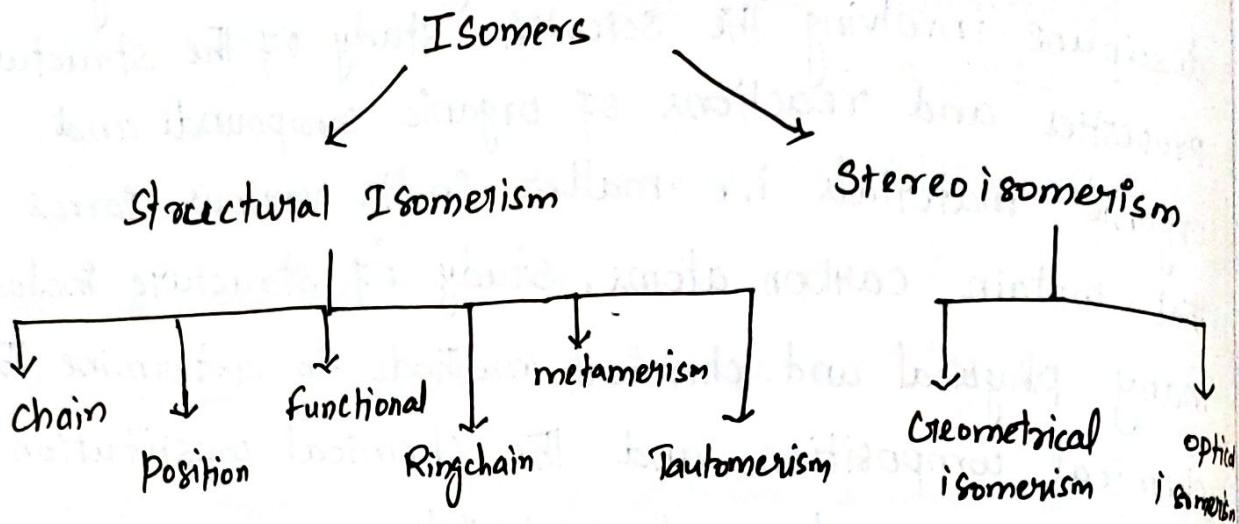


Classification of Isomerism



Structural Isomerism:

When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space the phenomenon is called Structural Isomerism.

In Otherwords Structural Isomers are compounds that have the same molecular formula but different structural formulas. Structural isomerism are classified into the following five types:

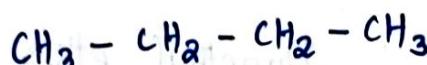
- (i) Chain Isomerism
- (ii) position Isomerism
- (iii) Functional Isomerism
- (iv) Metamerism
- (v) Tautomerism

chain Isomerism

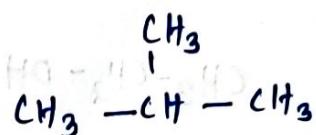
Chain Isomers have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

Example

n-Butane and Isobutane



n-Butane



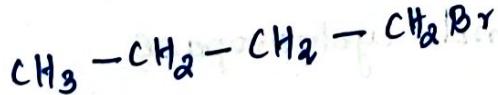
Isobutane

position Isomerism:

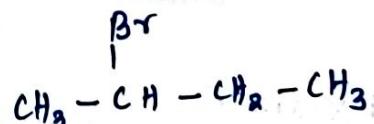
Position Isomers have the same molecular formula but differ in the position of a functional group on the carbon chain.

Example : 1

1-Bromobutane and 2-Bromobutane



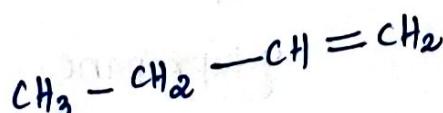
1-Bromobutane



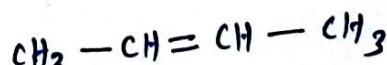
2-Bromo butane

Example : 2

1-Butene and 2-Butene



1-Butene



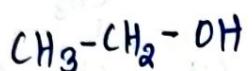
2-Butene

Functional Isomerism

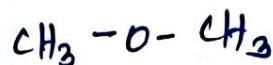
Functional isomers have the same molecular formula but different functional groups.

