03 Optical Isomerism

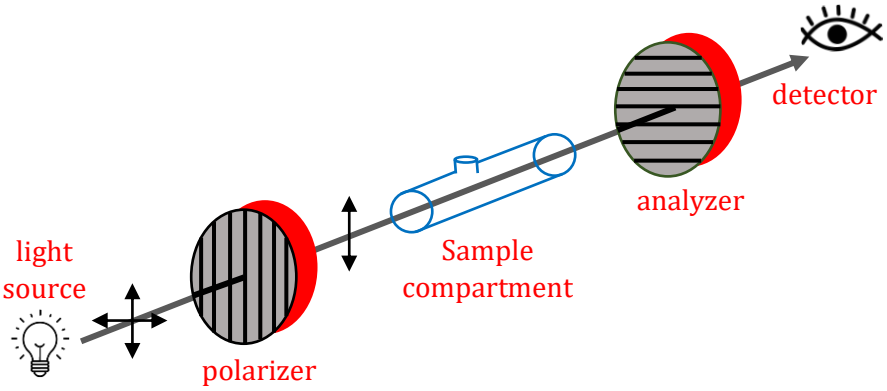
Optical Isomerism :

Compounds which have same molecular and structural formula but have different optical activity are known as optical isomers.

Optical activity :

Certain substances possess the property to rotate the plane of polarized light. Such substances are called optically active substances and this phenomenon is called optical activity.

Light has vibrations occur in all planes at right angles to the line of propagation. In plane polarized light the vibrations take place only in one plane. Plane polarized light can be obtained by passing ordinary light through a Nicol prism.



Certain organic compounds, when their solutions are placed in the path of a plane polarized light, have the remarkable property of rotating its plane through a certain angle which may be either to the left (or) to the right. This property of a substance of rotating the plane of polarized light is called optical activity and the substance possessing it is said to be optically active.

The observed rotation of the plane of polarized light [determined with the help of polarimeter] produced by a solution depends on :

(a) The amount of the substance in tube ;

(b) On the length of the sample tube;

(c) The temperature of the experiment and

(d) the wavelength of the light used.

The instrument used to measure angle of rotation is called polarimeter. The measurement of optical rotation is expressed in terms of specific rotation $[\alpha]_D^t$; this is given by the following relation :

$$[\alpha]_D^t = \frac{\alpha_{obs}}{l \times C}$$ [where α = observed angle of rotation]

$[\alpha]_D^t$ = specific rotation determined at t°C, using D-line of sodium light.

ℓ = length of solution in decimeters

C = concentration of the active compound in grams per millilitre.

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (–) indicates that the rotation is towards anti-clockwise, while positive (+) sign means that the direction of rotation is toward right clockwise.

If the substance rotates plane-polarised light to the right i.e. in clockwise direction it is called dextrorotatory and indicated by 'd' or (+)

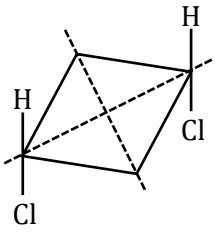
If the substance rotates plane-polarised light to the left i.e. in anti-clockwise direction it is called laevorotatory and indicated by 'l' or (–)

Condition of Optical Activity

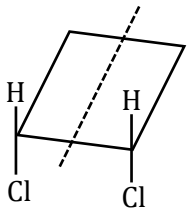
Compound must be asymmetrical.

Types of Symmetry :

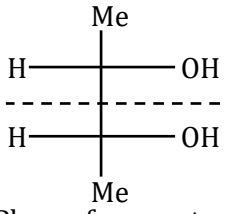
(i) Plane of symmetry (POS) : An imaginary plane which bisects any object or molecule into two equal parts which are mirror images of each other is known as POS.



