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CHEMISTRY

Target : JEE (Main)

STEREOISOMERISM

STEREOISOMERISM

Contents

JEE(MAIN) SYLLABUS

Some basic principles of Organic Chemistry :
Tetravalence of carbon, hybridization (s and p), shapes of simple molecules, functional groups: C=C,C≡C and those containing halogens, oxygen, nitrogen and sulphur; homologous series, Classification and isomerism.General introduction to naming of organic compounds-trivial names and IUPAC nomenclature.

JEE(ADVANCED) SYLLABUS

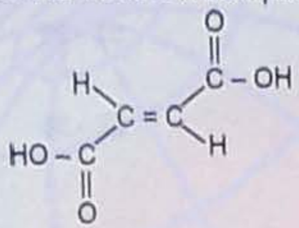
Geometrical isomerism; Optical isomerism of compounds containing up to two asymmetric centers, (R, S and E, Z nomenclature excluded); Conformations of ethane and butane (Newman projections).

STEREOISOMERISM

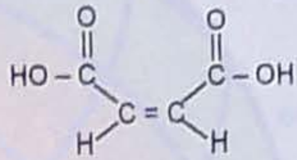
Introduction :

The particular kind of isomers that are different from each other only in the way the atoms are oriented in space are called stereoisomers. These isomers have same **connectivity** of atoms and groups. Stereoisomers have remarkably different physical, chemical and biological properties.

Ex. The two stereoisomers of butenedioic acid are maleic acid and fumaric acid. Fumaric acid is an essential metabolic intermediate in both plants and animals, but maleic acid is toxic and irritating to tissues.

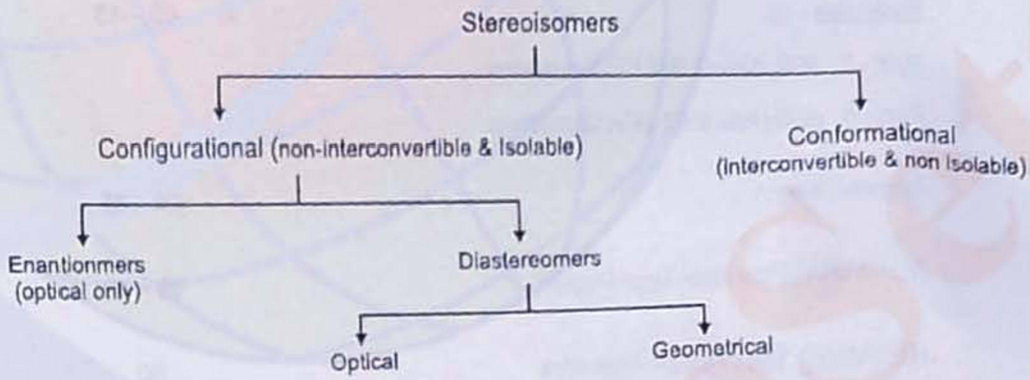


Fumaric acid
m.p. 287°C
essential metabolite



Maleic acid
m.p. 138°C
toxic, irritant

Classification of Stereoisomers :



1. Configurational Isomers :

(I) These isomers differ in the configuration (The spatial arrangement of atoms that characterises a particular stereoisomer is called its configuration).

(II) Configurational isomerism arises due to noninterconvertibility at room temperature. Since these are non interconvertible, therefore can be separated by physical or chemical methods.

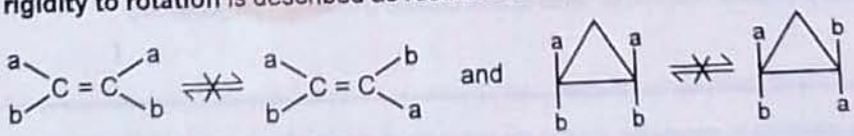
1.1 Geometrical isomerism :

D1 Isomers which possess the same **molecular and structural formula** but differ in the arrangement of atoms or groups in space due to **restricted rotation** are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

Conditions of geometrical isomerism :

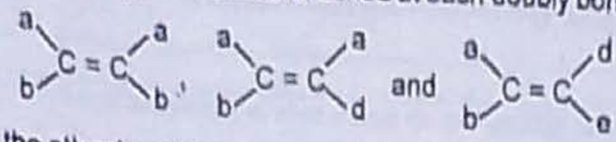
(I) Geometrical isomerism arises due to the presence of a double bond or a ring structure (i.e. >C = C<, >C = N –, –N=N– or ring structure)

Due to the rigidity of double bond or the ring structure the molecules exist in two or more orientations. This **rigidity to rotation** is described as restricted rotation / hindered rotation / no rotation.

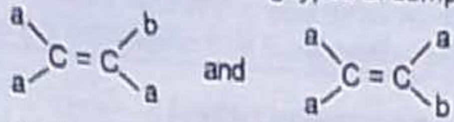


(Restricted Rotation)

(II) Different groups should be attached at each doubly bonded atom.



