negative charged containing groups is connected

with electron withdrawing groups then its donating ability decreases.



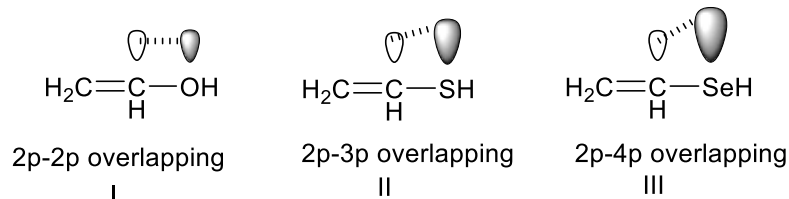
Cross Conjugation

Exception : (+M) effect of -OH group is more than -OCH₃ due to steric crowding of -CH₃ group change the plane of lone pair of oxygen.



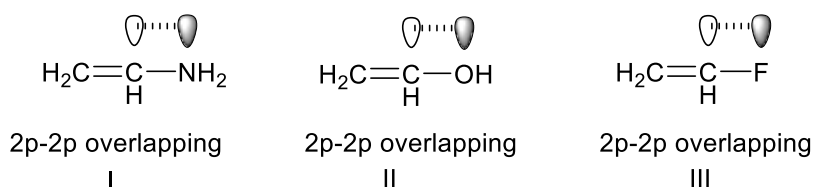
Strength of Mesomeric Effect:

- Extent of Overlapping:** If more effective overlapping of the atomic orbitals then more will be strength of mesomeric effect. 2p-2p overlapping of orbital is more effective than 2p-3p, 2p-4p, ... overlapping.



Stability : I > II > III

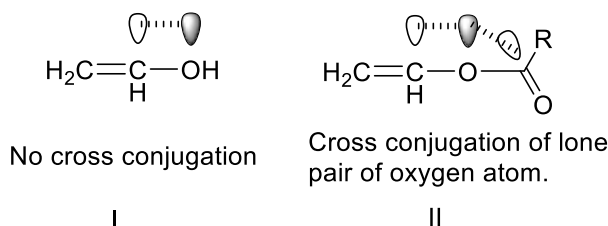
- Electronegativity:** If the extent of overlapping is same then less the electronegativity of donating atom the more will be (+M) effect and vice versa.



Electronegativity : F > O > N

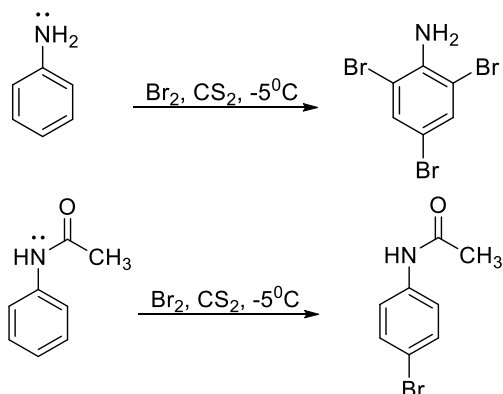
Stability : I > II > III

- Cross Conjugation:** Cross conjugation decreases the strength of (+M) effect.



+M effect : I > II

Example: Bromination of Aniline gives 2, 4, 6 trisubstituted aniline as lone -NH_2 group strongly activates the aromatic ring while if lone pair of -NH_2 is in cross conjugation then bromination take place at only para position.

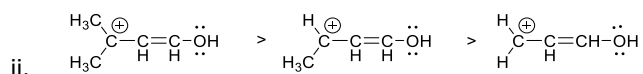
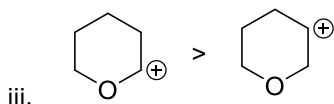


Application of Mesomeric Effect:

(1) Stability of Carbocation:

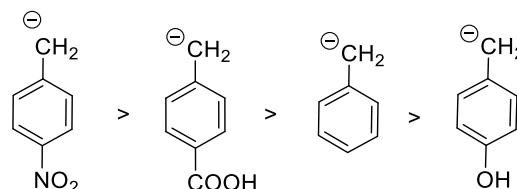
The stability of carbocation's increase when +M groups like -NH_2 , -OH etc. groups are present adjacent to positively charged carbon. The electron donating group reduce the positive charge on the carbon by donating electron density through electron donating mesomeric effect (+M). This results in greater stability of carbocation. Whereas, the electron withdrawing groups destabilize the carbocation as they increase the positive charge by withdrawing electron density.

- i. Electron donating effect of methyl stabilises carbocation with +I, while (+M) effect of -OH lone pair stabilises with +M effect.



(2) Stability of Carbanion:

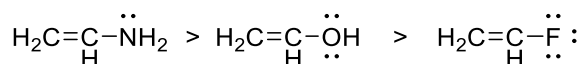
The stability of carbanion increase when -M groups like -NO_2 , -CN etc. are present adjacent to negatively charged carbon. The electron withdrawing group reduce the negative charge on the carbon by withdrawing electron density through electron withdrawing mesomeric effect (-M). This results in greater stability of carbanion. Whereas, the electron donating groups destabilize the carbanion as they increase the negative charge by donating electron density.



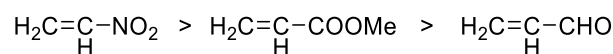
(3) Reactivity of Alkene:

When electron donating group (+M) groups like -NH_2 , -OH etc. groups are present adjacent to olefins. The electron donating group increases the electron density of double bond resultantly increases the nucleophilicity of double bond. When electron withdrawing group like -NO_2 , -CN etc. are present adjacent to olefin electron density of double bond decreases and electrophilicity of double bond increases.