Plane of symmetry

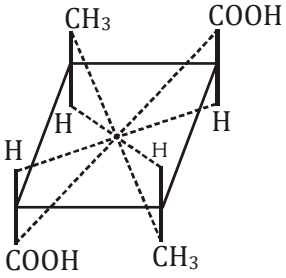


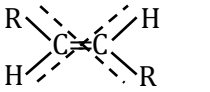
Plane of symmetry



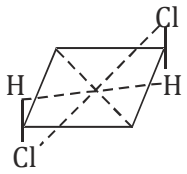
Plane of symmetry

(ii) Center of Symmetry (COS): It is a point inside a molecule from which on travelling equal distance in opposite directions one takes equal time.



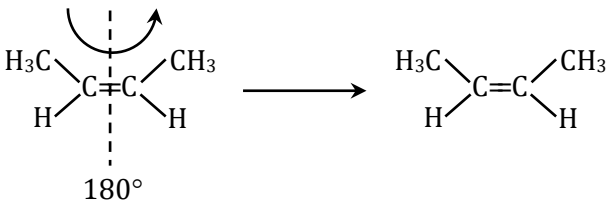


Centre of symmetry

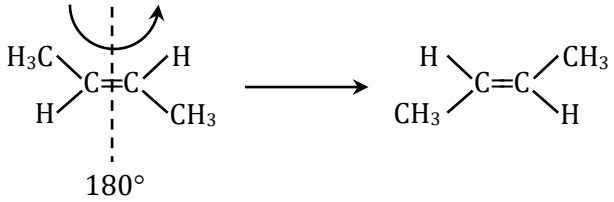


Centre of symmetry

(iii) Axis of Symmetry (AOS) (Cn) : Axis of symmetry is an axis such that if one rotates the molecule by $\frac{360^o}{n}$, the new position of molecule is superimposable with the original one.



(iv) Alternate axis of Symmetry (AAOS) : An imaginary plane around which rotation by angle x gives its mirror image is known as AAOS. It is represented by S_n where n = $\frac{360}{x}$



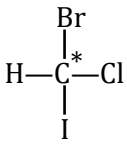
Chiral Compound:

Compound which is not super imposable on its mirror image is known as Chiral Compound. All optically active compounds are Chiral.

Asymmetric carbon (or) Chiral Carbon

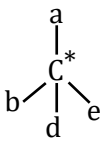
If all the four bonds of carbon are satisfied by four different atoms/groups, it is chiral. Chiral carbon is designated by an asterisk (*).

Example :

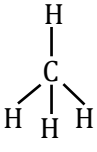
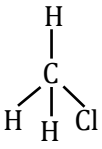


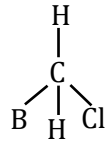
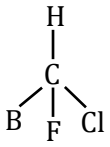
Optically Active Carbon Compounds:

If a carbon-atom is attached with four different group, then if does not have any element of symmetry. It is known as asymmetric carbon atom, which is represented as $*C_{abde}$.



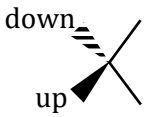
If a molecule contains only one asymmetric carbon atom, then the molecule as a whole becomes chiral and optically active and show optical isomers.

Compound	Centre of symmetric	Plane of symmetric	Optical active
(1) 	Absent	Yes	No
(2) 	Absent	Yes	No

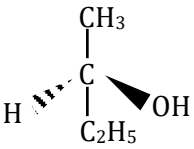
(3) 	Absent	Yes	No
(4) 	Absent	No	Yes

Projection Formula of Chiral Molecules:

(i) Wedge-Dash Projection formula



Example : (i) Butan-2-ol



(ii) Ficher Projection formula

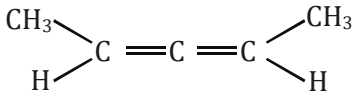
Rules of writing Fisher Projection formula

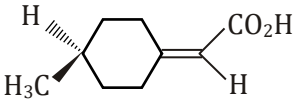
(a) Groups at Vertical line are away from observer.

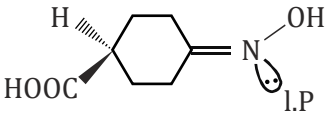
(b) Groups at Horizontal line are towards the observer.