Example 1

Ethyl alcohol and Dimethyl ether



Ethyl alcohol



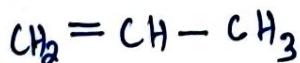
Dimethyl ether

Ring chain Isomerism

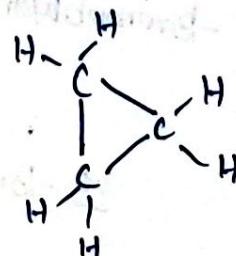
- The same molecular formula represents two or more compounds
- It differs in the mode of linkage of carbon atoms.
- The isomers have either open chain or closed chain

Example - 2

Propene and cyclopropane



Propene



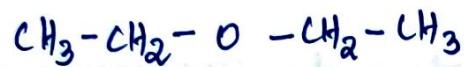
cyclopropane

Metamerism

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Members belong to the same homologous series.

Example :

Diethyl ether and Methyl propyl ether



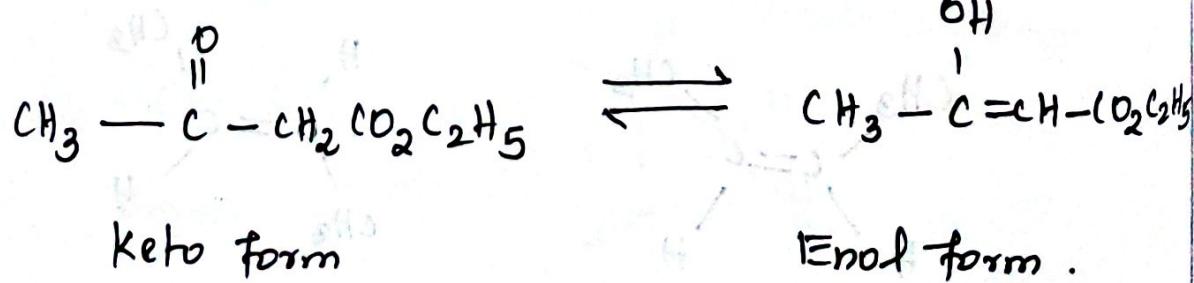
Diethyl ether



Methyl propyl ether

Tautomerism

It is a special type of functional isomerism in which the isomers are in dynamic equilibrium with each other. For example ethyl acetoacetate is an equilibrium mixture of the following two forms. At room temperature, the mixture contains 93% of keto-form plus 6% of the enol-form.



STEREOISOMERISM

This type of isomerism differs in the spatial arrangement of atoms or groups. It is two types.

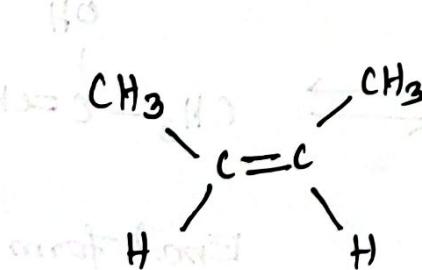
(i) Geometrical Isomerism

(ii) Optical Isomerism.

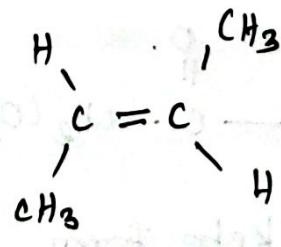
Geometrical Isomerism

- * The same molecular formula represents two or more compounds
- * It differs in the spatial arrangement of atoms or groups around carbon-carbon double bond.
- * It is of two types - If same group are on same side then it is called 'cis' isomers and if it is on opposite sides, then it is called 'trans' isomers.

Example ① cis-2-Butene and trans-2-Butene



cis-2-Butene



trans-2-Butene

Optical Isomerism

- * Optical isomerism is a type of Stereoisomerism.
- * In which the isomers are identical in molecular weight and most chemical & physical properties but differ in their effect on the rotation of polarized light.
- * Solution of some organic compounds have the ability to rotate the plane of polarized light. These compounds are said to be optically active. This property of a compound is called optical activity.
- * Optical activity in a compound is detected and measured by means of a polarimeter. When a solution of a known concentration of an optically active material is placed in the polarimeter, the beam of polarized light is rotated through a certain number of degrees, either to the right (clockwise) or to the left (anticlockwise).

Dextrorotatory (d) or (+) form :

Complexes that rotates the plane of polarized light towards right are said to be Dextrorotatory or 'd' form.

