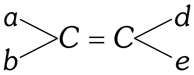
General Organic Chemistry Part 3

(3) ***E* and *Z* system of nomenclature :** '*Cis*' and '*Trans*' designations cannot be used if four different atoms or groups are attached to the carbon atoms of a double bond.

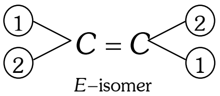


In such cases, *E* and *Z* system of nomenclature is used. This system is based on a priority system developed by *Cahn, Ingold* and *Prelog*.

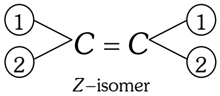
In this system, the two atoms or groups attached to each of the doubly bonded carbon are put in order of precedence on the basis of sequence rules.

The symbol '*E*' is assigned to an isomer in which the atoms or groups of higher precedence are on the opposite side (*E* from German word *Entgegen* = across or opposite).

The symbol '*Z*' is assigned to an isomer in which the atoms or groups of higher precedence are on the same side (*Z* from German word, *Zusammen* = together).



E–isomer



Z–isomer

Note: ✹1 signifies higher precedence and 2 signifies lower precedence. In most of the cases '*Z*' corresponds to *cis*-form and '*E*' to *trans*-form. However, there are many exceptions.

The following rules are followed for deciding the precedence order of the atoms or groups;

(i) Higher priority is assigned to the atoms of higher atomic number. For example, the order of precedence in the following atoms, H, Cl, I, Br is : I (at. no. 53) > Br (at. no. 35) > Cl (at. no. 17) > H (at. no. 1).

(ii) If isotopes of the same element are attached, the isotope with higher mass number is given higher order of precedence. For example, deuterium $\left({}_1^2D\right)$ is assigned higher priority in comparison to hydrogen $\left({}_1^1H\right)$.

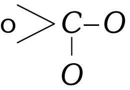
(iii) In the groups, the order of precedence is also decided on the basis of atomic number of fist atom of the group. For example, in the following set, $-Cl, -OH, -COOH, -NH-CH_3, -SO_3H$.

The order of the precedence is : $-\underset{(\text{ at.no17})}{\underset{\downarrow}{Cl}} > -\underset{(\text{at.no.16})}{\underset{\downarrow}{S}}O_3H > -\underset{(\text{at.no.8})}{\underset{\downarrow}{O}}H > -\underset{(\text{at.no.7})}{\underset{\downarrow}{N}}HCH_3 > -\underset{(\text{at.no. 6})}{\underset{\downarrow}{C}}OOH$

When the order of precedence of the groups cannot be settled on the first atom, the second atom or the subsequent atoms in the groups are considered. For example, in the set $-CH_2-CH_3, -CH_3, -COOH$, the order cannot be decided on the basis of first atom as it is same in all the groups. However, in $-CH_2-CH_3$, the second atom is carbon, in $-CH_3$, the second atom is hydrogen while in $-COOH$, the second atom is oxygen. Hence, the order of precedence is : $-C\underset{(\text{at.no.8})}{\underset{\downarrow}{O}}OH > -CH_2-\underset{(\text{at.no.6})}{\underset{\downarrow}{C}}H_3 > -C\underset{(\text{at.no.1})}{\underset{\downarrow}{H_3}}$

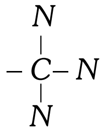
(iv) A doubly or triply bonded atom is considered equivalent to two or three such atoms. For example,

The group $>C=O$ is equal to



$>\underset{\substack{|\\O}}{C}-O$

and the group $-C\equiv N$ is equal to



$-\overset{\substack{N\\|}}{\underset{\substack{|\\N}}{C}}-N$.

(4) Number of geometrical isomers in polynes

(i) When compound has *n* double bonds and ends of a polyene are different, the number of geometrical isomers $= 2^n$

$$C_6H_5-CH=CH-CH=CH-CH=CH-CH=CH-Cl$$

The given compound has four double bonds and the two ends are different (One is C_6H_5 and other is *Cl*). Therefore, number of geometrical isomers $= 2^n = 2^4 = 16$.

(ii) When the ends of polyene are same.

Case I : When number of double bonds ($=n$) is even then the number of geometrical isomers $= 2^{n-1} + 2^{n/2-1}$

$$Cl-CH=CH-CH=\underset{n=4,\,\text{even}}{CH-CH}=CH-CH=CH-Cl$$

Number of geometrical isomers $= 2^{n-1} + 2^{(n/2)-1} = 2^3 + 2^1 = 8 + 2 = 10$.

Case II : When number of double bonds ($=n$) is odd.

Number of geometrical isomers $= 2^{(n-1)} + 2^{\left(\frac{n+1}{2}\right)/-1}$

$$C_6H_6-CH=CH-CH=CH-CH=CH-C_6H_5$$

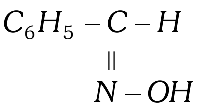
Number of geometrical isomers $= 2^2 + 2^{2-1} = 2^2 + 2^1 = 4 + 2 = 6$.

(5) Geometrical Isomerism in nitrogen compounds

(i) Geometrical isomerism due to $>C=N-$ bond.

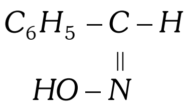
The important class of compounds exhibiting geometrical isomerism due to $>C=N-$bond are oximes, nitrones, hydrazones and semicarbazones. But the most common compound is oxime.

