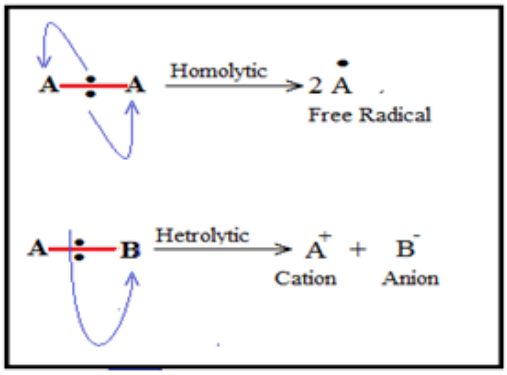
Bond Fission:

a) Homolytic fission: Each atom separates with one electron, leading to the formation of highly reactive entities called radicals, owing their reactivity to their unpaired electron.

b) Heterolytic fission: One atom holds on to electrons, leaving none for the other, the result in the above case being a negative and positive ion, respectively, the result being the formation of an *ion pair*.

Reactions involving radicals tend to occur in the gas phase and in solution in non-polar solvents, and to be catalyzed by light and by the addition of other radicals. Reactions involving ionic intermediates take place more readily in solution in polar solvents, because of the greater ease of separation of charges therein and very often because of the stabilization of the resultant ion pairs through solvation.



Electronic Displacement in Covalent Bonds

The following four types of electronic effects operates in covalent bonds

a) Inductive effect

b) Mesomeric and Resonance effect

c) Electromeric effects

d) Hyperconjugation

Inductive Effect:

a) Negative inductive Effect: (–I Effect): This is due to electron - attracting groups (X); it develops positive charge on the chain and is said to exert a negative inductive denoted by (– I)



1) It decreases as one goes away from group X (electron attracting): $X\text{-}C_1\text{-}C_2\text{-}C_3$

$C_1(d+) > C_2(dd+) > C_3(ddd+)$ and after third carbon charge is negligible

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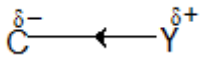
D and L configuration:

a) The configuration of an enantiomer is related to a standard, glyceraldehydes.

Order: $^{+}NH_3NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$

a) Positive Inductive Effect (+I): This is due to electron-releasing group (Y). It develops an negative charge on the chain and is said to exert a positive inductive effect denoted by

(+I)



1) It also decreases as we go away group Y (electron - releasing):$Y\text{-}C_1\text{-}C_2\text{-}C_3$

$C_1(d–) > C_2(dd–) > C_3(ddd–)$

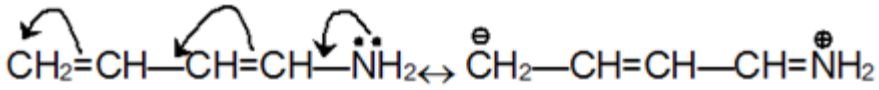
2) Order: $(CH_3)_3\,C\text{-}R > (CH_3)_2CH\text{-}R > CH_3CH_2\text{-}R > CH_3\text{-}R$

	(–I) effect	(+I) Effect
Acidic nature –	Increases	Decreases
Basic nature–	Decreases	Increases

Mesomeric Effect or Resonance Effect:

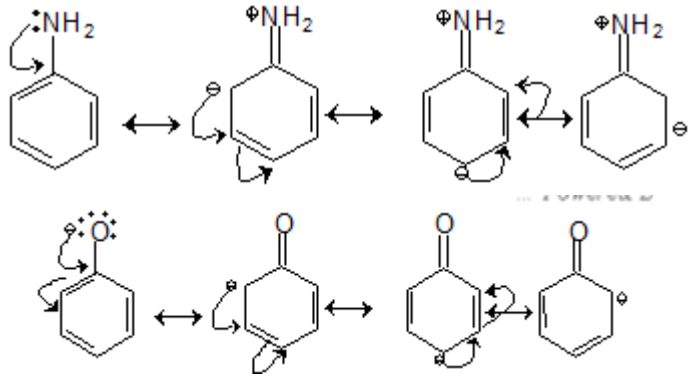
In conjugated systems, p-electrons shifting takes place consecutively giving permanent polarity on the chain.

a) Positive Mesomeric Effect (+M): A group or atom is said to have +M effect when the direction of electron -displacement is away from it.