Laevorotatory (l) or (-) form :

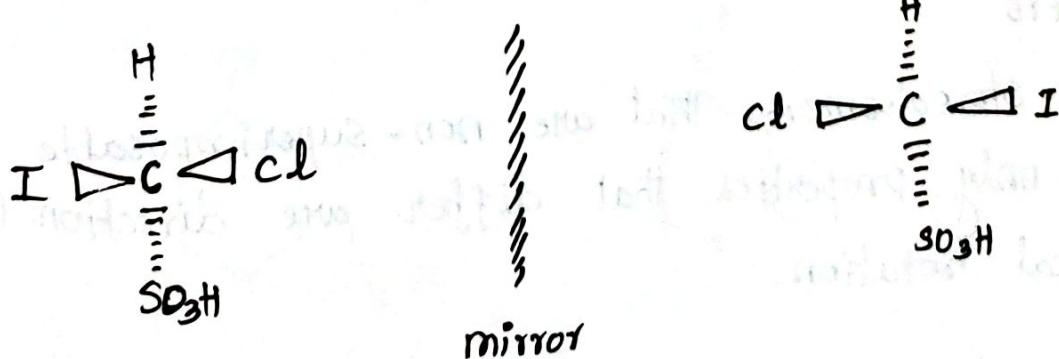
while the complexes rotates towards left are called Laevorotatory or 'l' form.

The 'd' and 'l' forms are mirror images of and cannot be superimposed on each other. Such molecules are

ions that cannot be superimposed are called chiral.
since these forms are related to each other as mirror
images these ~~forms~~ are commonly called Enantiomers.

chiral and Achiral - Superimposable & non-Superimposable

- ✓ Although everything has a mirror image, mirror images may or may not be superimposable.
- ✓ Some molecules are like hands. Left and right hands are mirror images, but they are not identical or non-Superimposable.
- ✓ A molecule (or object) that is not superimposable on its mirror image is said to be chiral.
- ✓ Other molecules are like socks. Two socks from a pair are mirror images that are superimposable. A socks and its mirror images are identical.
- ✓ A molecule or object that is superimposable on its mirror image is said to be 'achiral'



Chloriodomethane sulphonate acid

Sometimes diastereomers can include compounds that are ring structures. For example consider two compounds with six-membered ring that have two substituents each, a chlorine atom and an ethyl group. Note that the ethyl groups have the same configuration in both compounds, but the chlorine atoms labeled have opposite configurations.

These compounds are diastereomers because they have same bond configuration at one stereocenter but different configurations at another stereocenter.

Enantiomers

Diastereomers

- | | |
|---|--|
| 1. Enantiomers are stereoisomers that are mirror images of each other. | Diastereomers are stereoisomers that are not a mirror image of each other. |
| a. Have identical physical properties except for the ability to rotate plane polarized light. | Distinct physical properties. |
| 3. Present in pairs | There can be several molecules |
| 4. Similar molecular shape | Different molecular shape. |

Conformational analysis of n-Butane

conformational Analysis:

It is defined as the relative stabilities of the conformations of a compound and interpretation of its properties it depends on the following factors.

- (i) Torsional strain
- (ii) Angle strain
- (iii) Vander Waals strain
- (iv) Dipole - Dipole interactions

i) Torsional strain

The strain developed in a molecule by the bond-pair bond-pair repulsion, one on each C atom of a C-C single bond is called torsional strain. The greater the torsional strain the lower is the stability of a conformation.

ii) Angle strain

Any deviation from the usual bond angle will create a strain in the molecule which is called angle strain. The greater the angle strain, the lower is the stability of a conformation.

