

**Definition**

Compounds having same molecular formula but differ in at least one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

**Types of Isomerism:** (A) Structural isomerism (B) Stereo isomerism

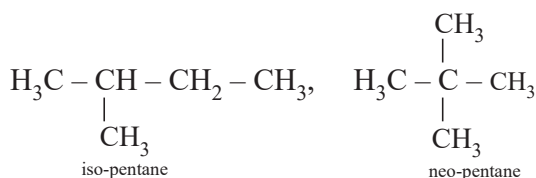
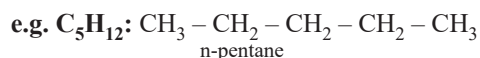
**(A) Structural isomerism**

Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

**Types of Structural Isomerism**

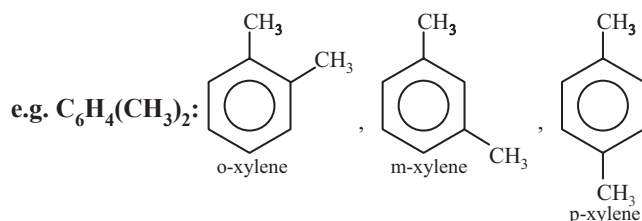
**Chain isomerism:** This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

**Key points:** Parent carbon chain or side chain should be different.

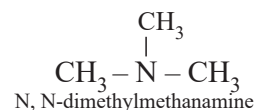
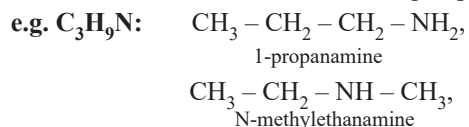


**Positional isomerism:** It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

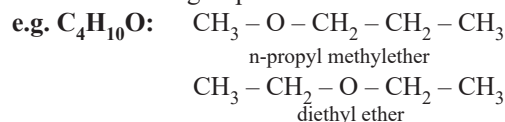
**Key points:** Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.



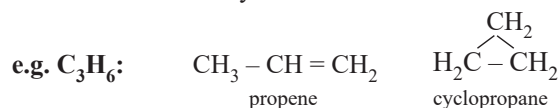
**Functional isomerism:** It occurs when compounds have the same molecular formula but different functional groups.



**Metamerism:** This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.



**Ring-Chain isomerism:** In this type of isomerism, one isomer is open chain but another is cyclic.



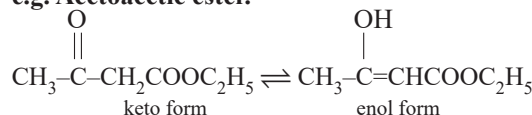
- ❖ For chain, positional and metamerism, functional group must be same.
- ❖ Metamerism may also show chain and position isomerism but priority is given to metamerism.

**Tautomerism:** This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

**Conditions:**

- (i) Presence of  $-\overset{O}{\parallel}C-$  or  $-\overset{O}{\parallel}N \rightarrow O$
- (ii) Presence of at least one  $\alpha$ -H atom which is attached to a saturated C-atom.

e.g. **Acetoacetic ester.**

**Enol content enhance by:**

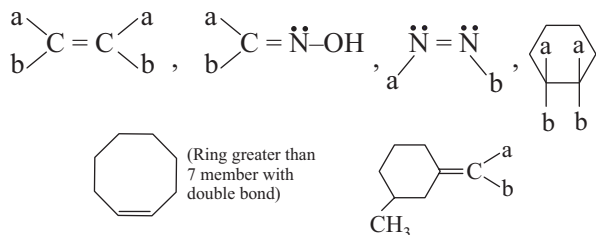
- ❖ Acidity of  $\alpha$ -H of keto form.
- ❖ Intra molecular H-Bonding in enol form.
- ❖ Resonance in enol form.
- ❖ Aromatisation in enol form.

**(B) Stereoisomerism**

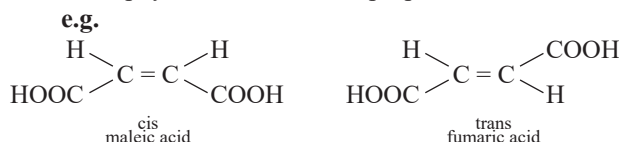
Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms of groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

## Types of Stereoisomerism

**Geometrical isomerism:** It is due to restricted rotation and is observed in following systems.



❖ **Cis-trans isomerism:** The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.



❖ General physical properties of geometrical isomer of but-2-ene

- |                     |             |
|---------------------|-------------|
| (i) Stability       | trans > cis |
| (ii) Dipole moment  | cis > trans |
| (iii) Boiling point | cis > trans |
| (iv) Melting point  | trans > cis |

**Calculation of number of geometrical isomers:**

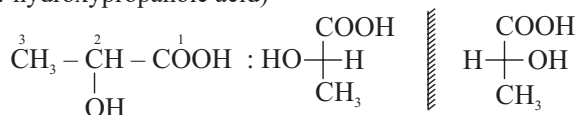
Unsymmetrical	$2^n$
Symmetrical	$2^{n-1} + 2^{m-1}$
	$m = \frac{n}{2}$ (If n is even)
	$m = \frac{n+1}{2}$ (If n is odd)

❖ Where n = number of sites where GI is possible.