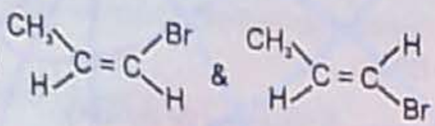
On the other hand, following types of compounds can not show geometrical isomerism :

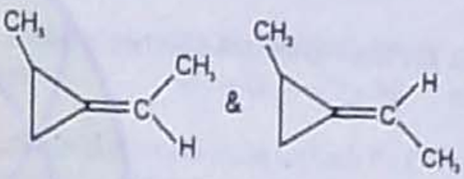
 are identical but not geometrical isomers.

(III) Groups responsible to show geometrical isomerism must be nearly in the same plane.

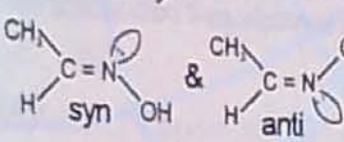
Examples of Geometrical isomers :

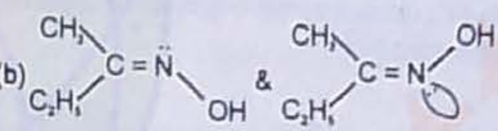
(I) Along >C=C< bond

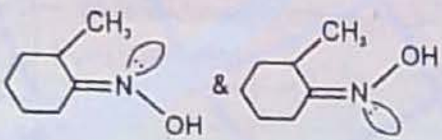
(a) 

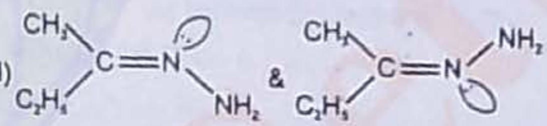
(b) 

(II) Along >C=N– bond

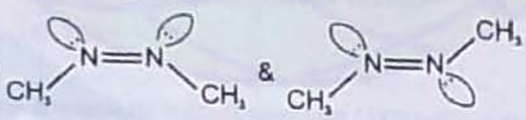
(a) 

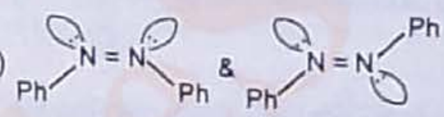
(b) 

(c) 

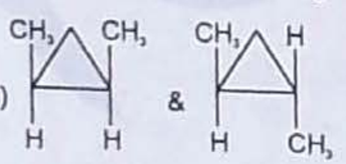
(d) 

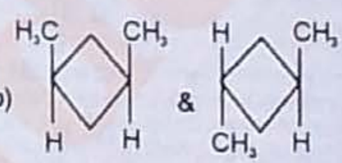
(III) Along –N=N– bond

(a) 

(b) 

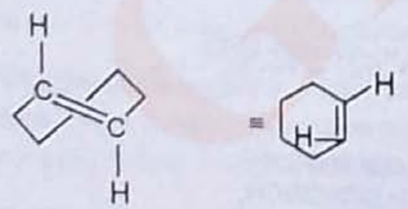
(IV) Along σ bond of cycloalkane

(a) 

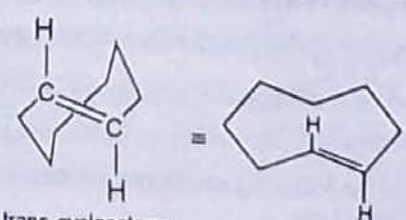
(b) 

(V) Along >C=C< in ring structures :

Usually in cycloalkenes double bond has cis configuration. Their trans isomers do not exist due to large angle strain. But if the ring is large enough then the trans stereoisomer is also possible. The **smallest trans cycloalkene** that is stable enough to be isolated & stored is **trans-cyclooctene.**

(a) 

trans-cyclohexene
highly unstable (not exist)

(b) 

trans-cyclooctene
less stable than cis
(isolable at – 90°C)

Configurational nomenclature in geometrical isomerism :

Configuration	Criteria	Remarks
cis / trans	Similarity of groups	If the two similar groups are on same side of restricted bond the configuration is cis otherwise trans.
E/Z	Seniority of groups	If the two senior groups are on same side of restricted bond the configuration is Z (Z = zusammen = together) otherwise E (E = entgegen = opposite).

Sequence rules (Cahn - Ingold - Prelog sequence rules) :

For deciding the seniority of groups following (CIP) rules are applied :

Rule I : The group with the first atom having higher atomic number is senior. According to this rule the seniority of atoms is :

$I > Br > Cl > S > F > O > N > C > H$

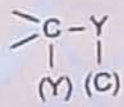
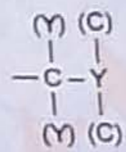
Rule II : The higher mass isotope is senior.

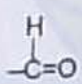
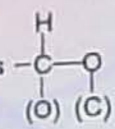
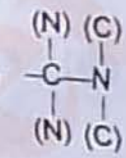
Thus (a) $-T > -D > -H$. (b) $-C^{14}H_3 > -C^{12}H_3$

Rule III : If the first atom of group is identical then second atom is observed for seniority.