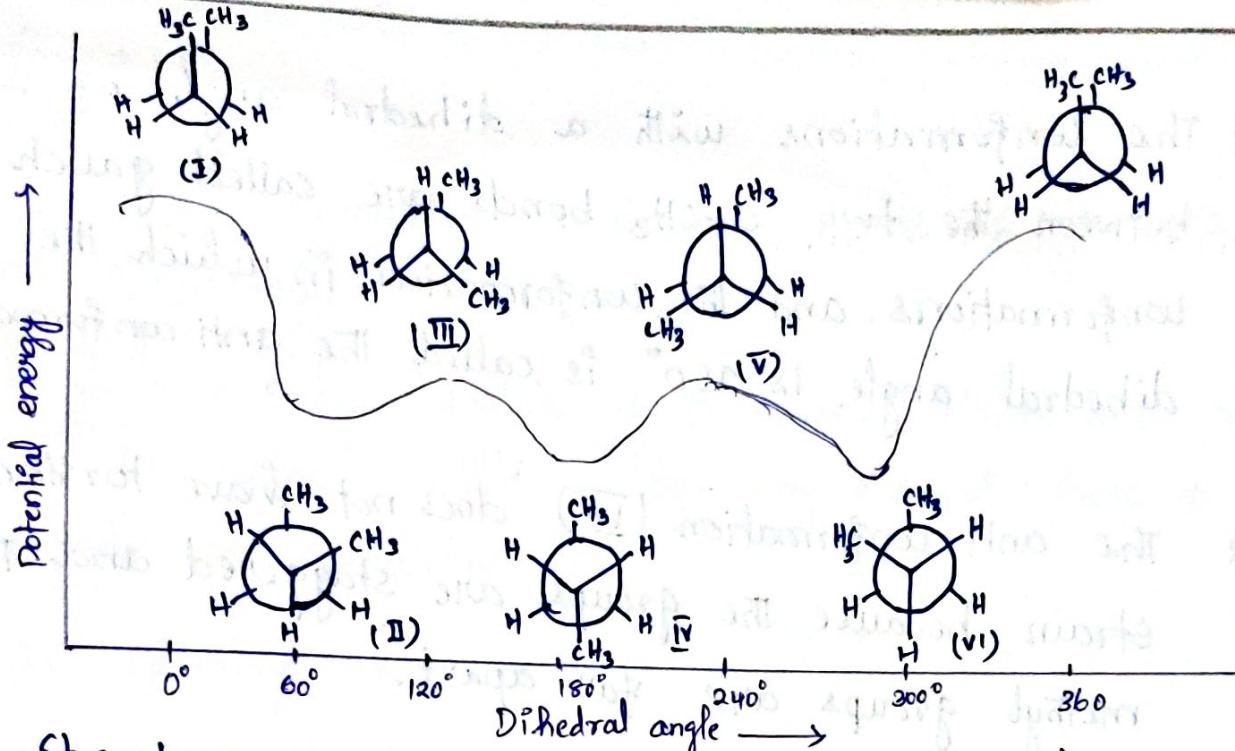
(iii) steric strain (or) Vander Waals strain :

If the distance between two substituents is less than the sum of their Vander Waals radii then a repulsive force generates due to repulsion between the electron clouds of the interacting substituents. The destabilizing interaction creates a strain in the molecule which is known as Vander Waals strain. The greater the size of the non-bonded substituents, the greater is the vander waals strain and less stability.

(iv) Dipole - Dipole Interactions :

Non-bonded substituents on each carbon atom of a C-C single bond may undergo dipole-dipole interactions of which the H-bonding force is the strongest. If the non-bonded atoms have opposite charges, the stability of the conformation increases otherwise the non-bonded atom have same charge the stability of the conformation decreases.

The potential energy of butane as a function of dihedral angle is given below.

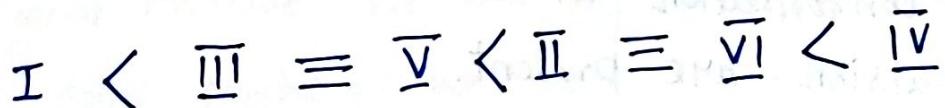


Structure I - Total eclipsed (0° & 360°)

II & VI - Gauch conformation (60° & 300°)

III & V - partially eclipsed (120° & 240°)

The order of increasing stability of the conformation of butane is as follows:



* The staggered conformations (II, IV and VI) of butane are at energy minima and are thus the stable conformations of butane.

* However not all of the staggered conformations of butane are similar.