**Optical isomerism:** Compounds having similar molecular and structural formula but differing in the stereo chemical formula and behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomerism.

## Types of optical isomers

- (1) Optically active
    - ❖ Dextrorotatory (d)
    - ❖ Laevorotatory (l)
  - (2) Optically inactive
    - ❖ Meso
    - ❖ **Condition** Molecule should be asymmetric or chiral i.e. symmetry elements (POS & COS) should be absent.
    - ❖ The carbon atom linked to four different groups is called **chiral carbon**.
    - ❖ **Fischer projection** An optical isomer can be represented by Fischer projection which is planar representation of three dimensional structure.
- Fischer projection representation of lactic acid (2-hydroxypropanoic acid)



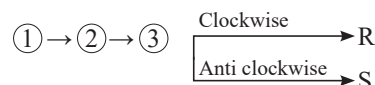
## ❖ Configuration of optical isomer

- (a) Absolute configuration (R/S system)
- (b) Relative configuration (D/L system)

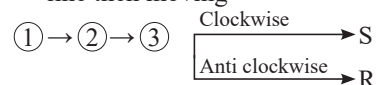
## ❖ Determination of R/S configuration

**Rule-1** Assign the priority to the four groups attached to the chiral carbon according to priority rule.

**Rule-2** If lowest priority (4) is bonded to vertical line then moving



**Rule-3** If lowest priority (4) is bonded to horizontal line then moving



## Determination of D/L system

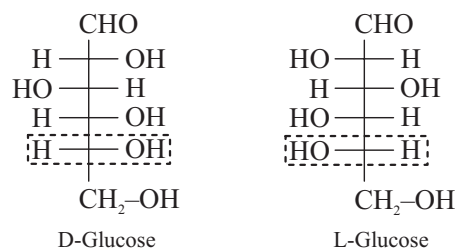
- ❖ Reference molecule glyceraldehyde
- ❖ It is used to assign configuration in carbohydrate amino acid and similar compounds.

**Rule:** Arrange parent carbon chain the vertical line

- ❖ Placed most oxidised carbon on the top or nearest to top.
- ❖ On highest IUPAC numbered chiral carbon

If OH group on RHS → D

If OH group on LHS → L



## CIP Sequence Rule

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

- (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
  - (ii) In case of isotopes, isotopes having higher atomic mass is given priority.
  - (iii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2<sup>nd</sup> atom or subsequent atoms in group.
  - (iv) If there is a double bond or triple bond, both atoms are considered to be duplicated for triplicated.
- ❖ Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.
  - ❖ **Diastereomers** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.

- ❖ **Meso compounds** are those compounds whose molecules are superimposable on their mirror images in spite of the presence of asymmetric carbon atom.
- ❖ An equimolar mixture of the enantiomers (*d* & *l*) is called **racemic mixture**. The process of converting *d*- or *l*- form of an optically active compound into racemic form is called **racemisation**.
- ❖ The process by which *d/l* mixture is separated into *d* and *l* forms with the help of chiral reagents or chiral catalyst is known as **resolution**.
- ❖ Compound containing chiral carbon may or may not be optically active but show optical isomerism.
- ❖ For optical isomer chiral carbon is not the necessary condition.

#### Calculation of number of optical isomers

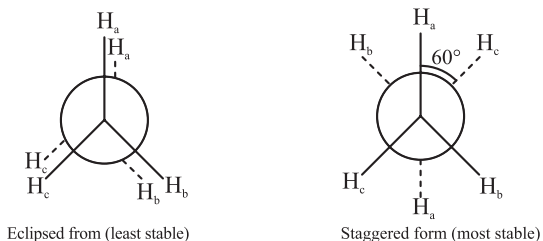
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	$2^n$	Zero
Symmetrical If $n = \text{even}$	$2^{(n-1)}$	$2^{\frac{n}{2}-1}$
Symmetrical If $n = \text{odd}$	$2^{(n-1)} - 2^{(n-1)/2}$	$2^{(n-1)/2}$

\* Where  $n$  = no. of chiral carbon

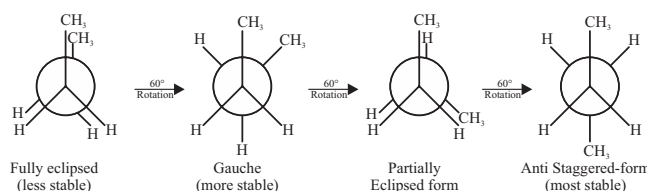
The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by  $0$ - $360^\circ$  are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomers.

## Conformational Isomerism

**Newman projection:** Here two carbon atoms forming the  $\sigma$  bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C–H bonds of front carbon are depicted from the centre of the circle while C–H bond of the back carbon are drawn from the circumference of the circle.



❖ **Conformations of butane:**  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$



- ❖ The order of stability of conformations of *n*-butane.  
Anti staggered > Gauche > Partially eclipsed > Fully eclipsed.
- ❖ Relative stability of various conformation of cyclohexane is  
Chair > twist boat > boat > half chair.