(a) $-CH_2Cl > -CH_2OH > -CH_2NH_2 > -CH_2CH_3 > -CH_3$

Rule IV : Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated that

>C=Y is written hypothetical as  & $-C\equiv Y$ is written hypothetical as 

 is written hypothetical as  & $-C\equiv N$ is written hypothetical as 

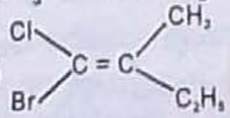
To decide seniority of multiple bonded groups ($-C\equiv CH$, $-CH=CH_2$) their hypothetical equivalents are compared.

(for $-C\equiv C-H$) > (for $-CH=CH_2$)

Rule V : Bond pair is senior to lone pair.

e. In which compound, Cis-Trans nomenclature cannot be used

(1) $CH_3-CH=CH-CH_3$ (2) $CH_3-CH=CH-COOH$

(3)  (4) $C_6H_5-CH=CH-CHO$

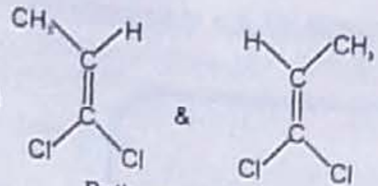
s. (3)

e. Which of the following structures will display geometrical isomerism ?

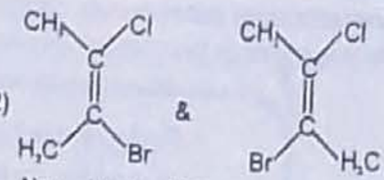
(1) $CH_3CH=CCl_2$ (2) $CH_3CCl=CBrCH_3$

(3) $CH_3CH=CHBr$ (4) Ph–CH=N–OH

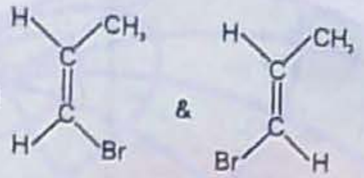
s. (2,3,4)

Sol. (1) 

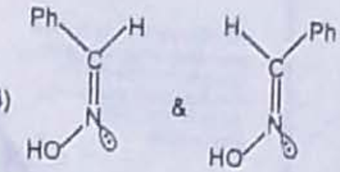
Both are identical

(2) 

Non – Identical (Geometrical Isomer)

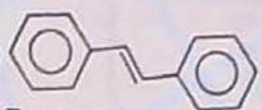
(3) 

Non–identical (Geometrical Isomer)

(4) 

Non–identical (Geometrical Isomer)

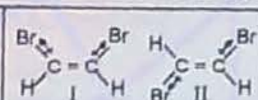
Que. Identify E and Z form of stilbene

(a) 

(b) 

Ans. (a) E (b) Z

Physical Properties of Geometrical Isomers :

Physical properties		Remarks
Dipole moment	I > II	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out
Boiling point	I > II	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction
Solubility (in H_2O)	I > II	More polar molecules are more soluble in H_2O.
Melting point	II > I	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis
Stability	II > I	The molecule having more vander waal strain are less stable. In cis isomer the bulky groups are closer they have larger vander waals strain.

1.2 Optical Isomers :

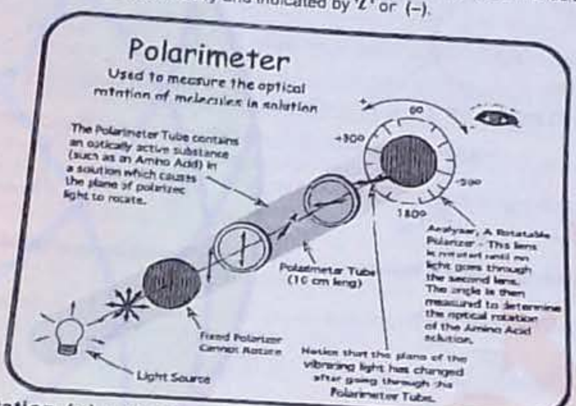
Introduction and Definitions :

(1) Optical activity & plane-polarised light : Ordinary light is an electromagnetic wave, which has oscillation in all the directions perpendicular to the path of propagation. When ordinary light is passed through Nicol prism it has all its oscillations in the same plane and is called plane-polarised light.

D2 Certain compounds rotate the plane of polarised light in a characteristic way when it is passed through their solutions. These compounds are referred to as **optically active compounds**. The angle of rotation can be measured by an instrument called polarimeter.

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

(III) laevorotatory compounds : If light is rotated towards left (i.e. in anticlockwise direction) then substance is said to be laevorotatory and indicated by '*l*' or (–).



D3 **Specific rotation (α) :** Specific rotation is the number of degrees of rotation observed if a 1-dm (10-cm) tube is used and the compound has concentration 1 gm/mL. Thus specific rotation [α] is

$$[\alpha]_t^{\lambda} = \frac{\theta}{\ell \times C}$$

[α] = Specific rotation ; θ = observed angle of rotation (degree)
ℓ = Pathlength (dm) ; C = concentration (gm/ml)
λ = wavelength (nm) ; t = temperature (25°C)

Note :- Specific rotation of a compound is **independent** of the length of tube and concentration of the solution.