Oximes : In aldoxime, when hydrogen and hydroxyl groups are on the same side, the isomer is known as syn. (analogous to *cis*) and when these groups are on the opposite side, the isomer is known as anti (analogous to *trans*)



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ \quad N-OH \end{array}$$

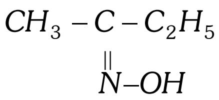
Syn-benzaldoxime



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ HO-N \quad \end{array}$$

Anti–benzaldoxime

In ketoximes the prefixes **syn** and **anti** indicate which group of ketoxime is syn or anti to hydroxyl group. For example:



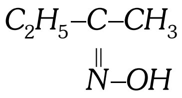
$$\begin{array}{c} CH_3-C-C_2H_5 \\ \| \\ N\text{–}OH \end{array}$$

this compound will be named as;

(a) Syn-ethyl methyl ketoxime $\Rightarrow HO$ and C_2H_5 are syn or

(b) Anti-methyl ethyl ketoxime $\Rightarrow HO$ and C_2H_3 are anti.

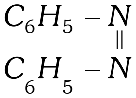
Similarly consider the following structure



$$\begin{array}{c} C_2H_5\text{–}C\text{–}CH_3 \\ \| \\ N\text{–}OH \end{array}$$

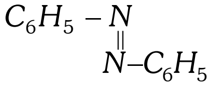
Syn–methyl ethyl ketoxime
or Anti–ethyl methyl ketoxime

(ii) Geometrical isomerism due to $N=N$ bond.



$$\begin{array}{c} C_6H_5-N \\ \| \\ C_6H_5-N \end{array}$$

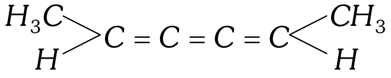
Syn-azobenzene



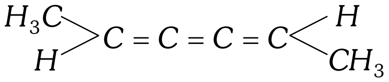
$$\begin{array}{l} C_6H_5-N \\ \qquad\quad \| \\ \qquad\quad N\text{–}C_6H_5 \end{array}$$

Anti–azobenzene

(6) Geometrical isomerism show by cumulatrienes : Cumulatrienes (Trienes with three adjacent double bonds) show only geometric isomerism. This is because their molecule is planar, as such the terminal $-CH_3$ groups and H- atoms lie in the same plane. Therefore, in this case their planar structure can exist in two diastereoisomeric forms, *cis*- and *trans*- but no enantiomeric forms are possible.

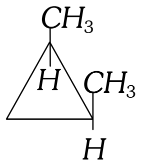


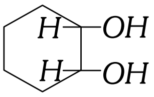
cis–Hexa–2,3,4–triene

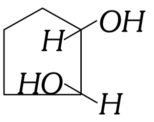


trans–Hexa–2,3,4–triene

(7) Geometrical isomerism in cycloalkanes : Disubstituted cycloalkanes show geometrical isomerism.


Cis-1,2-dimethylcyclopropane


Cis-1,2-cyclohexanediol


Trnas-1,2-cyclopentanediol

Note : ✹Certain compounds show geometrical as well optical isomerism. Such type of isomerism is know as **geometrical enantiomerism**.

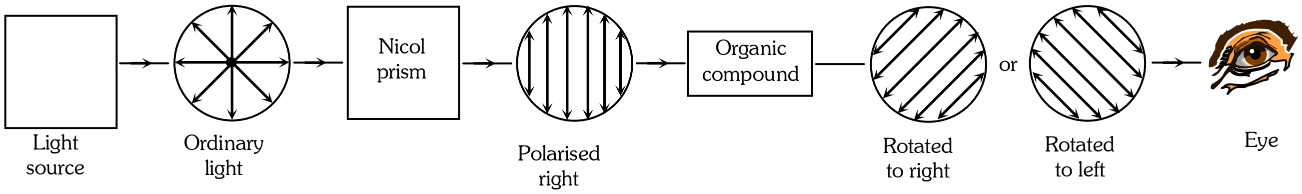
Optical isomerism.

(1) Compounds having similar physical and chemical properties but they have the ability to rotate the plane of polarised light either to the right (Clockwise) or to the left (Anticlockwise) are termed as optically active or optical isomer and the properly is called optical activity or optical isomerism.

The optical activity was first observed in organic substances like quartz, rock-crystals and crystals of potassium chlorate $(KClO_3)$, potassium bromate $(KBrO_3)$ and sodium periodate $(NaIO_4)$.

Biot (In 1815) suggested that optical activity of an organic compound was a molecular phenomenon, *i.e.*, it was due to constitution of an organic compound rather than its crystalline nature.

The light whose vibrations occur only in one plane is termed plane polarised or simply polarised light. The device that brings polarisation in light is called a polariser (Nicol prism, made of calcite, $CaCO_3$). The apparatus which measures the extent of rotation of polarised light is called polarimeter.



(2) **Measurement of optical activity :** The measurement of optical activity is done in terms of **specific rotation which is defined as the rotation produced by a solution of length of 10 centimetres (One decimetre) and unit concentration (1 *g/mL*) for the given wavelength of the light at the given temperature**.

$$\text{Specific rotation, } [\alpha]^{t°C}_{\text{wavelength}} = \frac{\alpha_{obs}}{l \times C}$$

Where α_{obc} is the rotaion observed, l is the length of the solution in decimeters and C is the number of grams in 1mL of solution. The specific rotation of the sucrose at 20°C using sodium light (D-line, λ=5893Å) is +66.5°C and is denoted as: $[\alpha]_D^{20°C} = +66.5°C (C = 0.02\, g/mL\, \text{water})$

+ sign indicates the rotation in clockwise direction.