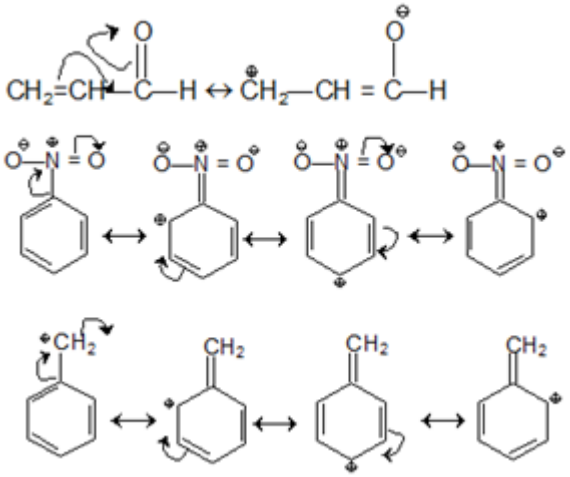


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This effect extends the degree of delocalization and imparts stability to the molecule

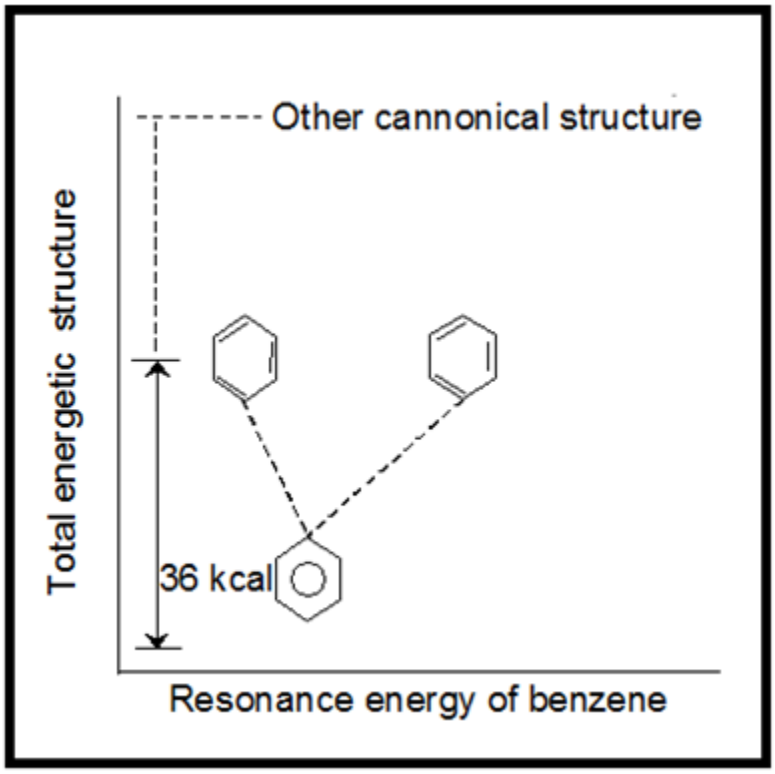


a) Negative Mesomeric Effect (–M): A group or atom is said to have +M effect when the direction of electron -displacement is toward it.



a) Resonance Energy: The difference in energy between the hybrid and the most stable canonical structure is called as Resonance energy

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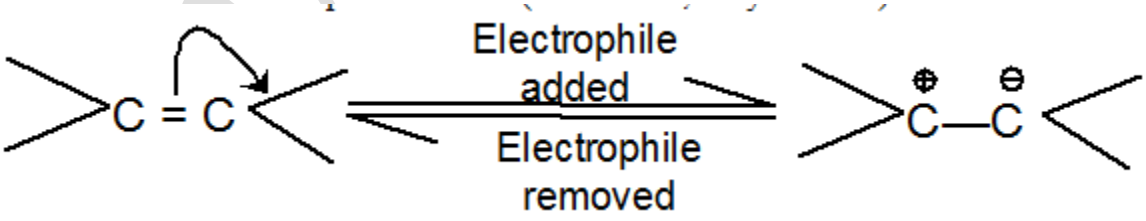


Electromeric Effect:

Complete transfer of p-electrons from one atom to other to produce temporary polarity on atoms joined by multiple bonds, in the presence of an electrophile is known as electro-meric effect. Effect is reversible and temporary.