Cause of optical activity :

The foundation of modern theory of stereochemistry was laid by Louis Pasteur when he observed two different kind of crystals, which were mirror images of each other. Aqueous solution of both types of crystals showed optical rotation that was equal in magnitude but opposite in direction. Pasteur believed that this difference in optical activity was associated with the three dimensional arrangement of atoms in the two types of crystals. Later van't Hoff and LeBel proposed that all the four valencies of carbon are directed towards the four corners of regular tetrahedron, and if all the four substituent attached to such a carbon are different the resulting molecule lack symmetry and such a molecule is referred to as asymmetric molecule and **asymmetry** of the molecule is responsible for optical activity in such organic compounds.

D4 **Chirality :**

A compound which is non-superimposable to its mirror image is called **chiral** while a compound which is superimposable to its mirror image is called **achiral**.

D5 **Chiral centre :**

A compound in which a carbon is atttached with four different groups lacks symmetry and is called chiral carbon or asymmetric carbon. It is represented by C*.

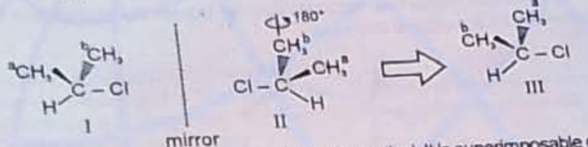
(III) Asymmetric and dissymmetric compounds :

A molecule which does not possess any element of symmetry (there are all 23 elements of symmetry) is called asymmetric. A molecule which does not possess plane of symmetry, centre of symmetry and alternating axis of symmetry is called dissymmetric.

(IV) Condition for optical activity :
The minimum condition for a compound to show optical activity is molecular dissymmetry i.e. absence of plane of symmetry, centre of symmetry and alternating axis of symmetry.

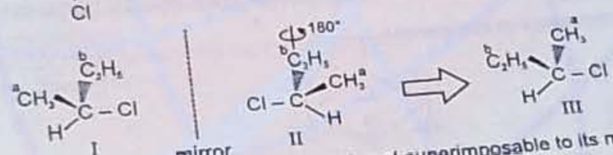
For Examples :

(a) $CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$ (2-chloropropane) :



I has no chiral centre since two groups (a & b) are identical. It is superimposable on its mirror image II (≡ III).

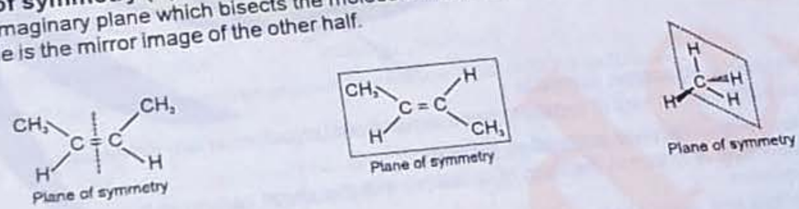
(b) $CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{*}{C}H}}-C_2H_5$ (2-chlorobutane) :

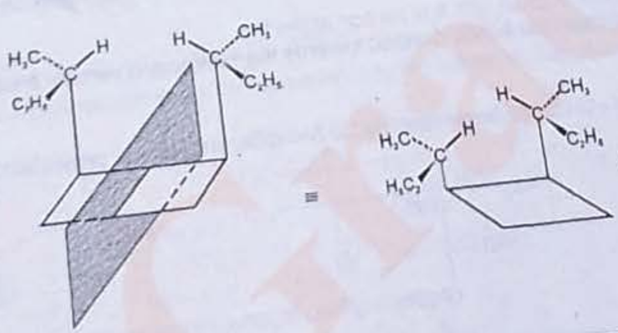


I has one chiral centre it is asymmetric & it is not superimposable to its mirror image II (≡ III).
The necessary condition for chirality is not just the presence of asymmetric carbon atoms but the dissymmetry of the molecule as a whole.

Element of symmetry and concept of molecular dissymmetry/asymmetry and chirality.

D6 **Plane of symmetry (σ) :**
It is an imaginary plane which bisects the molecule in two equal halves in such a way that each half of the molecule is the mirror image of the other half.





Cis-(1R, 2S)-Disec-butylcyclobutane

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D7 Centre of symmetry (i) :

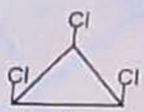
A centre of symmetry is a point from which lines, when drawn on one side and produced an equal distance on the other side, will meet identical points in the molecule.

centre of symmetry

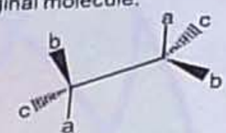
centre of symmetry absent

D8 Axis of symmetry (C_n) :

Axis of symmetry is a line about which the molecule can be rotated by 360°/n and thereby produce a molecule indistinguishable from the original molecule.



C_3 axis of symmetry



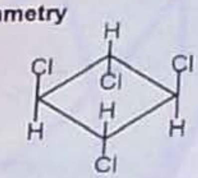
C_2 axis of symmetry

D9 Alternating axis of symmetry (S_n) :

A molecule possess an n-fold alternating axis of symmetry if when rotated through an angle of 360°/n about this axis and then followed by reflection in plane perpendicular to the axis ; the molecule is indistinguishable from the original molecule.