(3) On the basis of the study of optical activity, the various organic compounds were divided into four types :

(i) The optical isomer which rotates the plane of the polarised light to the rigth (Clockwise) is known as dextrorotatory isomer (Latin: *dextero* = *right*) or *d*-form or indicated by +*ve* sign.

(ii) The optical isomer which rotates the plane of the polarised light to the left (Anticlockwise) is known as laevorotatory isomer (Latin; *laevo* = *left*) or *l*-form or indicated by *–ve* sign.

(iii) The optical powers of the above two isomers are equal in magnitude but opposite in sign. An equimolar mixture of the two forms, therefore, will be optically inactive due to external compensation. This mixture is termed racemic mixture or *dl*-form or (±) mixture.

(iv) Optical isomer with a plane of symmetry is called *meso* form. It is optically inactive due to internal compensation, *i.e.*, the rotation caused by upper half part of molecule is neutralised by lower half part of molecule.

(4) Chirality

(i) ***Definition*** : A molecule (or an object) is said to be chiral or dissymmetric, if it is does not possess any element of symmetry and not superimposable on its mirror image and this property of the molecule to show non-superimposability is called chirality.

On the other hand, a molecule (or an object) which is superimposable on its mirror image is called achiral (non-dissymmetric or symmetric).

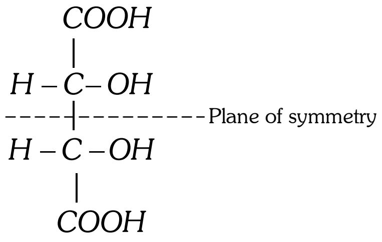
To understand the term chiral and achiral let us consider the alphabet letters '*P*' and '*A*' whereas '*P*' is chiral, '*A*' is achiral as shown in fig.

Non-superimposable
(Chiral or dissymmetric)

Superimposable
(Achiral or non-dissymmetric)

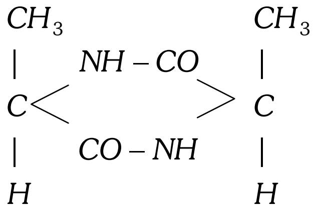
(ii) ***Elements of symmetry*** **:** There are three elements of symmetry,

(a) *Plane of symmetry* : It may be defined as a plane which divides a molecule in two equal parts that are related to each other as an object and mirror image. *e.g.*,



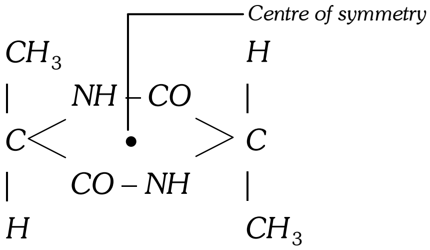
$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ \text{-----}|\text{---------} \text{Plane of symmetry} \\ H-C-OH \\ | \\ COOH \end{array}$$

(b) *Centre of symmetry* : It may be defined as a point in the molecule through which if a line is drawn in one direction and extended to equal distance in opposite direction, it meets another similar group or atom, *eg*.



cis–Dimethyl diketo piperazine

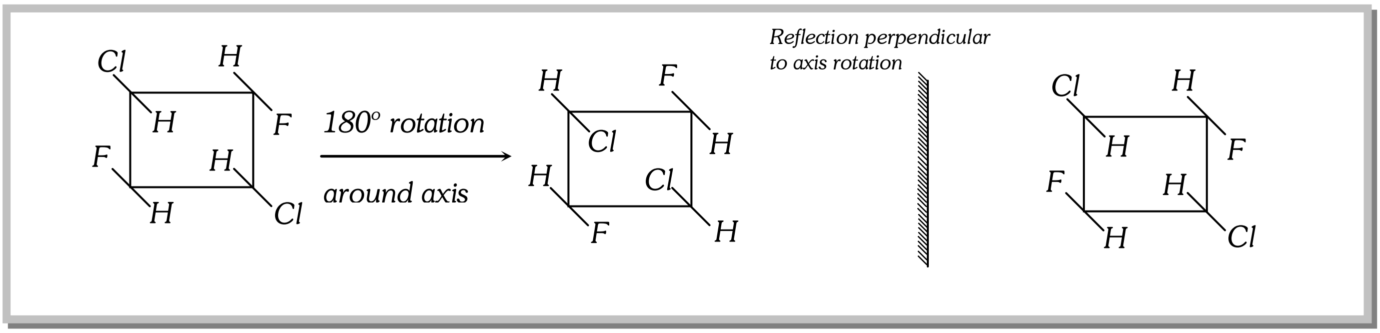
and



trans–Dimethyl diketo piperazine

Since *trans* form contains a centre of symmetry, it is optically inactive.

(c) *Alternating axis of symmetry* : A molecule is said to possess an alternating axis of symmetry if an oriention indistinguishable from the original is obtained when molecule is rotated Q degree around an axis passing through the molecule and the rotated molecule is reflected in a mirror that is perpendicular to the axis of rotation in step (I).

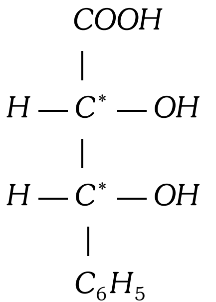


(iii) Symmetric, Asymmetric and Dissymmetric molecules

(a) *Symmetric molecules* : If any symmetry is present in the molecule then molecule will be symmetric molecule.