- * The conformations with a dihedral angle of $\pm 60^\circ$ between the two C-CH₃ bonds are called gauche conformations and the conformation in which the dihedral angle is 180° is called the anti conformation (vi).
- * The anti conformation (iv) does not have torsional strain because the groups are staggered and the methyl groups are far apart.
- * The methyl groups in the gauche conformations are close enough to each other and for this, the gauche conformation are destabilized by vander waals repulsion between non-bonded hydrogen on the two CH₃ groups.
- * This repulsion causes the gauche conformation to have approximately 0.9 kcal/mol more energy than anti conformation in which no such vander waals repulsion are present.
- * Therefore the anti conformation is more stable than gauche conformation.
- * The eclipsed conformations (I, III, & V) represent energy maxima in the potential energy diagram.
- * Eclipsed conformations III and V not only have torsional strain, they have vander waals repulsions

arising from the eclipsed methyl groups and hydrogen atoms.

- * The eclipsed conformation (I) has greater energy (least stable) of all because in addition to torsional strain, there is larger vander Waals repulsive force between the eclipsed methyl groups.

PROJECTION FORMULAS OF STEREOISOMERS

Formulas used to represent molecules having three-dimensional structures on a two-dimensional surface (paper or blackboard) are called projection formulas.

The important projection formulas that are used to represent chiral or achiral molecule are

- (i) Fischer projection Formula
- (ii) Sawhorse projection Formula
- (iii) Newman projection formula

Fischer projection Formula

structures for three-dimensional chiral molecules are sometimes represented with two-dimensional formulas. These two dimensional-formulas are called Fischer projection formulas.

In this representation the chiral carbon lies in the plane of the paper and the four bonds are shown by two vertical lines (which represent bonds projecting behind the plane of the paper, i.e. pointing away from the viewer) and two horizontal lines (which represent bonds projecting behind the plane of the paper, i.e., pointing towards the viewer).



Three-dimensional representation of lactic acid

Fischer projection
of Lactic acid.

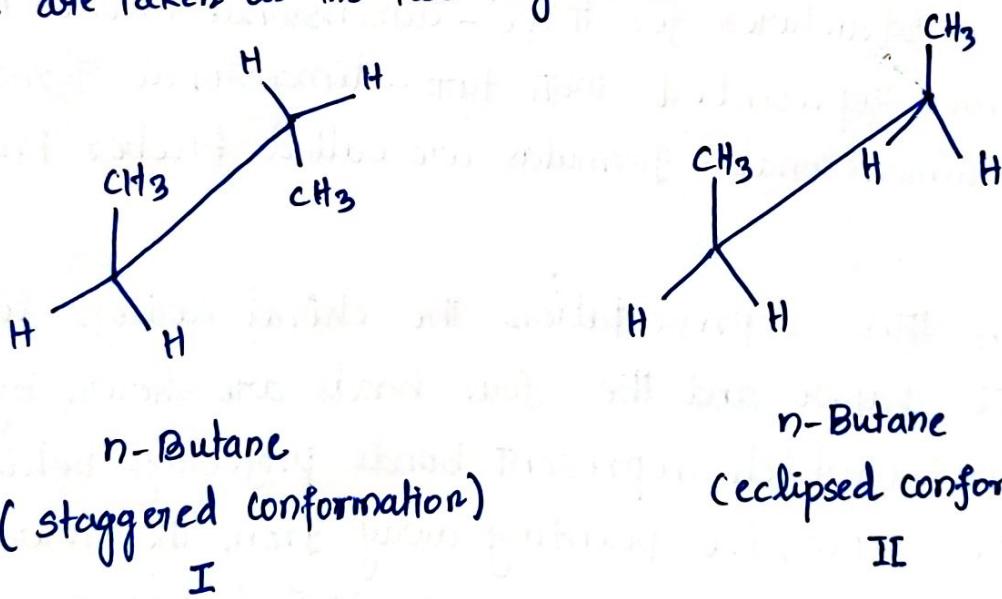
Sawhorse projection formula

The sawhorse projection formula provides a graphic three-dimensional perspective picture used to specify a conformation.

This projection shows the spatial relationship between the substituents attached to two adjacent carbon atoms (chiral or achiral).

In this representation, the bond between the two carbon atoms is drawn diagonally and is slightly elongated. The remaining bonds are shown by small lines.

For example, n-butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$) can be represented by the following sawhorse projections when C-2 and C-3 carbon atoms are taken as the two key carbon atoms.