It is also called **Improper axis of symmetry**

S_2

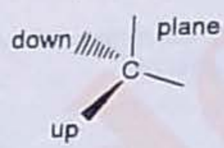


S_4

Projection formulas in optical isomerism :

(I) Wedge-dash projection formula :

It is a convenient way of depicting three dimensional structure in two dimension. In this projection four bonds of a tetrahedral molecule is shown by two lines (in the plane), one wedge (up the plane) and one dash line (down the plane)



(II) Fischer projection formula :

It is also a convenient way of depicting three dimensional structure in two dimension.

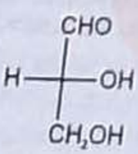
Rules for writing Fischer projection formula :

(i) The molecule is drawn in the form of cross (+) with the chiral carbon at the intersection of horizontal & vertical lines.

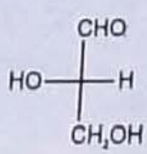
(ii) On vertical line, main chain is taken with first carbon at the top.

(iii) The horizontal lines represent the bonds directed towards the viewer and vertical lines represent away from the viewer

Ex. (a) glyceraldehyde $\underset{OH}{CH_2}-\underset{OH}{\overset{*}{CH}}-CHO$ can be represented in two different Fischer projection as

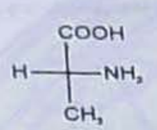


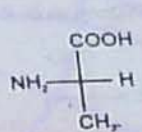
I



II

(b) Alanine $CH_3-\overset{*}{C}H(NH_2)-COOH$ can be represented in two different Fisher projections as

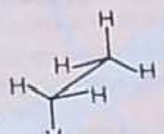

I

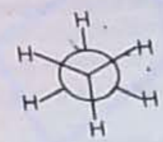

II

(III) Saw horse projection formula :
The molecule is veiwed slightly from above, from the right and projected on the paper. The bond between the carbon atoms is drawn diagonally. The lower left hand carbon is considered to be towards front and upper right hand side carbon towards back.

(IV) Newman projection Formula :
(i) These projection formulae are obtained by veiwing the molucule along the bond joining the two carbon atoms.
(ii) The carbon atoms near the eye is represented by a point and three other atoms/ groups attached to it by 3 equally spaced lines.
(iii) The carbon atom further from the eye is represented by a circle and three atoms / groups attached to it by 3 equally spaced lines.

Ex.


Staggered (Saw horse)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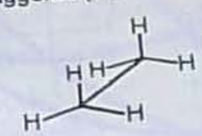
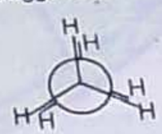
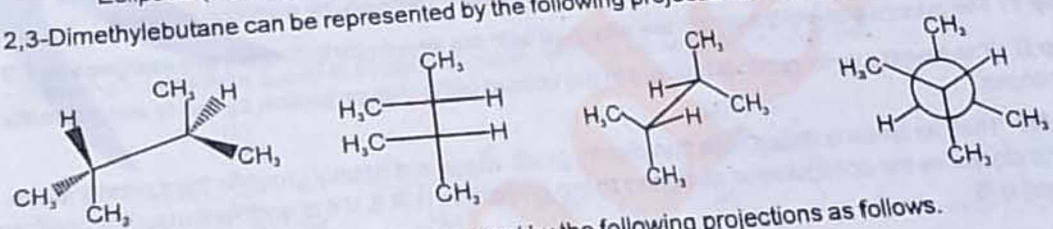
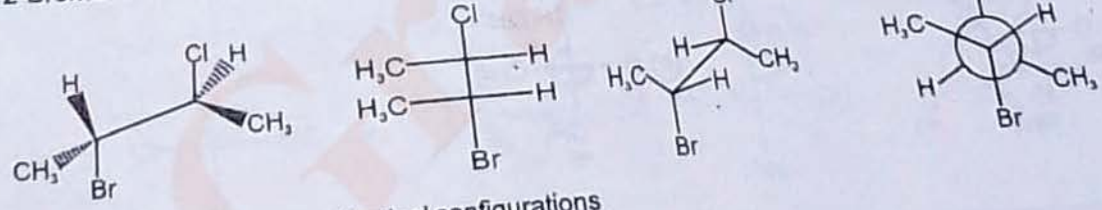

Eclipsed (Saw horse)


Eclipsed (Newman)

Ex. 2,3-Dimethylebutane can be represented by the following projections as follows.



Ex. 2-Bromo-3-chlorobutane can be represented by the following projections as follows.