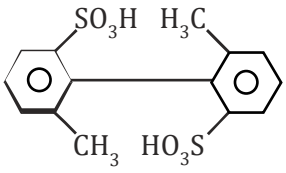
(c) High priority group lies at the top of vertical line (Numbering starts from top).

Optically active compounds having no asymmetric carbon:

(i) 

(ii) 

(iii) 

(iv) 

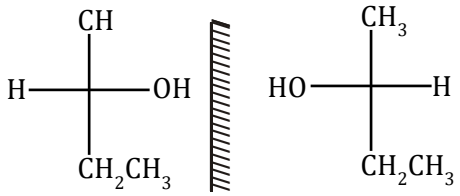
Optically

Enantiomers :

Stereoisomers which are mirror-image of each other are called enantiomers (or) enantiomorphs. Thus (i) and (ii) are enantiomers. All the physical and chemical properties of enantimoers are same except two :

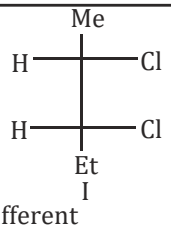
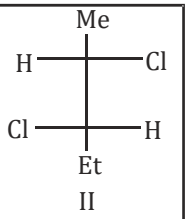
(i) They rotate PPL to the same extent but in opposite direction. One which rotates PPL in clockwise direction is called dextro-rotatory [dextro is latin word meaning thereby right] and is designated by d(or) (+). One which rotates PPL in anti-clockwise direction is called laevo rotatory [means towards left] and designated by l (or) (–).

(ii) They react with optically active compounds with different rates.

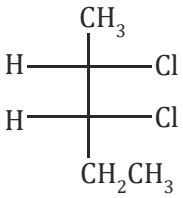


Diastereomerism :

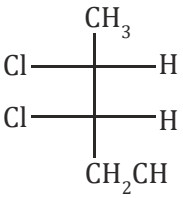
The optical isomer which are not mirror images to each other are called diastereomers.

Properties	 I	 II
(i) Dipole moment	Different	
(ii) Melting point	Different	
(iii) Boiling point	Different	
(iv) Solubility & Density	Different	
(v) Specific rotation	Different	

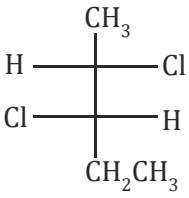
Example :



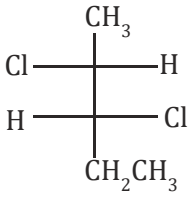
(I)



(II)



(III)



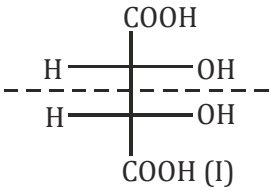
(IV)

I, II = Enantiomers, III, IV = Enantiomers

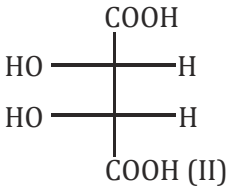
I, III = Diastereomers, II, IV = Diastereomers

II, III = Diastereomers, I, IV = Diastereomers

Example :



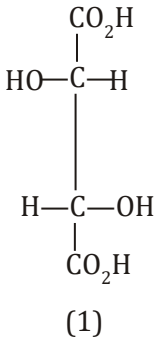
Achiral



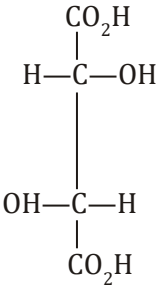
I and II are identical

Stereoisomerism in Tartaric Acid:

Tartaric acid exists in only three stereomeric forms. Two of them (1 and 2) are non superimposable mirror images of each other so they are enantiomers of each other. The 3rd isomer is non mirror image stereomers of (1) and (2) so it is diastereomer of (1) and (2). 3rd isomer containes plane of symmetry so, it is optically inactive. It is known as meso tartaric acid.



(1)



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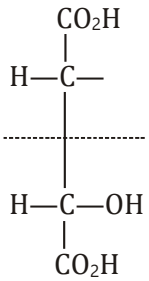


(3)

Meso tartaric acid

Meso isomers:

(i) Achiral compound which have chiral centers is known meso compound.

