



Some Basic Principles of Organic Chemistry

Hybridisation in Organic Compounds

The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as *hybridisation*.

Type of hybridisation	Number of orbitals used	Bond	Bond angle	Geometry
sp^3	1s and 3p	Four $-\sigma$	109.5°	Tetrahedral
sp^2	1s and 2p	Three $-\sigma$ One $-\pi$	120°	Trigonal planar
sp	1s and 1p	Two $-\sigma$ Two $-\pi$	180°	Linear

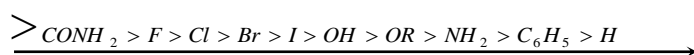
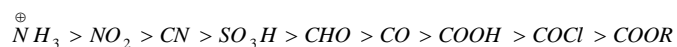
Inductive effect or Transmission effect

When an electron withdrawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to displacement of shared electron



of a covalent bond towards a more electronegative atom. This is called *inductive effect* or simply as *I – effect*.

Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to have –I effect whereas atoms or groups which have a greater electron releasing power are said to have +I effect.

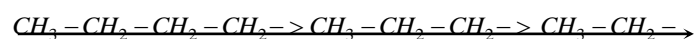


–I power of groups in decreasing order with respect to the reference *H*



+ I power in decreasing order with respect to the reference *H*

+ I power \propto number of carbon in the same type of alkyl groups



+ *I* power in decreasing order in same type of alkyl groups



Resonance effect or mesomeric effect

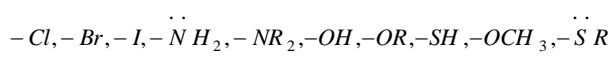
The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (*s*) of electrons from an atom to the adjacent single covalent bond is called



mesomeric effect or simply as **M-effect**. In case of the compound with conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.

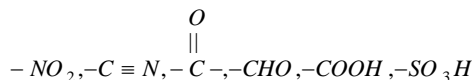
(a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+M$ effect or $+R$ effect.

$+M$ effect groups :

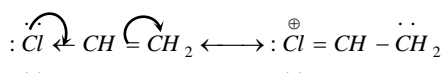


(b) The groups which withdraw electrons from the double bond or from a conjugated system towards itself due to resonance are said to have $-M$ effect or $-R$ effect.

$-M$ effect groups :



(3) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to $-I$ effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.



Hyperconjugative effect

When a $H-C$ bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of



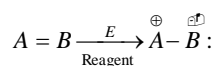
the $H-C$ bond interact or enter into conjugation with the unsaturated system. *The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single $H-C$ bonds) of the substituent groups in organic compounds is called **hyperconjugation**. The concept of hyperconjugation was developed by Baker and Nathan and is also known as *Baker and Nathan effect*.*

Inductomeric effect

Inductomeric effect is the temporary effect which enhances the inductive effect and it accounts only in the presence of an attacking reagent.

Electromeric effect

The phenomenon of movement of electrons from one atom to another in multibonded atoms is electromeric effect.



Attacking reagents

There are basically two types of reagents used in organic chemistry, the *electrophiles* and *nucleophiles*.

(a) **Electrophiles**(Electron-loving)–Electrophilic reagents or electrophiles are the electron-deficient species which tend to attack the substrate at a position (or positions) of high electron



density, e.g. H^{\oplus} , $\text{H}_3\text{O}^{\oplus}$, $\overset{\oplus}{\text{N}}\text{O}_2$, R^{\oplus} , $\text{R}_2\overset{\oplus}{\text{C}}\text{H}$, $\text{R}_3\text{C}^{\oplus}$, Cl^{\oplus} , $\text{R}-\overset{\oplus}{\text{C}}\text{O}$, $\overset{*}{\text{S}}\text{O}_3$, $\overset{*}{\text{C}}\text{O}_2$, $\overset{*}{\text{B}}\text{F}_3$, $\overset{*}{\text{A}}\text{lCl}_3$ etc.

(b) Nucleophiles (Nucleus-loving)– Nucleophilic reagents or nucleophiles are the electron-rich reagents which tend to attack the substrate at a position (or positions) of low electron density.

e.g. H^- , $\text{H}\overset{*}{\text{S}}\text{O}_3^-$, OH^- , RO^- , CN^- , $\text{H}_2\ddot{\text{O}}$ etc.