All the presentations have identical configurations

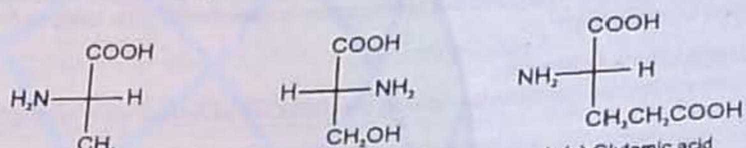
Configurational nomenclature in optical isomers :

(I) D-L System (Relative configuration) :

This method is used to relate the configuration of sugars and amino acids by the help of enantiomers of glyceraldehyde. The configuration of (+)-glyceraldehyde 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

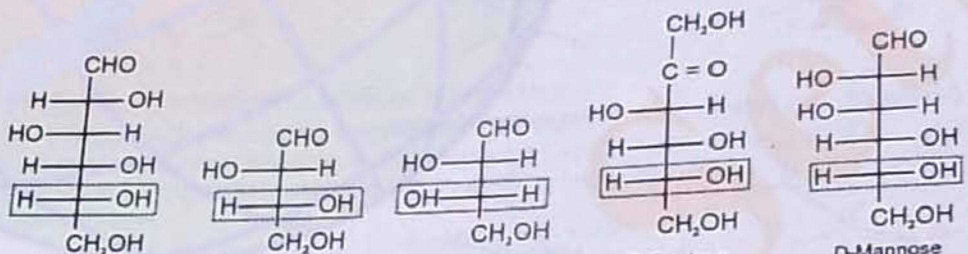
Ex.



L-Alanine | D(+)-serine | L-(+)-Glutamic acid

Sugars have several asymmetric carbons. A sugar whose highest numbered chiral centre (the penultimase 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.

Ex.



D-(+)-Glucose | D-Threose | L-Erythrose | D-Fructose | D-Mannose

(II) R and S configurations in Fischer projection : (Absolute configuration)

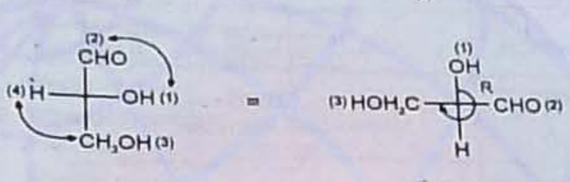
Step I : The priorities of groups which are attached with the asymmetric C-atom are assigned by CIP rule.

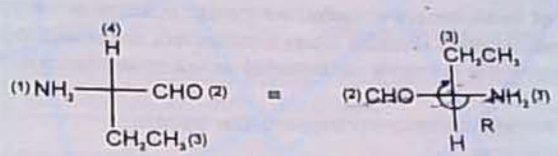
Step II : The lowest priority group is brought to the bottom of Fischer projection by two or even simultaneous exchanges.

Step III : Then an arrow is drawn from first priority group to second priority group to third priority group. If the arrow is clockwise the configuration assigned to the projection is **R** & If it is anticlockwise the configuration assigned is **S**.

Ex.

(c) 

(d) 

(e) 

(III) R and S configurations in wedge-dash formula : (Absolute configuration)

Step 1 : Decide the priority of groups by sequence rule.

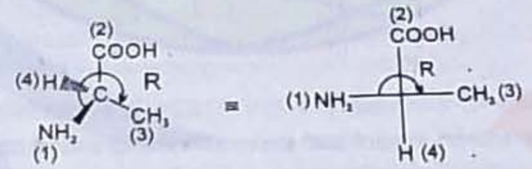
Step 2 : Bring the lowest prior group to dash by even simultaneous exchanges.

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

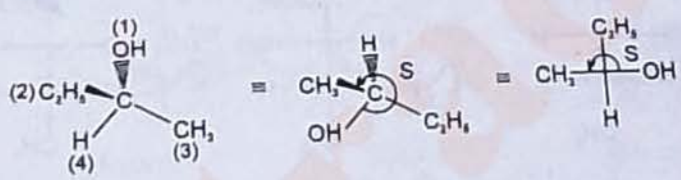
Step 4 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

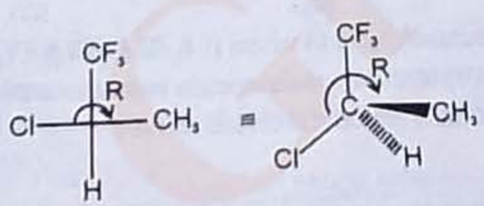
Converting a wedge-dash formula into Fischer projection formula :

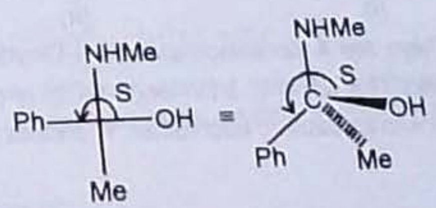
Draw the Fischer projection formula having equivalent configuration to the wedge-dash formula.

Ex. (a) 

Here the lowest prior group is already on dash, there is no need for exchanges.

(b) 

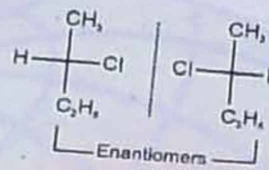
(c) 

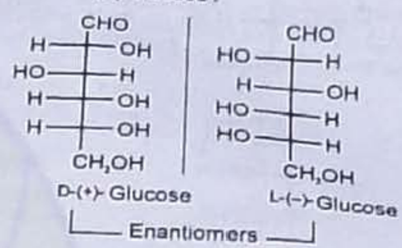
(d) 

D10 Enantiomers :

Stereoisomers which are non-superimposable mirror images of each other are called enantiomers.