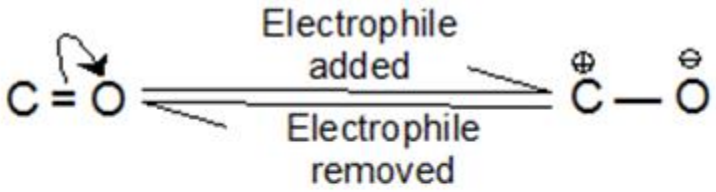
a) Positive Electromeric Effect:

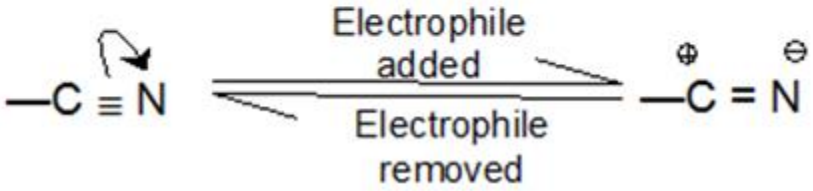
p-electrons transfer takes place C to C (as alkenes, alkynes etc.)



a) Negative Electromeric Effect:

p-electrons transfer takes place to more electronegative atom (O,N,S) joined by multiple bonds.





Hyperconjugation:

Delocalization of sigma electrons also known as sigma-pi – conjugation or no bond resonance. It is a permanent effect.

a) Occurrence

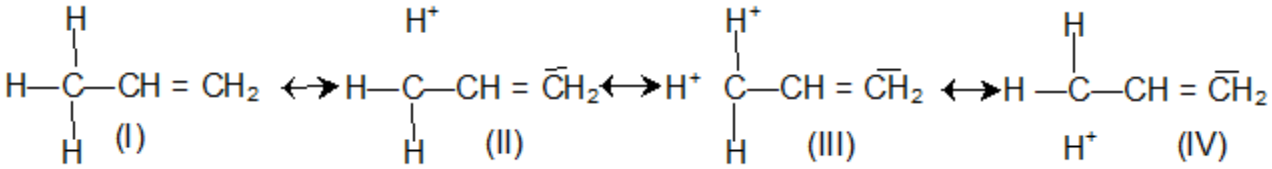
Alkene, alkynes

Free radicals (saturated type) carbonium ions (saturated type)

b) Condition

Presence of a–H with respect to double bond, triple bond carbon containing positive charge (in carbonium ion) or unpaired electron (in free radicals)

Example



Note: Number of hyperconjugative structures = number of a-Hydrogen. Hence, in above examples structures I,ii,iii,iv are hyperconjugate structures (H-structures).

a) Effects of Hyperconjugation:

Bond Length: Hyperconjugation also affects bond lengths because during the process the single bond in compound acquires some double bond character and vice-versa

Dipole moment: Since hyperconjugation causes this development of charges, it also affects the dipole moment of the molecule.

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Stability of carbonium Ions: Tertiary > Secondary > Primary

Stability of Free radicals:

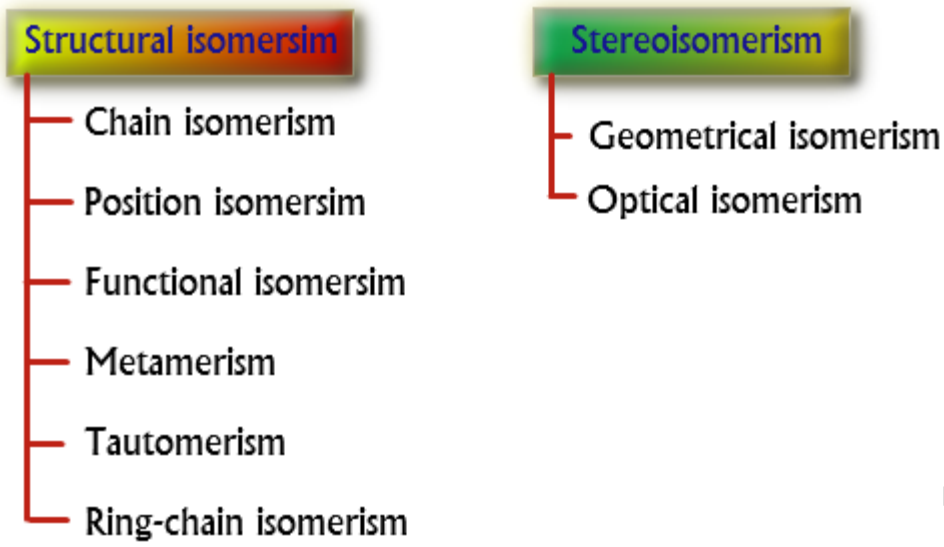
$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

Reactive Intermediates:

Species	Geometry	Stability
Carbocation	sp^2 hybridized with a planar structure and bond angles are of about 120°. There is a vacant unhybridized p orbital which (e.g. in the case of CH_3^+) lies perpendicular to the plane of C—H bonds	Any structural feature which tends to reduce the electron deficiency at the tricoordinate carbon stabilizes the carbocation Order: 3°> 2° > 1° > CH_3^+
Carbanions	sp^3 hybridized with the unshared pair occupying one apex of the tetrahedron. Pyramidal structures similar to those of amines.	Any structural feature which tends to reduce the electron deficiency at the tricoordinate carbon stabilizes the carbocation Order: 3°< 2° < 1° < CH_3^-
Free Radicals	sp^2 hybridized with planar (trigonal) structure.. and sp^3 hybridized with pyramidal structure.	Hyperconjugation increases the stability of free radical. Order: : 3°> 2° > 1°

Isomerism:

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Structural Isomerism:

Isomerims	Description	Example
Chain Isomerism	This type of isomerism arises from the difference in the structure of carbon chain which forms the nucleus of the molecule.	Butane and Isobutane
Position Isomerism	It is the type of isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain.	n-propyl alcohol and isopropyl alcohol
Functional Isomerism	In this type of isomerism two compounds have the same molecular formula but possess different functional groups.	Diethyl ether(C2H5-O-C2H5) and butyl alcohol (C4H9OH)
Metamerism	This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group in the molecule of compounds belonging to the same class	For example, methyl propyl ether and diethyl ether both have the molecular
Tautomerism	It is the type of isomerism in which two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as tautomers.	Acetoacetic ester has two tautomers – one has a keto group and other has an enol group

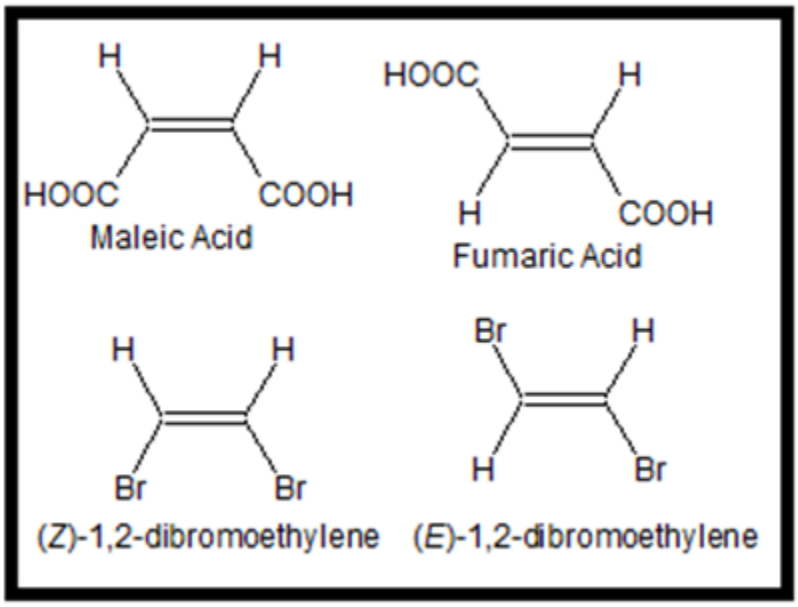
Geometrical Isomerism:

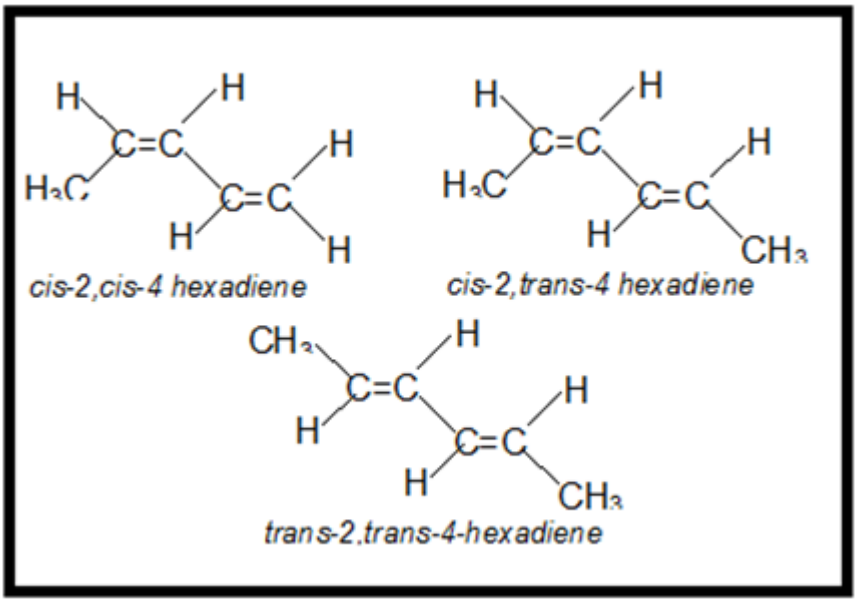
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The isomers possess the same structural formula containing a double bond and differ only in respect of the arrangement of atoms or groups about the double bond.

This isomerism is shown by alkenes or their derivatives in which two different atoms or groups are attached to each carbon containing the double bond.

Thus the compounds having the formula abC = Cxy or the simple structure *abC = Cab* occur in two forms and exhibit geometrical isomerism.





a)The *trans* isomers of alkenes are usually more stable than their corresponding *cis* isomers.

b) The *trans* isomers have normally less dipole moments than their corresponding *cis* isomers.

c) The *trans* isomer has greater symmetry than the corresponding *cis* isomer. Thus it packs more easily in the crystal lattice and hence has higher melting points.

Optical Isomerism:

a) Optical Activity: The property of a substance of rotating the plane of polarized light.

b) Specific Rotation: The number of degrees of rotation observed when light is passed through 1 decimeter (10 centimeters) of its solution having concentration 1 gram per milliliter.

$$[\alpha]_D^{t^o} = \frac{a_{obs}}{l \times c}$$

a) Laevorotatory or (-) - form: rotates the plane of polarized light to the left.

b) Dextrorotatory or (+)- form : rotates the plane of polarized light to the right.

c) Racimic Mixture or (±)– mixture : An inactive from which does not rotate the plane of polarized light at all. This is a mixture of equal amounts of (+)– and (–)– forms and hence its optical inactivity

Asymmetric Carbon atom: A carbon atom which is attached to four different atoms

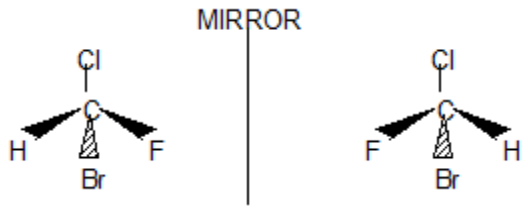
Chirality:

a) All organic compounds which contain an asymmetric carbon (C* *abde*) atom are *chiral* and exist in two tetrahedral forms.

b) A molecule must have chirality in order to show optical activity.