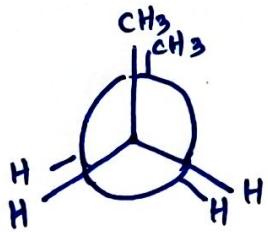
The conformation I in which the groups on C-2 and C-3 are oriented as far away from each other as possible is known as the staggered conformation. and the conformation II in which the groups C-2 and C-3 are nearest is known as the eclipsed conformation.

Newman projection formula

Another common way to represent a conformation is by a Newman projection. This is also a perspective formula.

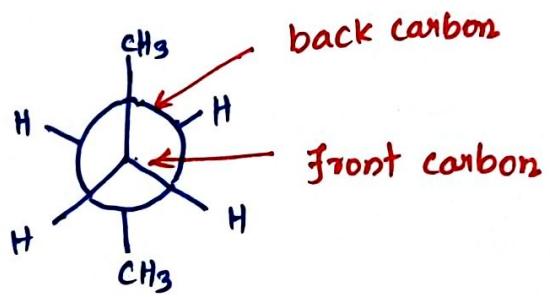
In the Newman projection, the molecule is viewed along the bond joining the key carbon atoms. The front carbon atom is represented by a central point from which the remaining three bonds emerge (\nearrow).

The rear carbon atom is depicted by a circle with the remaining three bonds pointing out from it (\nwarrow).



eclipsed
conformation

\equiv



back carbon
front carbon
staggered
conformation

Symmetry

Symmetry is defined in terms of elements and operations.

Each operation is performed relative to a point line or plane - called a symmetry element. There are 5 kinds of operations:

1. Identify E
2. n-Fold rotations C_n
3. Reflection σ
4. Inversion i
5. Improper n-fold Rotation S_n

1. Identity (E) :

In identity operation no change is made in the original molecule. we can say identity is the operation of not doing anything. we leave the system unchanged and identical to the original system.

2. Rotation axis (or) Proper axis of symmetry (C_n):

If an imaginary axis can be constructed in a molecule around which the molecule can be rotated through an angle (θ) to get an indistinguishable ~~possible~~ configuration, the molecule is said to possess a rotation axis.

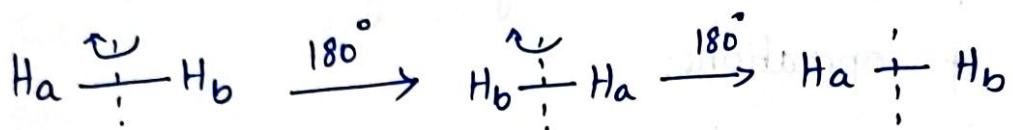
The value of n (order of axis) can be calculated by

$$n = \frac{360^\circ}{\theta}$$

ex:

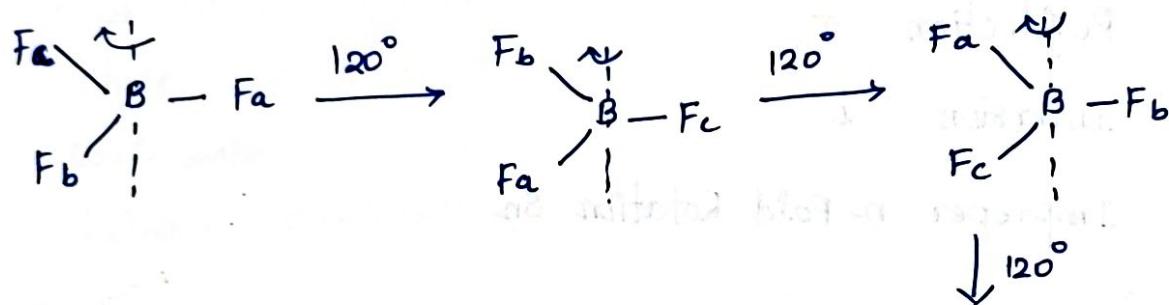
C_2 axis

$$n = \frac{360^\circ}{180^\circ} = 2$$



C_3 axis

$$n = \frac{360^\circ}{120^\circ} = 3$$

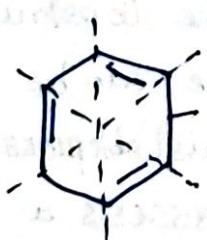


other examples



$$n = \frac{360^\circ}{72^\circ} = 5 \quad (\text{C}_5 \text{ axis})$$

cyclopentane

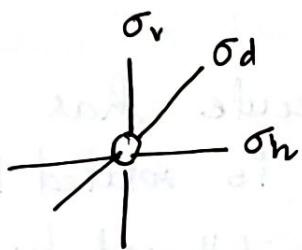


$$n = \frac{360^\circ}{60^\circ} = 6 \quad (\text{C}_6 \text{ axis})$$

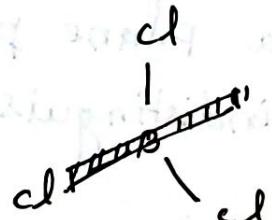
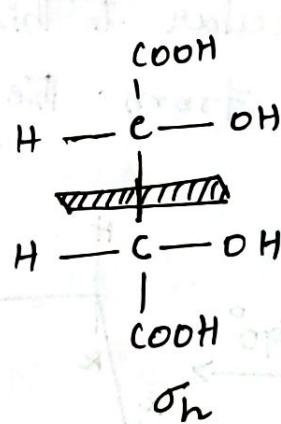
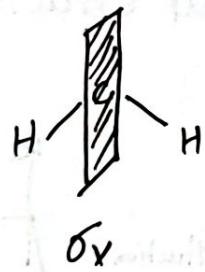
3. plane of Symmetry

An imaginary plane that bisects molecule in such a way that the two parts are mirror images of each other. This element of symmetry is represented by symbol (σ)

A symmetry plane parallel with the principle axis is known vertical (σ_v) and one perpendicular to it horizontal (σ_h). A third type, the angle between two (2-fold) rotation axis perpendicular to the principle axis is dihedral (σ_d)



ex:

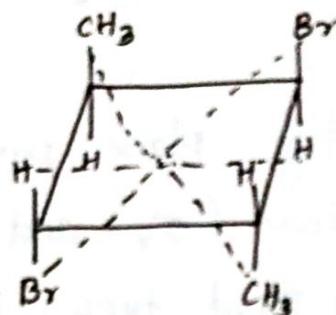
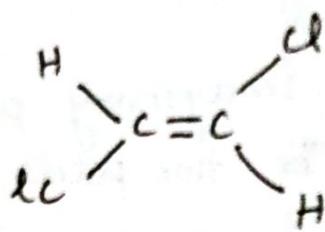
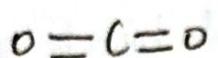


Other examples: NH_3 , SF_4 , O_2 , BaH_6 etc.

4. centre of Symmetry (i):

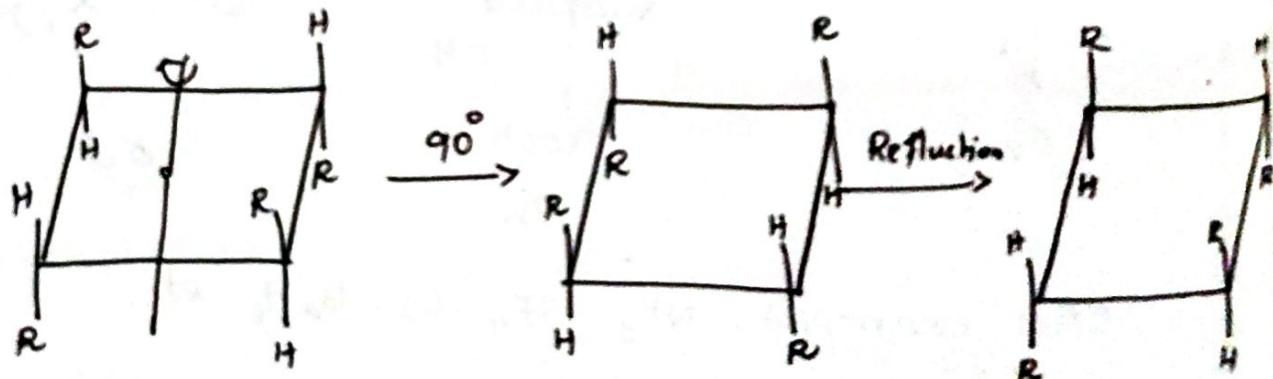
This is such a point through if a line drawn meets identical atoms of equal distance from the point in two opposite directions.

ex:



5. Alterating axis of Symmetry (or) Improper axis of symmetry (S_n):

When a molecule has a n -fold alternating axis of symmetry is rotated through an angle $360^\circ/n$ about this axis then followed by the reflection in a plane perpendicular to this axis. The molecule is indistinguishable from the original structure.