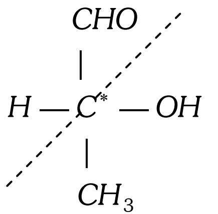
(b) *Dissymmetric molecules* : Molecule will be a dissymmetric molecule if it has no plane of symmetry, no centre of symmetry and no alternating axis of symmetry.

(c) *Asymmetric molecules* : Dissymmetric molecule having at least one asymmetric carbon is known as assymmetric molecule. All asymmetric molecules are also dissymmetric molecules but the reverse is not necessarily true.



$$\begin{array}{c} COOH \\ | \\ H - C^* - OH \\ | \\ H - C^* - OH \\ | \\ C_6H_5 \end{array}$$

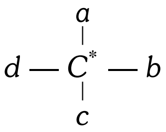
No plane of symmetry
⇓
Dissymmetric molecule
⇓
Asymmetric molecule



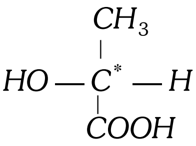
$$\begin{array}{c} CHO \\ | \\ H - C^* - OH \\ | \\ CH_3 \end{array}$$

No plane of symmetry
⇓
Dissymmetric molecule
⇓
Asymmetric molecule

(iv) **Chiral or asymmetric carbon atom :** A carbon bonded to four different groups is called a chiral carbon or a chirality centre. The chirality centre is indicated by asterisk. *e.g.*,



$$\begin{array}{c} a \\ | \\ d - C^* - b \\ | \\ c \end{array}$$

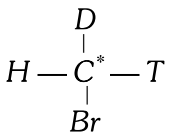


$$\begin{array}{c} CH_3 \\ | \\ HO - C^* - H \\ | \\ COOH \end{array}$$

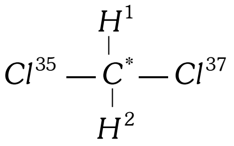
Lactic acid

Note : ✹Carbons that can be chirality centres are sp^3-hybridised carbons; sp^2 and sp-hybridised carbons cannot be chiral carbons because they cannot have four group attached to them.

✹Isotopes of an atom behave as different group in stereoisomerism.



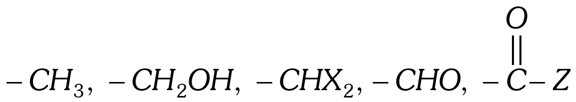
$$H - \overset{\displaystyle D}{\underset{\displaystyle Br}{C^*}} - T$$



$$Cl^{35} - \overset{\displaystyle H^1}{\underset{\displaystyle H^2}{C^*}} - Cl^{37}$$

Lactic acid

✸Carbon of the following groups will not be a chiral carbon



$$-CH_3,\ -CH_2OH,\ -CHX_2,\ -CHO,\ -\overset{\displaystyle O}{\overset{\|}{C}}-Z$$

✸Maleic acid $(HOOC-CH=CH-COOH)$ show geometrical isomerism while malic acid $(HOOC-CH_2-CHOH-COOH)$ show optical isomerism.

(5) Calculation of number of optical isomers

(i) If molecule is not divisible into two identical halves and molecule has n asymmetric carbon atoms then

Number of optically active forms $= 2^n = a$

Number of enantiomeric pair $= a/2$

Number of racemic mixture $= a/2$

Number of *meso* form $= 0$

Examples : $C_6H_5-\overset{*}{C}HOH-\overset{*}{C}HOH-\overset{*}{C}HOH-CH_3$

This molecule cannot be divided into two identical halves and it has three asymmetric carbons. Hence number of optical active isomers $= a = 2^n = 2^3 = 8$.

$$CH_2OH-\overset{*}{C}HOH-\overset{*}{C}\underset{n=4}{HOH}\,\vdots\,-\overset{*}{C}HOH-\overset{*}{C}HOH-CHO$$

Number of optically active forms $= a = 2^4 = 16$

$$CH_3-\overset{*}{C}\underset{n=2}{HOH}\,\vdots\,-\overset{*}{C}HCl-CH_3$$

Number of optically active forms $= 2^2 = 4$

(ii) If molecule is divisible into two identical halves, then the number of configurational isomers depends on the number of asymmetric carbon atoms.

Case I : When compound has even number of carbon atoms, i.e., $n = 2, 4, 8, 10, 12, \ldots\ldots$:

(i) Number of optically by active forms $= a = 2^{n-1}$

(ii) Number of enantiomeric pairs $= a/2$

(iii) Number of racemic mixture $= a/2$

(iv) Number of *meso* forms $= m = 2^{(n/2)-1}$

(v) Total number of configurational isomers $= a + m$

Example :

$$COOH - \underset{(I)}{\overset{*}{C}HOH} \,\vert\, - \underset{(II)}{\overset{*}{C}HOH} - COOH$$

Two idenitcal halves (I) and (II) having $n = 2$.

Thus number of optical isomers $= a = 2^{2-1} = 2$

Number of *meso* form $= m = 2^{(n/2)-1} = 2^{(2/2)-1} = 2^0 = 1$

Total number of configurational isomers $= 2 + 1 = 3$

$$C_6H_5 - \underset{n=4,\,\text{even}}{\overset{*}{C}HCl} - \overset{*}{C}HCl - \,\vert\, - \overset{*}{C}HCl - \overset{*}{C}HCl - C_6H_5$$

$$a = 2^{4-1} = 2^3 = 8$$

$$m = 2^{(n/2)-1} = 2^1 = 2$$

Total number of configurational isomers $= 8 + 2 = 10$

Case II : When compound has odd number of carbon atoms, *i.e.*, $n = 3, 5, 7, 9, 11, \ldots\ldots$:

(i) Number of optically active forms $= a = 2^{n-1} - 2^{(n-1)/2}$

(ii) Number of enantiomeric pairs $= a/2$

(iii) Number of racemic mixutre $= a/2$

(iv) Number of *meso* forms $= m = 2^{(n-1)/2}$

(v) Total number of configurational isomers $= a + m$

Example :

$$CH_2OH - \underset{(I)}{\overset{*}{C}HOH} - \overset{*}{C}H\vert OH - \underset{(II)}{\overset{*}{C}HOH} - CH_2OH$$

Compound has two identical halves and has three asymmetric carbons.