Ex. (a) 2-Chlorobutane : (b) Glucose :





D11 Racemic mixture :

A mixture of equal amounts of enantiomers is called a racemic mixture or racemic modification. A racemic modification is always **optically inactive** when enantiomers are mixed together, the rotation caused by a molecule of one enantiomer is exactly cancelled by an equal and opposite rotation caused by a molecule of its enantiomer.

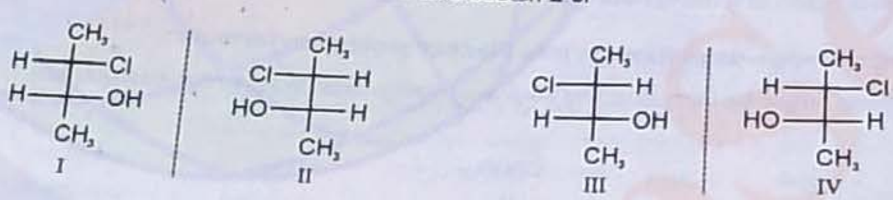
The prefix (±) is used to specify the racemic nature of the particular sample.

e.g. (±) Lactic acid, or ($d + \ell$) Lactic acid.

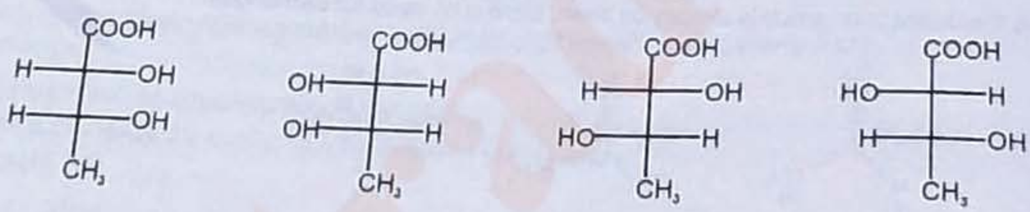
D12 Optical diastereomers :

The optical isomers which are neither mirror image nor superimposable to each other are called diastereomers. Diastereomers have different physical and chemical properties and they can be easily separated by physical methods.

Ex. Let us consider the stereoisomers of 3-chlorobutan-2-ol



There are 4 stereoisomers of 3-chlorobutan-2-ol. In which (I & II) & (III & IV) are enantiomeric pairs. (I & III) or (I & IV) or (II & III) or (II & IV) all the isomers in each pair are neither mirror image nor superimposable to each other. Therefore these pairs are optical diastereomers.



(I) (II) (III) (IV)

There are 4 stereoisomers of 2,3-Dihydroxybutanoic acid In which (I & II) & (III & IV) are enantiomeric pairs. (I & III) or (I & IV) or (II & III) or (II & IV) all the isomers in each pair are neither mirror image nor superimposable to each other. Therefore these pairs are optical diastereomers.

Properties of Enantiomers & Diastereomers :

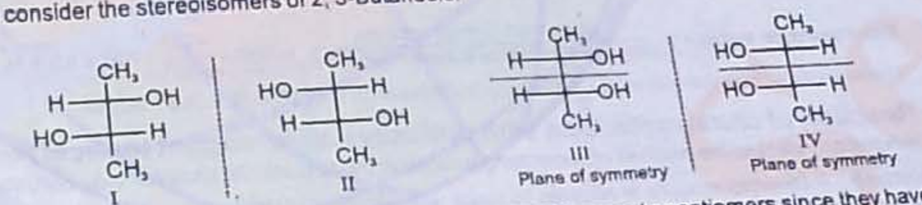
	Properties	Enantiomers	Diastereomers
(1)	Molecular formula	Same	Same
(2)	Structural formula	Same	Same
(3)	Stereochemical formula (structure formula with orientation)	Different	Different
(4)	Dipole moment	Same	Different
(5)	Physical properties (m.p., b.p., density, solubility, refractive index etc.)	Same	Different
(6)	Specific rotation	Different sign but same magnitude	Different
(7)	**Chemical properties**		
	(a) with optically inactive compound	Same	Different
	(b) with optically active compound	Different	Different

D13 Meso compound :

An optical inactive molecule whose atleast one diastereomer is optically active.

* Mirror image of meso compound is superimposable over each other & nonresolvable.
* Molecule contains chiral centres & symmetry but optically inactive.