- **Nucleophilicity of double bond due to (+M) is given below in order,**



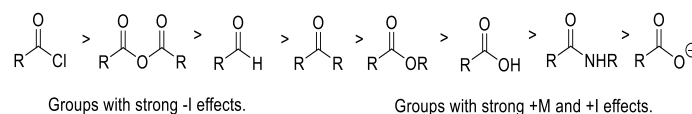
- **Electrophilicity of double bond due to (-M) is given below in order,**



(4) Reactivity of Carbonyl Compounds:

In carbonyl compounds carbonyl carbon is electrophilic, when group with (+M/+I) effect attached to carbonyl carbon then its electrophilicity decreases and group with (-M/-I) effect increases the electrophilicity of carbonyl compound.

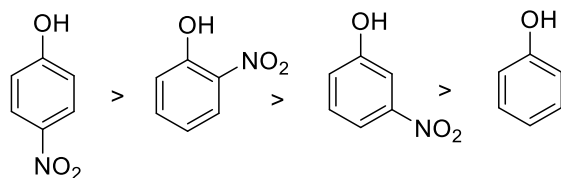
Electrophilicity order of carbonyl functional groups given below,



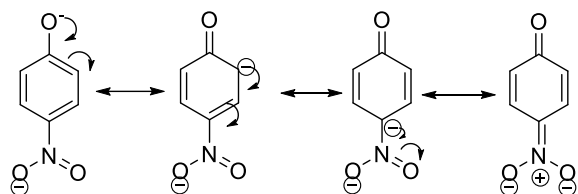
(5) Acidic Strength:

Acidity of substituted phenol is affected by substituents and its position on benzene ring. When groups with (-M) effect attach to the phenol at ortho and/or Para position they stabilize the phenoxide ion by conjugation. When groups with (+M) effect attach to the phenol at ortho and/or Para position they destabilize the phenoxide ion.

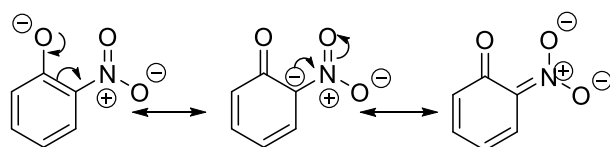
Acidity order of Substituted phenol is given as,



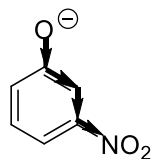
Stabilisation of negative charge by (-M) effect of -NO_2 group at para position of phenoxide ion,



Stabilisation of negative charge by (-M) and (-I) effect of -NO_2 group at ortho position of phenoxide ion,



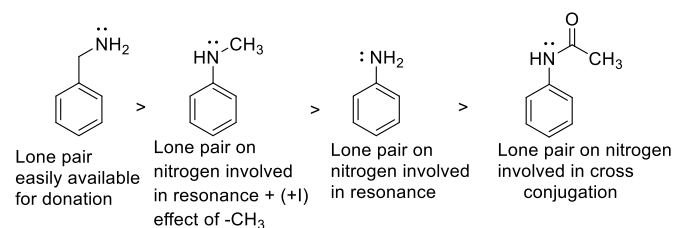
Stabilisation of negative charge by (-I) effect of -NO_2 group at meta position of phenoxide ion,



-I effect of -NO_2 group stabilises phenoxide ion

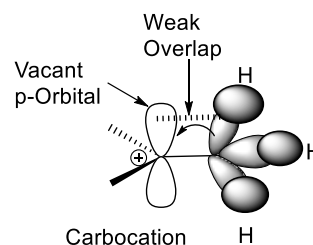
(6) Basic Strength of Amines:

If the lone pair of amines is already involved in conjugation the basicity of amines is decreases.



(D) Hyperconjugation Effect:

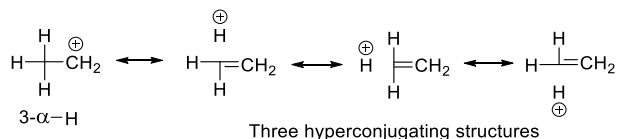
In Hyperconjugation effect localization of σ electrons of C-H bond of an alkyl group with adjacent empty or partially filled or non-bonding or antibonding σ/π or filled π orbital take place.



- Hyperconjugation effect is a permanent effect.
- Hyperconjugation effect results in stabilization of Alkene, Alkynes, Saturated carbocations, Saturated Free radicals.
- More the number of hydrogen atom present at α -position of unstabilized system more be the stability of the system.
- Total number of hyperconjugation structures are equals to total number of α -H atoms.
- In hyperconjugation there is no definite bond between carbon and one hydrogen atom hence it is also known as No bond resonance.

Type of Hyperconjugation Effect:

- 1) **C-H σ -Bond to Carbocation/empty orbital hyperconjugation:** This type of hyperconjugation occurs in compounds contain carbocation or element with vacant orbitals.



- 2) **C-H σ -Bond to π -Bond hyperconjugation:** This type of hyperconjugation occurs in compounds contain alkene or alkyne.



- 3) **C-H σ -Bond to radical hyperconjugation:** This type of hyperconjugation occurs in compounds contain free radicals.