Thus, $a = 2^{n-1} - 2^{(n-1)/2} = 2^2 - 2^1 = 4 - 2 = 2$

$$m = 2^{(n-1)/2} = 2^1 = 2$$

Hence total number of configurational isomers $= 2 + 2 = 4$

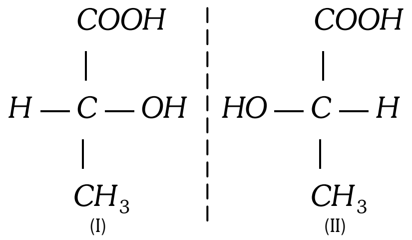
$$COOH - \overset{*}{C}\underset{\underset{n=5}{(I)}}{HCl} - \overset{*}{C}HOH - \overset{*}{C}H\vert Br - \overset{*}{C}HOH - \overset{*}{C}\underset{(II)}{HCl} - COOH$$

(6) Optical activity of compounds containing one asymmetric carbon

Examples : $CH_3 - \overset{*}{C}HOH - COOH$; $CH_3 - \overset{*}{C}HOH - CHO$

$CH_2OH - \overset{*}{C}HOH - CHO$; $C_6H_5 - \overset{*}{C}HCl - CH_3$

Any molecule having one asymmetric carbon atom exists in two configurational isomers which are nonsuperimposible mirror images.



$$\begin{array}{c} COOH\\ | \\ H-C-OH\\ | \\ CH_3 \end{array} \;\vdots\; \begin{array}{c} COOH\\ | \\ HO-C-H\\ | \\ CH_3 \end{array}$$

(I) (II)

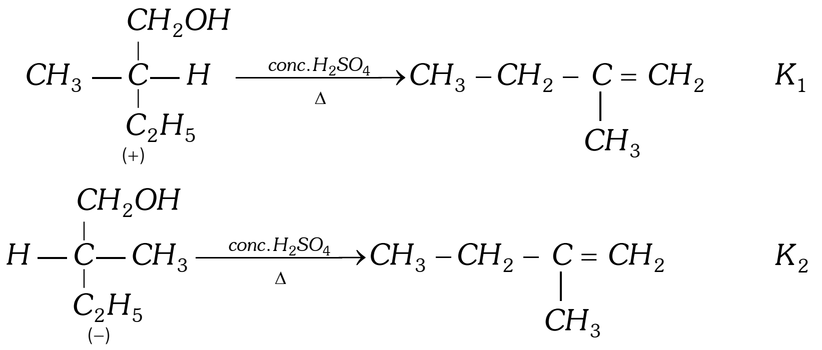
(I) and (II) have the same molecular formula, the same structure but different configurations, hence (I) and (II) are known as configurational isomers. (I) and (II) are nonsuperimposable mirror images, hence (I) and (II) are optical isomers. Configurational isomers which are nonsuperimposable mirror images are known as **enantiomers**. Thus (I) and (II) are enantiomers. Pair of (I) and (II) is known as enantiomeric pair.

(i) ***Properties of Enantiomers*** **:** All chemical and physical properties of enantiomers are same except two physical properties.

(a) *Mode of rotation* : One enantiomer rotates light to the right and the other by an **equal magnitude** to the left direction. For example

Enantiomer	***[α]***	***bp***	***d***
(+) 2-methyl-1-butanol	**+ 5.78**	**128.9**	**1.41**
(–2) -methyl-1-butanol	**– 5.78**	**128.9**	**1.41**

(b) **Rate of chemical reaction with an optically active compound** : Both the enantiomers of 2-methyl-1-butanol are converted to 2-methyl butene when treated with conc. H_2SO_4. The rate of the reactions is the same.



$$CH_3-\underset{C_2H_5}{\overset{CH_2OH}{C}}-H \xrightarrow[\Delta]{conc.H_2SO_4} CH_3-CH_2-\underset{CH_3}{C}=CH_2 \qquad K_1$$

(+)

$$H-\underset{C_2H_5}{\overset{CH_2OH}{C}}-CH_3 \xrightarrow[\Delta]{conc.H_2SO_4} CH_3-CH_2-\underset{CH_3}{C}=CH_2 \qquad K_2$$

(–)

$$\mathbf{K_1 = K_2}$$

When both these compounds are treated with lactic acid, the rate of the reaction is different.

(+) –2–methyl-1-butanol

K_3 ↓ (–) lactic acid

Ester

(–) –2-methyl-1-butanol

K_4 ↓ (–) lactic acid

Ester

$K_3 \neq K_4$

Thus rate of reactions of enantiomers with optically active compound is different.

(ii) ***Racemic Mixture*** : An equimolar mixture of two enantiomers is called a racemic mixture (or racemate, ± form, (*dl*) form or racemic modification). Such a mixture is optically inactive because the two enantiomers rotate the plane polarised light equally in opposite directions and cancel each other's rotation. This phenomenon is called **external compensation**.