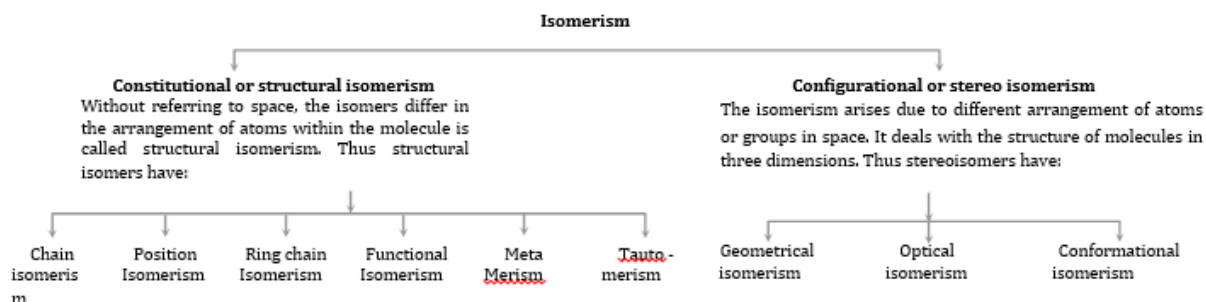
The star indicates the atom that accepts electrons from or donates electrons to the substrate, depending on the case.

Distinction between $\text{S}_{\text{N}}2$ and $\text{S}_{\text{N}}1$ reactions

Factors	$\text{S}_{\text{N}}2$ Reactions	$\text{S}_{\text{N}}1$ Reactions
Number of steps	One: $\text{R} : \overset{\ominus}{\text{L}} + : \overset{\ominus}{\text{Nu}} \rightarrow \text{R} : \text{Nu} + : \text{L}$	Two: (i) $\text{R} : \text{L} \xrightarrow{\text{Slow}} \text{R}^+ + : \text{L}^-$ (ii) $\text{R}^+ + : \text{Nu}^- \xrightarrow{\text{Fast}} \text{R} : \text{Nu}$
Reaction rate and order	Second order: Rate \propto [Substrate] [Nucleophile] or Rate = $\text{K}_2[\text{RL}][: \text{Nu}^-]$	First order: Rate \propto [Substrate] or Rate = $\text{K}_1[\text{RL}]$
Molecularity	Bimolecular	Unimolecular
TS of slow step	$\delta^- \quad \delta^-$ $: \text{Nu} \text{---} \text{C} \text{---} : \text{L}$	$\delta^+ \quad \delta^-$ $: \text{Nu} \text{---} \text{C} \text{---} \text{L} \text{---} \text{Nu} :$
Reacting nucleophile	The nucleophile attacks the carbon of the substrate exclusively from the back side.	The nucleophile can attack the carbon of the substrate both from the back and front sides although the back side attack predominates.
Stereochemistry	Complete inversion of configuration takes place.	Inversion and retention takes place.



Reactivity order of alkyl halides	Methyl > 1° > 2° > 3° halides. (I > Br > Cl > F)	3° > 2° > 1° > methyl halides. (I > Br > Cl > F)
Rearrangement	No rearranged product is formed (except for allylic).	Rearranged products can be formed.
Nature of nucleophiles	Favoured by strong and high concentration of nucleophiles.	Favoured by mild and low concentration of nucleophiles.
Polarity	Favoured by solvents of low polarity.	Favoured by solvents of high polarity.
Reaction rate determining factor	By steric hindrance.	By electronic factor (stability of R^{\oplus}).
Catalysis	Not catalysed by any catalyst (phase transfer).	Catalysed by Lewis and Bronsted acids, e.g., Ag^{\oplus} , $AlCl_3$, $ZnCl_2$ and strong HA .

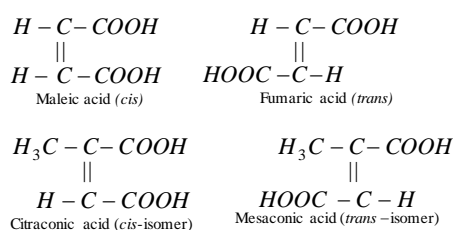


Geometrical or cis-trans isomerism



Geometric isomers are molecules that are locked into their spatial positions with respect to one another due to a double bond or a ring structure. The isomer in which same groups or atoms are on the same side of the double bond is known as *cis* form and the isomer in which same groups or atoms are on the opposite side is called *trans*-isomer.

Examples :



Conditions for geometrical isomerism :

- (i) It must contain a carbon-carbon double bond in the molecule.
- (ii) Two unlike atoms or groups must be linked to each doubly bonded carbon atoms.