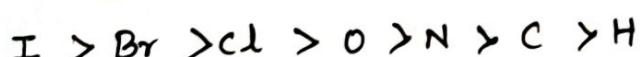


Cahn - Ingold - Prelog Rule:

- * The four atoms (or) groups attached to the chiral carbon are ranked in order of priority.

Rule: 1

- * Atom of higher atomic number gets priority
- * High priority '1', Least priority '4'



Rule: 2

- * If first atom is the two groups have same atomic number

↓ Then

Relative priority of the group is decided by a comparison of the atomic number of the next atom in the two groups

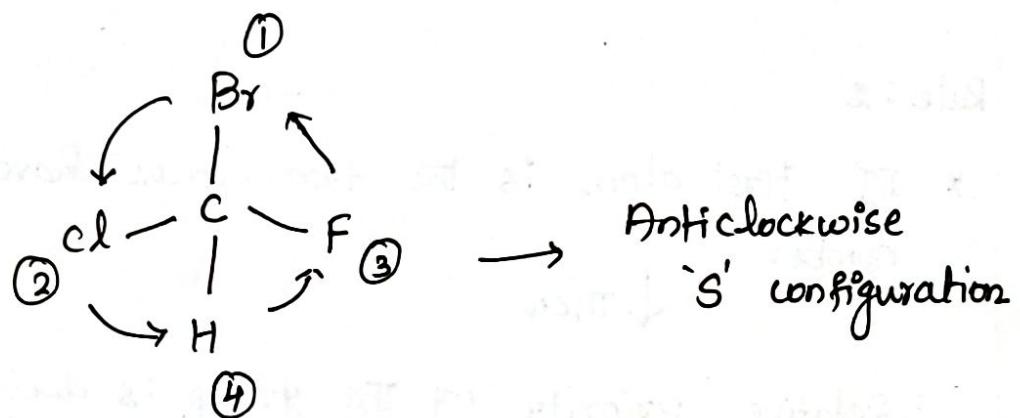
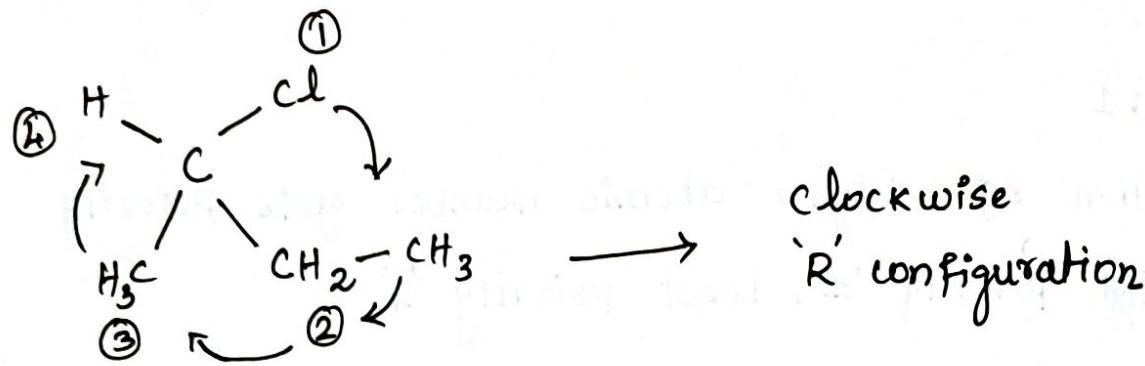
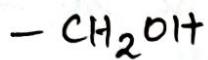


- * 'C' is attached with 'O' in CHO , but 'C' is attached with 'N' in $-\text{CN}$
- * $\text{O} > \text{N}$ → 'O' is high in priority

Rule 3:

Multiple bonds are treated as separate single bonds

$\text{C}^{\text{H}}=\text{O}$ is given priority over



Note In case of isotopes higher mass number gets higher priority