⇒ Racemic mixture can be separated into (+) and (–) forms. The separation is known as **resolution**.

⇒ The conversion of (+) or (–) form of the compound into a racemic mixture is called **racemisation**. It can becaused by heat, light or by chemical reagents.

⇒ Racemic mixture is designated as being ($\pm$) or (*dl*).

(iii) ***Enantiomeric Excess*** **:** A sample of an optically active substance that consists of a single enantiomer is said to be **enantiomerically pure** or to have an **enantiomeric excess** of 100%. An enantiomeric pure sample of (+)-2-butanol shows a specific rotation of 13.52^o. On the other hand, a sample of (+)-2-butanol that contains less than an equimolar amount of (–)-2-butanol will show a specific rotation that is less than $+13.52^o$ but greater than 0^o.

Such a sample is said to have an enantiomeric excess less than 100%. The **enantiomeric excess** (*ee*) is defined as follows :

$$\text{\% Enantiomeric excess} = \frac{(\text{moles of one enantiomer} - \text{moles of other enantiomer}) \times 100}{\text{Total number of moles of both enantiomers}}$$

The enantiomeric excess can be calcualted from optical rotation :

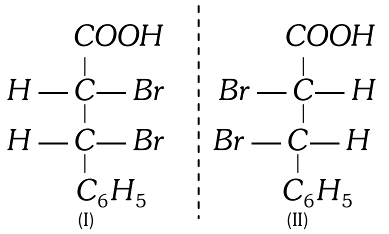
$$\text{\% Enantiomeric excess} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of pure enantiomer}} \times 100$$

Enantiomeric excess is also known as **optical purity**.

(7) Optical activity of compounds containing two asymmetric carbon

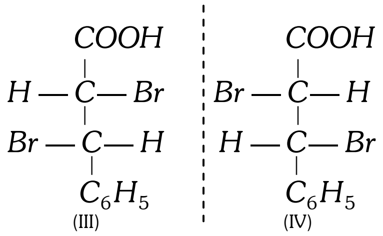
Case I : When molecule is not divisible into two identical halves.

The number of optical isomers possible in this case is four $(a = 2^2 = 4)$. Further there will be two pairs of enantiomers and two racemic modifications. In practice also it is found to be so. For example dibromocinnamic acid exists in the following four optically active forms.



(I) (II)

First pair of enantiomers



(III) (IV)

Second pair of enantiomers

Thus there are two pairs (I), (II) and (III), (IV) of enantiomers. Further, more equimolar mixtre of (I) and (II) will give one racemic mixture. Similarly, equimolar mixture of (III) and (IV) will give other racemic mixutre.

Now let us examine the relationship between the structures (I) and (III), (I) and (IV), (II) and (III) and (II) and (IV). These are configurational isomers but these are not mirror images. Configurational isomers which are not mirror images are known as **diastereomers**.

Thus (I) and (III) are diastereomers

(I) and (IV) are diastereomers

(II) and (III) are diastereomers

(II) and (IV) are diastereomers

Properties of Diastereomes : Diastereomers have different physical properties, *e.g.,* melting and boiling points, refractive indices, solubilities in different solvents, crystalline structures and specific rotations. Because of differences in solubility they often can be separated from each other by fraction crystallisation; because of slight differences in molecular shape and polarity, they often can be separated by chromatography.

Diastereomers have different chemical properties toward both **chiral** and **achiral** reagents. Neither any two diastereomers nor their transition states are mirror images of each other and so will not neccessarily have the same energies. However, since the diastereomers have the same functional groups, their chemical properties are not too dissimilar.

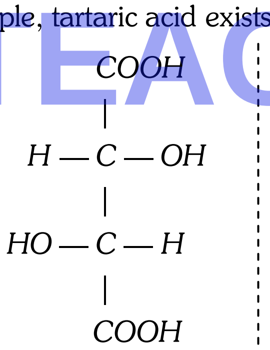
Case II : *When molecule is divisible into two identical halves.*

Number of optical isomers $= a = 2^{2-1} = 2$

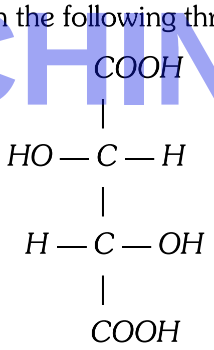
Number of meso forms $= m = 2^0 = 1$

Total number of configurational isomers $= 3$

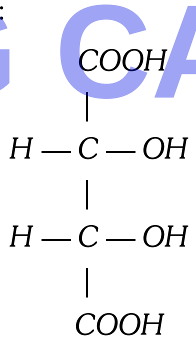
For example, tartaric acid exists in the following three forms :



(I)



(II)



(III) No non-super imposible mirror image because it has a plane of symmetry

(I) and (II) are enantiomers

(I) and (III) diastereomers

(II) and (III) are diastereomers

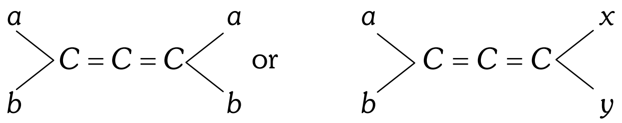
(III) is optically inactive due to symmetry of the molecule. It is known as **meso form.**

(8) **Optical activity in compounds containing no assymmetric carbon :** Although the largest number of known optically active compounds are optically active due to the presence of chiral carbon atom, some compounds are also known which do not possess any chiral carbon atom, but on the whole their molecules are chiral (such molecules were earlierly called **dissymmetric**); hence they are optically active. Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spirans) and properly substituted biphenyls.