(ii) They are achiral (optical rotation = 0).

(iii) They have [α] = 0 due to internal compensation of optical rotation.

(iv) They are diastereomer of d – ℓ pair. So, it has different physical properties than d –ℓ -pair.

(v) Presence of more than one asymmetric 'C' atoms.

(vi) They are non resolvable.

Internal compensation :

In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one 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 asymmetric carbon atoms has a plane (or) point of symmetry. Since the optical inactivity of such a compound arises within the molecule, the question of separating into active components does not arise.

Racemic mixture (External compensation):

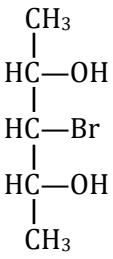
If equimolar amounts of d and ℓ-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced (or) compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to external compensation. Such mixtures of (+) and (–) isomer (Racemic mixtures) can be separated into the active components.

A meso compound is optically inactive due to internal compensation.

Pseudo Chiral Centre:

A chiral center which becomes achiral on changing the configuration of one of its substituents and vice versa

Pseudo chiral center ⟶



Calculation of number of optical isomers:

The number of optical isomers of an organic compound depends on its structure and number of asymmetric carbon atoms. Thus, the number of optical isomers may be determined from the knowledge of the structure of the compound as follows :

(a) When the molecule is unsymmetrical

No. of optically active isomers, $a = 2^n$

Number of meso forms (m) = 0

$\therefore$ Total no. of optically isomers = $(a + m) = 2^n$

(b) When the molecule is symmetrical and has even no. of asymmetric carbon atoms.

No. of optically active isomers, $a = 2^{(n-1)}$

No. of meso forms, $m = 2^{\frac{n}{2}-1}$

$\therefore$ Total no. of optically isomers = a + m

(c) When the molecule is symmetrical and has an odd no. of asymmetrical carbon atoms.

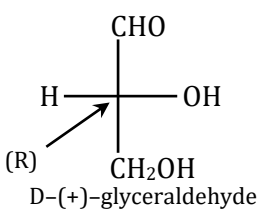
no. of optically active isomers, $a = 2^{(n-1)} - 2^{\frac{n-1}{2}}$

No. of meso forms, $m = 2^{\frac{n-1}{2}}$

$\therefore$ Total no. of optically isomer = $(a + m) = 2^{(n-1)}$

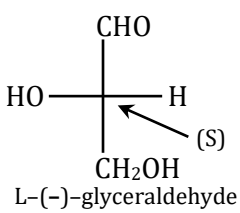
D-L System (Relative configuration) : Application on correct Fischer Projection Formula:

This method is used to relate the configuration of sugars and amino acids to the enantiomers of glyceraldehyde. The configuration of (+)-glyceraldenyde has been assigned as D and the compounds with the same relative configuration are also assigned as D, & those with (-) glyceraldehyde are assigned as L.