Enantiomers: Two optical isomers which are non superimposable mirror images of each other.

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a) **Meso compounds**: Compound containing two or more chiral carbon which do not show optical activity due to presence of centre of symmetry (indicated by thick dot).

b) Compounds which have unsymmetrical molecule with one or more chiral centres: In such compounds if 'n' is the number of chiral carbons, then

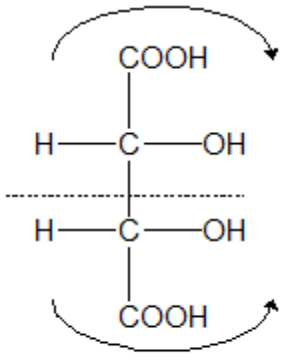
No. of optically active isomers (a) = 2^n

No. of racemic forms (r) = a/2

No. of meso forms (m) = 0

c) compounds having a symmetrical molecule (compounds having chiral carbons but molecule as a whole is achiral): (a) compounds with even number of carbons atoms: In such compounds if number of chiral carbons in n, we have a = 2^{n-1}, r = a/2, and m=$2^{(n/2-1)}$

d) Compounds with odd number of carbon atoms: In such compounds if n is the number of asymmetric carbons then total optical isomers are given by 2^{n-1} whereas m = $2^{(n-2)/2)}$. Thus, a = $2^{n-1} - 2^{(n-1)/2)}$.



Inactivity of Meso Tartaric acid by Internal Compesnation

The force of rotation due to one half of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to **internal compensation.** It occurs whenever a compound containing two or more

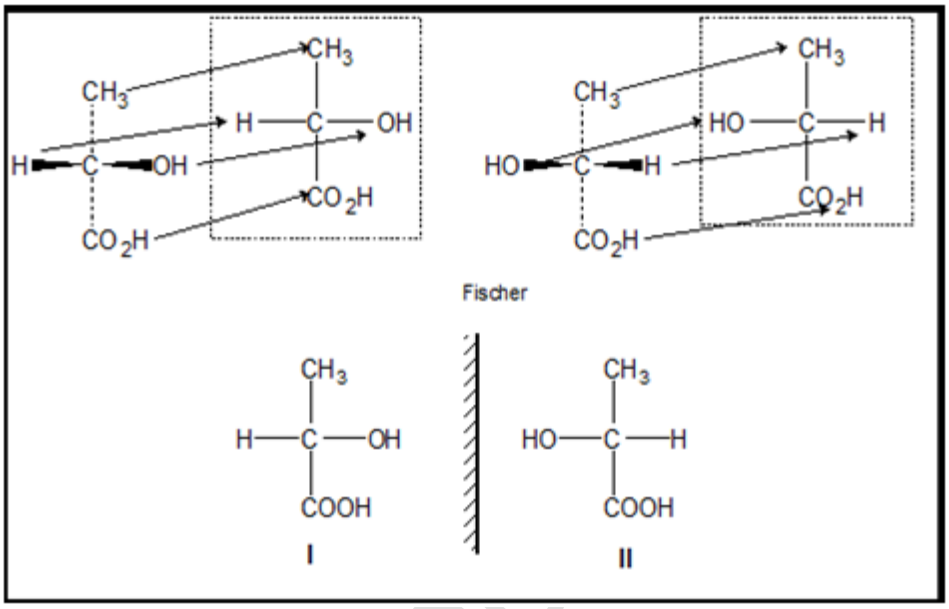
Fischer Projections:

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a) Representing three dimensional structures on a two dimensional surface.