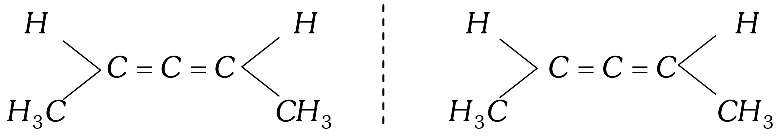
(i) **Allenes** : Allenes are the organic compounds of the following general formulae.

$$>C=C=C<$$

Allenes exhibit optical isomerism provided the two groups attached to each terminal carbon atom are different, *i.e.*,

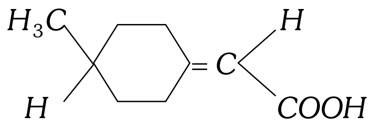


For example, 2 3-pentadiene shows enantiomerism (optical isomerism)

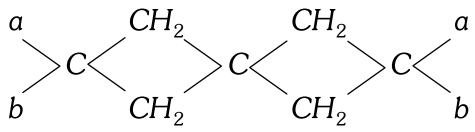


Non-superimposable mirror images of 2, 3-pentadiene

(ii) **Alkylidene cycloalkanes and spiro compounds :** When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes are spirans.

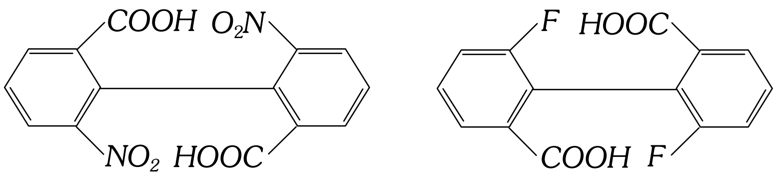


1-Methylcyclohexylidene-4- acetic acid (Alkylidene cycloalkane)



Spirans

(iii) **Biphenyls :** Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other. *Such types of stereoisomerism which is due to restricted rotation about single bond, is known as atropisomerism* and the stereoisomers are known and **atropisomers**. Examples



The above discussion leads to the conclusion that the *essential condition for optical isomerism is the molecular disymmetry or molecular chirality* and not the mere presence of a chiral centre. However, it may be noted that the **molecules having only one chiral centre are always chiral and exhibit optical isomerism**.

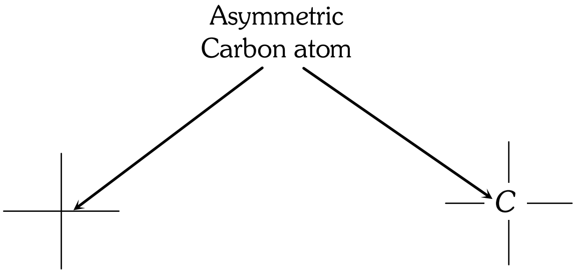
(9) **Fischer projection formulae :** The arrangement of the atoms or groups in space that characterizes a stereoisomer is called its configuration.

Emil Fischer (1891) provided an easy method to represent the three dimensional formulae of various organic molecules on paper. **Fischer projection is, thus, a planar representation of the three dimesional structure**.

By convention, the following points are followed in writing the Fischer formula.

(i) The carbon chain of the compound is arranged vertically, with the most oxidised carbon at the top.

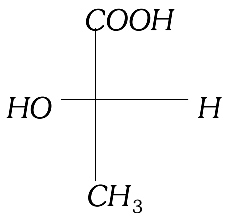
(ii) The asymmetric carbon atom is in the paper plane and is represented at the interaction of crossed lines.



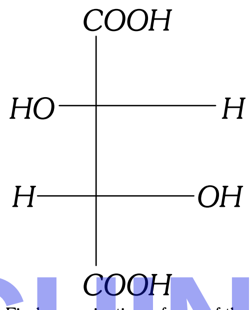
(iii) Vertical lines are used to represent bonds going away from the observer, *i.e.*, groups attached to the vertical lines are understood to be present behind the plane of the paper.

(iv) Horizontal lines represent bonds coming towards the observer, *i.e.*, groups attached to the horizontal lines are understood to be present above the plane of the paper.

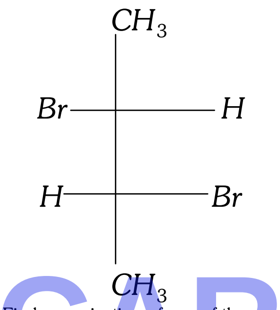
Some Fischer projections are given below :



Fischer projection of one of the enantiomers of Lactic acid



Fischer projection of one of the enantiomers of Tartaric acid

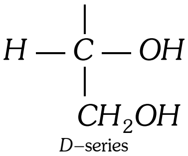


Fischer projection of one of the enantiomers of 2,3-dibromobutane

(10) **Name of optical isomers :** Following three nomenclatures are used for optically active compounds,

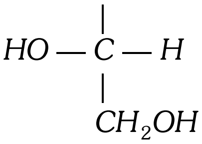
(i) ***D,L. System of nomenclature* :** This nomenclature is mainly used in sugar chemistry or optically active polyhydroxy carbonyl compounds. This nomenclature was given by Emil Fischer to designate the configurations of various sugars relative to the enantiomeric (+) and (–) glucose as reference.