D–(+)–glyceraldehyde

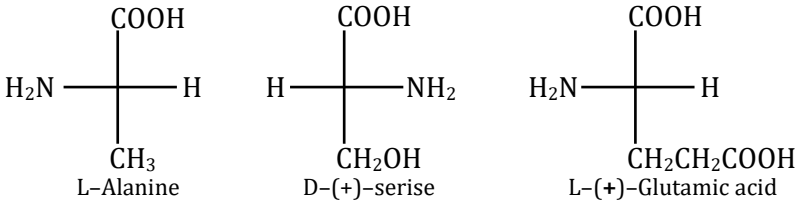
–OH group on right side



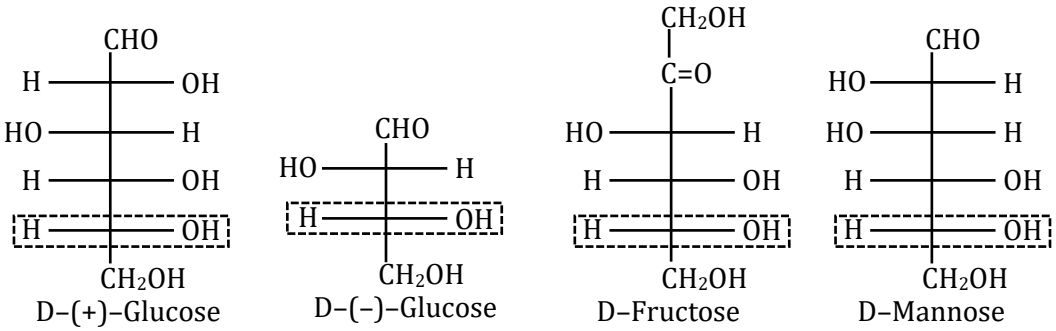
L–(–)–glyceraldehyde

–OH group on left side

Examples :



Sugars have several asymmetric carbons. A sugar whose highest numbered chiral centre (the penultimate carbon) has the same configuration as D-(+)-glyceraldehyde (– OH group on right side) is designated as a D-sugar, one whose highest numbered chiral centre has the same configuration as L-glyceraldehyde is designated as an L-sugar.



Absolute Configuration (R, S configuration)

The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed **absolute configuration**.

System which indicates the absolute configuration was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (R) and (S) system or the Cahn–Ingold system. The letter (R) comes from the latin rectus (means right) while (S) comes from the latin sinister (means left).

(R) (S) nomenclature is assigned as follows :

Step 1 : Assign priority to the groups which are attached with chiral carbon.

Step 2 : Bring the lowest priority group to dash by even simultaneous exchanges.

Step 3 : Draw an arrow from first priority group to second priority group till third priority group.

Step 4 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

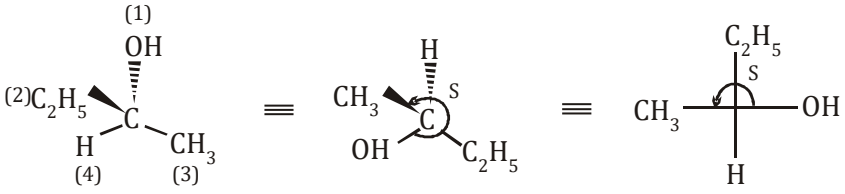
RS Nomenclature in Fischer formula :

Step 1 : Assign priority to the groups which are attached with chiral carbon.

Step 2 : Bring the lowest priority group to vertical line.

Step 3 : Draw an arrow from first priority group to second priority group till third priority group.

Step 4 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

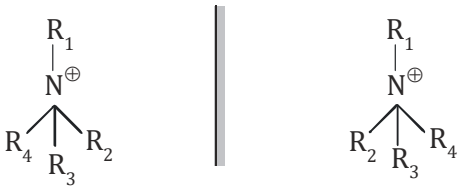


Important:

Note that the designation of a compound as R or S has nothing to do with the sign of rotation. the Cahn-Ingold rule can be applied to any three dimensional representation of a chiral compound to determine whether it is R or S only. For example in above case (i.e. lactic acid), R configuration is laevo rotatory is designated as R-(–)-lactic acid. Now the other configuration of it will have opposite sign of rotation i.e. S-(+)- lactic acid.

Amine inversion:

(i) Chiral nitrogen containing tetra alkyl ammonium ion show optical isomerism.

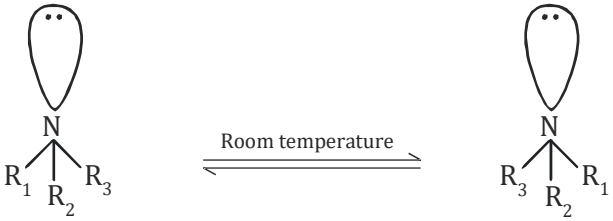


(I) (II)

I and II enatiomers

(ii) Chiral nitrogen containing tertiary amine do not show optical isomerism

Reason :- Rapid umbrella inversion.