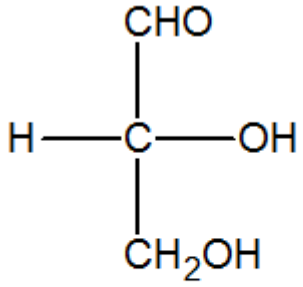
b) Asymmetric carbon atom drawn in a prescribed orientation and then projected into a planar surface.

c) Planar formulas of the asymmetric carbon are obtained by placing it so that the two substituents are horizontal and project out towards the viewer (shown by thick wedge-like bonds), while the two other substituents are vertical and project away from the viewer (shown by dotted bonds).



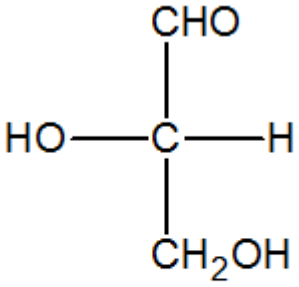
D and L configuration:

a) The configuration of an enantiomer is related to a standard, glyceraldehydes.



(+)-glyceraldehyde

D configuration



(-)-glyceraldehyde

L configuration

b) If the configuration at the asymmetric carbon atom of a compound can be related to D (+)-glyceraldehyde, it belongs to D-series.

c) By convention for sugars, the configuration of the highest numbered asymmetric carbon is referred to glyceraldehyde to determine the overall configuration of the molecule.

R and S System:

The **sequence rules** to determine the order of priorities of groups are :

The atoms or groups directly bonded to the asymmetric carbon are arranged in order of decreasing atomic number and assigned priority 1, 2, 3, 4, accordingly

a) Thus in chlorobromofluoromethane (CHClBrF), the substituents Br (at no = 35), Cl (at no = 17), F (at no = 9) and H (at no = 1) give the order of priorities.

Br > Cl > F > H

(1) (2) (3) (4)

b) When two or more groups have identical first atoms attached to asymmetric carbon, the priority order is determined by considering the atomic numbers of the second atoms; and if the second atoms are also identical the third atoms along the chain are examined.

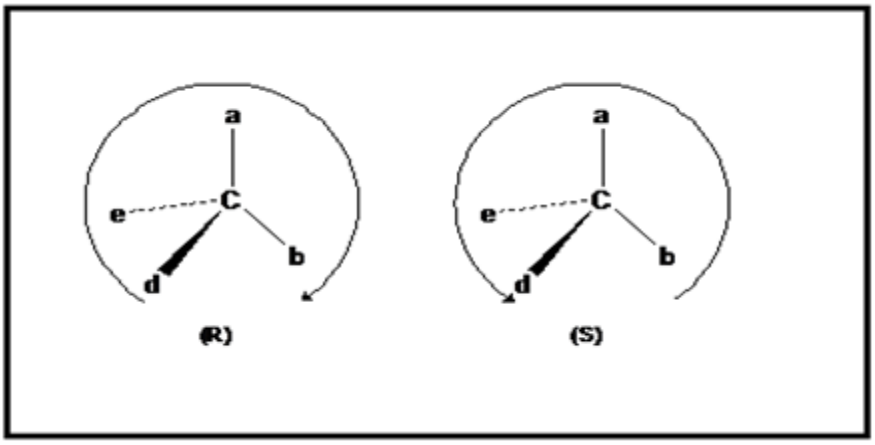
c). If the first atoms of the two groups have same substituents of higher atomic number, the one with more substituents takes priority.

Thus —$CHCl_2$ has a higher priority than —CH_2Cl.

d) A doubly or triply bonded atom 'A' present in a group appended to asymmetric carbon, is considered equivalent to two or three singly bonded 'A's, respectively. Thus, R= A equals A-R-A.

If in a molecule, order of priority for groups a,b,c,d, & e is $a > b > d > e$

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Diastereomers :

Stereoisomers which are optically active isomers but not mirror images, are called diasteriomers.

Diastereoisomers have different physical properties. Thus they have different melting points, boiling points, solubilities in a given solvent, densities, and refractive indices.

They also differ in specific rotations; they may have the same or opposite signs of rotations.

Like geometrical isomers, the diastereoisomers may be separated from each other :–

by fractional distillation due to their difference in boiling points;

by fractional crystallisation due to their difference in solubility;

by chromatography due to their different molecular shapes and polarity.

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