All sugars whose Fischer projection formula shows the OH group on the chiral carbon atom adjacent to the terminal CH_2OH group on the right hand side belong to the D-series. Similarly if OH is on the left hand side, then the sugars belong to the L-series.



$$\begin{array}{c} | \\ H - C - OH \\ | \\ \quad CH_2OH \end{array}$$

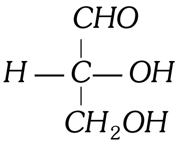
D–series



$$\begin{array}{c} | \\ HO - C - H \\ | \\ \quad CH_2OH \end{array}$$

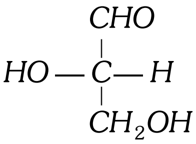
L–series

Examples :



$$\begin{array}{c} CHO \\ | \\ H - C - OH \\ | \\ \quad CH_2OH \end{array}$$

$D(d)$glyceraldehyde
or
$D(+)$glyceraldehyde



$$\begin{array}{c} CHO \\ | \\ HO - C - H \\ | \\ \quad CH_2OH \end{array}$$

$L(l)$glyceraldehyde
or
$L(-)$glyceraldehyde

⇒ It must be noted that there is no relation between the sign of rotation (+, – or *d, l*) and the configuration (*D* and *L*) of an enantiomer.

⇒ Any compound that can be prepared from, or converted into $D(+)$ glyceraldehyde will belong to D-series and similarly any compound that can be prepared from, or converted into $L(-)$ glyceraldehyde will belong to the L-series.

⇒ This nomenclature is also used in α-amino acids.

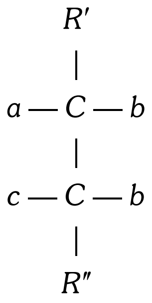
(ii) ***Erythro* and *Threo* System of Nomenclature :** This nomenclature is used only in those compounds which have

(a) Only two chiral carbons and

(b) The following structure, $R' - Cab - Cbc - R''$

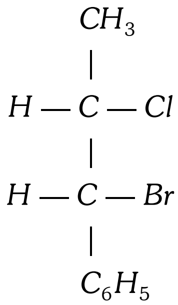
i.e., out of six substituents on two asymmetric carbons, at least two should be same.

When two like groups (in the given example, group is b) in Fischer projection formula are drawn on the same side of the vertical line, the isomer is called *erythro* form; if these are placed on the opposite sides, the isomer is said to be *threo* form.



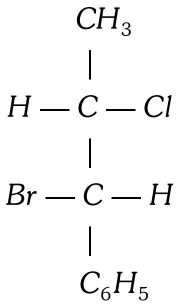
$$\begin{array}{c} R' \\ | \\ a - C - b \\ | \\ c - C - b \\ | \\ R'' \end{array}$$

Erythro form



$$\begin{array}{c} CH_3 \\ | \\ H - C - Cl \\ | \\ H - C - Br \\ | \\ C_6H_5 \end{array}$$

Erythro form



$$\begin{array}{c} CH_3 \\ | \\ H - C - Cl \\ | \\ Br - C - H \\ | \\ C_6H_5 \end{array}$$

Threo form

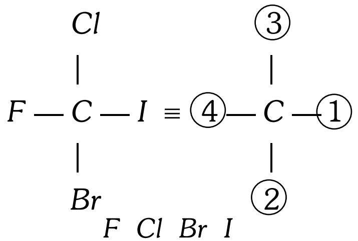
(c) *R,S Nomenclature* (Absolute configuration)

The order of arrangement of four groups around a chiral carbon (stereocentre) atom is called the absolute configuration around that atom. 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 Prelog** system. The letter (R) comes from the latin **rectus** (means right) while (S) comes from the latin **sinister** (means left). Any chiral carbon atom has either an (R) configuration or an (S) configuration. Therefore, one enantiomer is (R) and other is (S). A racemic mixture may be designated (R) (S), meaning a mixture of the two. (R) (S) nomenclature is assigned as follows :

Step I : By a set of sequence rules given below the atoms or groups connected to the chiral carbon are assigned a priority sequence.

Sequence Rules for Order of Priority

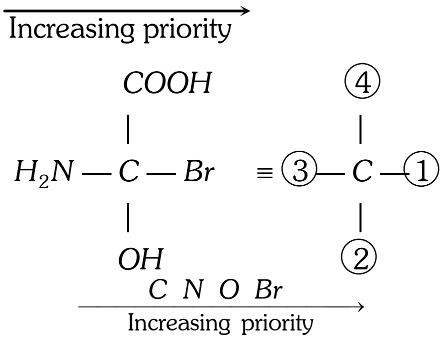
Rule 1 : If all four atoms directly attached to the chiral carbon are different, priority depends on their atomic number. The atom having highest atomic number gets the highest priority, *i.e.,* (1). The atom with the lowest atomic number is given the lowest priority, *i.e.,* (4), the group with next higher atomic number is given the next higher priority (3) and so on. Thus,



$$\begin{array}{c} Cl \\ | \\ F - C - I \\ | \\ Br \end{array} \equiv \begin{array}{c} ③ \\ | \\ ④ - C - ① \\ | \\ ② \end{array}$$

$$\xrightarrow[\text{Increasing atomic number}]{F\ \ Cl\ \ Br\ \ I}$$

④ ③ ② ①



$$\xrightarrow[\text{Increasing priority}]{}$$

$$H_2N-\overset{\displaystyle COOH}{\underset{\displaystyle OH}{C}}-Br \equiv \textcircled{3}-\overset{\textcircled{4}}{\underset{\textcircled{2}}{C}}-\textcircled{1}$$

$$\xrightarrow[\text{Increasing priority}]{C\ \ N\ \ O\ \ Br}$$