(I) (II)

(iii) Energy required for this interconversion is available at room temperature so I and II are identical

Optical Purity:

Some times we deal with mixtures that are neither optically pure nor racemic mixture. In these cases, we specify the optical purity of the mixture. It is defined as the ratio of its rotation to the rotation of pure enantiomer.

$$\Rightarrow \text{Optical purity} = \frac{\text{observed optical rotation}}{\text{optical rotation of pure enantiomer}} \times 100$$

e.g. If we have some 2-butanol with observed rotation of +9.72, we compare this rotation with +13.5 rotation of the pure (+) enantiomer.

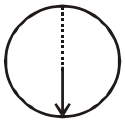
$$\text{Optical purity} = \frac{9.72}{13.5} \times 100 = 72\%$$

That means 72% is pure (+) 2-Butanol and 28% is (± mixture)

Total (+) isomer = 72 + 14 = 86%, (–) isomer = 14%

Specific Rotation(∝) :-

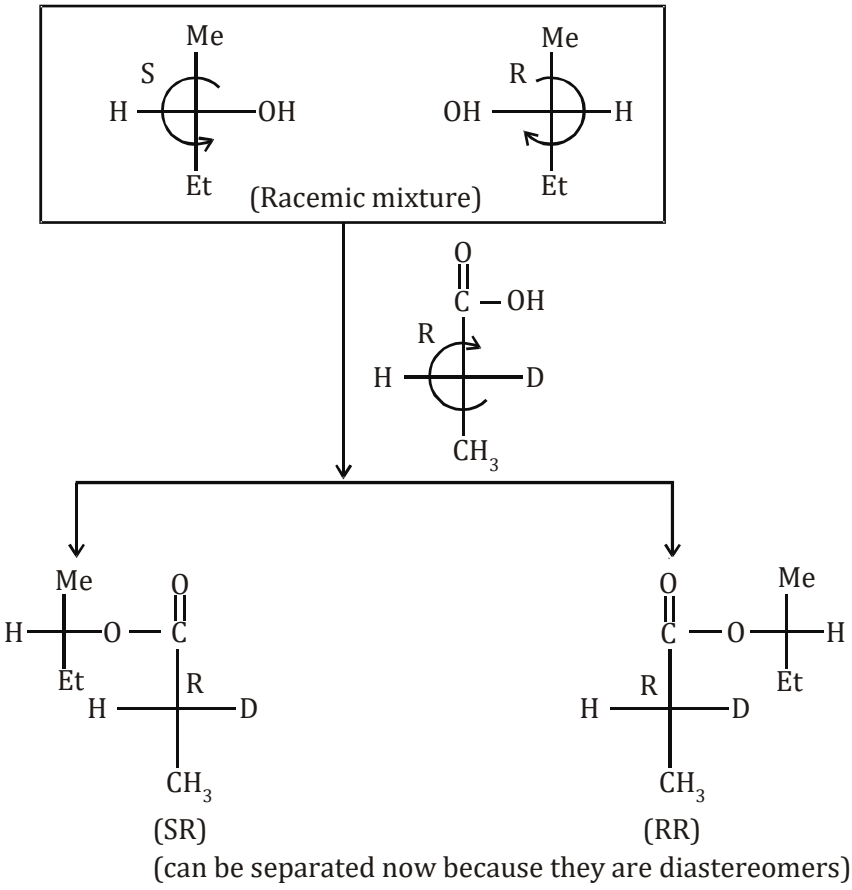
Rotation caused by 1gm/ml of solution in 1 dm length polarimeter tube at specific temperature and fixed wavelength of light.

Confusion  q = + 180° or – 180°

If concentration is halfed and becomes + 90° then d if – 90° then ℓ

Resolution:- Separation of enantiomers from enantiomeric mixture is known as resolution.

When optically active compound is introducted in racemic mixture than we obtain diasteriomeric pair which is easily separated by fractional distillation.



(SR) (RR)

(can be separated now because they are diastereomers)