Ex. Let us consider the stereoisomers of 2, 3-Butanediol



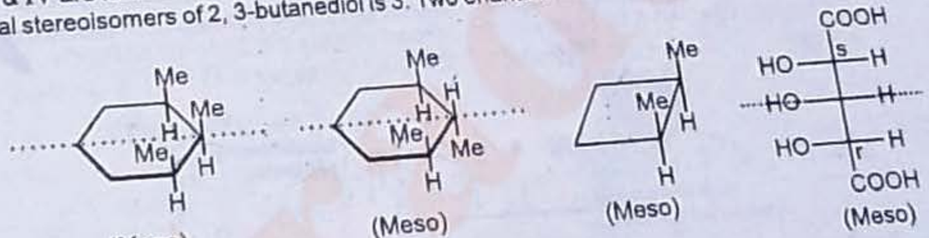
In all the possible isomers I & II are enantiomers but III & IV are not enantiomers since they have plane of symmetry and are superimposable to each other

Note :- All symmetrical compounds are superimposable to their mirror images.

Thus III & IV are identical & meso compounds.

Thus total stereoisomers of 2, 3-butanediol is 3. Two enantiomers and one meso isomer.

Ex.



Optical purity :

Sometimes we deal with mixture that is 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.

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

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

optical purity = $\frac{9.72}{13.5} \times 100 = 72\%$.

That means 72% is pure (+) 2-Butanol and 28% is racemic (± mixture)
Total (+) isomer = 72 + 14 = 86%, (–) isomer = 14%

Enantiomeric excess :

To compute the enantiomeric excess of a mixture we calculate the excess of predominant enantiomer as a percentage of the entire mixture. The calculation of enantiomeric excess gives the same result as the calculation of optical purity.

$$\therefore \text{ Optical purity} = \text{Enantiomeric excess} = \frac{|d-\ell|}{d+\ell} \times 100 = \frac{\text{excess of one enantiomer over other}}{\text{entire mixture}} \times 100$$

Thus for above example optical purity = enantiomeric excess = $d - \ell = 72\%$ & $d + \ell = 100\%$
so, $2d = 172 \Rightarrow d = 86\%$ & $\ell = 14\%$ (composition of mixture)

Ex. Cholesterol, when isolated from natural sources, is obtained as a single enantiomer. The observed rotation α of a 0.3 g sample of cholesterol in 15 mL of chloroform solution contained in a 10 cm polarimeter tube is –0.78°. Calculate the specific rotation of cholesterol. A sample of synthetic cholesterol was prepared consisting entirely of (+) -cholesterol. This synthetic (+)- cholesterol was mixed with some natural (–)-cholesterol. The mixture had a specific rotation $[\alpha]_D^{20}$ of –13°. What fraction of the mixture was (+)-cholesterol ?

Sol. Specific rotation, $[\alpha]_t^{\lambda} = \frac{\theta}{\ell \times C} = -\frac{0.78}{1 \times \frac{0.3}{15}} = -39^\circ$

Enantiomeric excess = $\frac{\text{observed optical rotation}}{\text{optical rotation of pure enantiomer}} \times 100 = \frac{-13^\circ}{-39^\circ} \times 100 = 33.3\%$.

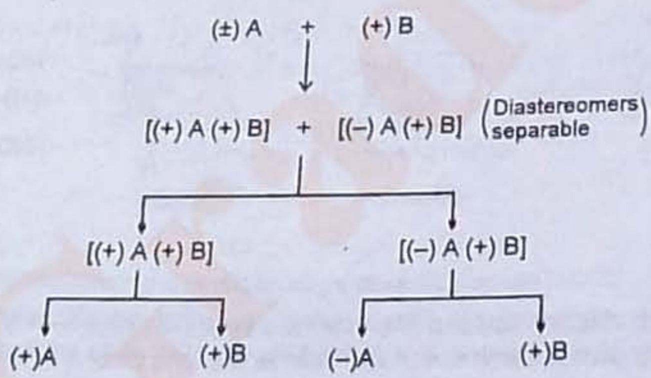
Therefore (+)-cholesterol is of 33.3 % and (–)-cholesterol is of 66.6 % in the mixture.

Reaction of chiral molecules with optically active reagent (optical resolution) :

Resolution refers to the method of separating a racemic mixture into its enantiomeric constituents.

Method : A racemic mixture is allowed to react with another optically pure compound. This changes a racemic mixture into a mixture of diastereomers which have different melting and boiling point and solubilities. These can be separated from one anoth er by conventional method of separation of compounds. The separated diastereomers is then broken down to give pure enantiomers.

Suppose a racemic mixture (±) A is to be separated. It is reacted with an optically pure compound (+) B. Thus the schematic diagram for resolution will be.



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JAIPUR
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NANDED
Tel.: 02462-250220, 606066
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MUMBAI
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UDAIPUR
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BHUBANESWAR
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e-mail: bbsr@resonance.ac.in

AHMEDABAD
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e-mail: abad@resonance.ac.in

PATNA
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JODHPUR
Tel.: 0291- 6060660
e-mail: jodhpur@resonance.ac.in

AJMER
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INDORE
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SIKAR
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e-mail: sikar@resonance.ac.in

AGRA
Tel: 0562-3192222, 6060660
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RANCHI
Tel.: 0651-6060660
e-mail: ranchi@resonance.ac.in

ALLAHABAD.
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e-mail: nashik@resonance.ac.in

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GWALIOR
Tel.: 0751-6060660
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CHANDRAPUR
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