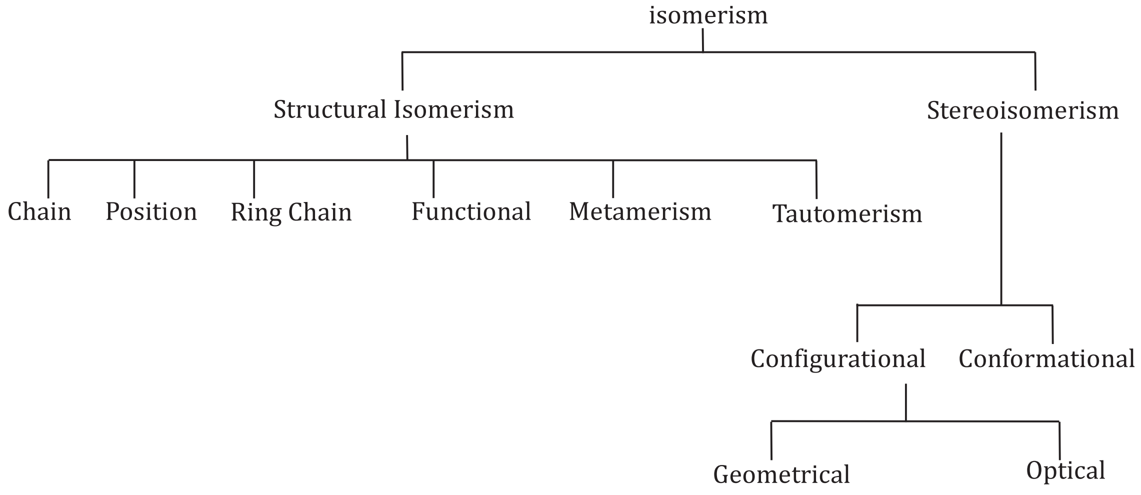
ISOMERISM

Two or more than two compounds having the same molecular formula but different physical /chemical or both properties are called isomers and the phenomenon is called isomerism.



(A) Structural Isomerism

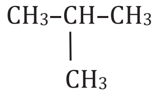
Structural isomers, alternatively referred to as constitutional isomers, are compounds characterized by identical molecular formulas yet possess distinct structures. This phenomenon, known as structural isomerism or constitutional isomerism, highlights the diverse arrangements of atoms within these compounds despite their shared chemical composition.

(1) Chain Isomerism (C.I.)

The compounds which have same molecular formula, same functional group but different arrangement of carbon chain (Parental or side chain) show chain isomerism.

Ex. $CH_3–CH_2–CH_2–CH_3$

(Butane (4C)



$$\underset{\displaystyle CH_3}{CH_3–\underset{|}{CH}–CH_3}$$

2-Methyl propane (3C)

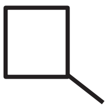
Ex. $CH_3–CH_2–CH_2–CH_2–$

1-Butanol (4C)

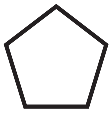
|
CH_3

2-Methyl-1-propanol (3C)

Ex.



Methylcyclobutane



Cyclopentane

(2) Position Isomerism (P.I.)

The compounds which have same molecular formula. Same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, show position isomerism.

Ex. $CH_2 = CH - CH_2 - CH_3$

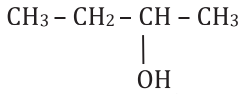
But-1-ene

$CH_3 - CH = CH - CH_2$

But-2-ene

Ex. $CH_3 - CH_2 - CH_2 - CH_2 - OH$

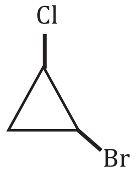
1-Butanol



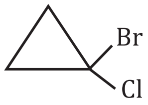
$CH_3 - CH_2 - \underset{\substack{|\\OH}}{CH} - CH_3$

2-Butanol

Ex.



1-Bromo-2-chlorocyclopropane



1-Bromo-1-chlorocyclopropane

Example of Cl and PI

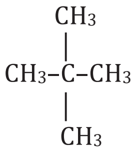
(i) C_5H_{12} has three structural isomers

$CH_3–CH_2–CH_2–CH_2–CH_3$

Pentane

$CH_3–CH_2–CH–CH_3$

2-Methyl butane



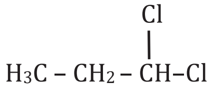
$CH_3–\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{C}}–CH_3$

2,2-Dunethylpropane

(ii) $C_3H_6C_{l2}$ has 4 isomers

Position of chlorine atom is different in all the structure, so these are position isomers.

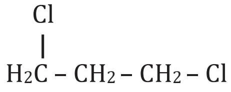
(a)



$H_3C - CH_2 - \overset{\substack{Cl\\|}}{CH}–Cl$

1,1-Dichloropropane

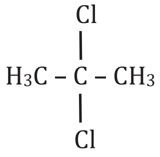
(b)



$H_2\overset{\substack{Cl\\|}}{C} - CH_2 - CH_2 - Cl$

1,3-Dichloropropane

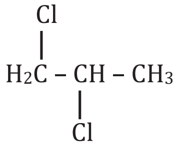
(c)



$H_3C - \underset{\substack{|\\Cl}}{\overset{\substack{Cl\\|}}{C}} - CH_3$

2,2-Dichloropropane

(d)



$H_2\overset{\substack{Cl\\|}}{C} - \underset{\substack{|\\Cl}}{CH} - CH_3$

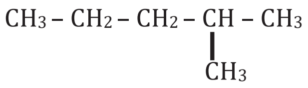
1,2-Dichloropropane

(iii) C_6H_{14} has 5 structural isomers

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

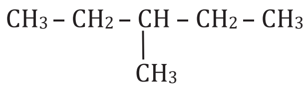
(b)



$CH_3 - CH_2 - CH_2 - \underset{\substack{|\\CH_3}}{CH} - CH_3$

2-Methyl pentane

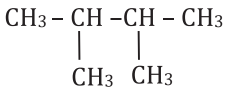
(c)



$CH_3 - CH_2 - \underset{\substack{|\\CH_3}}{CH} - CH_2 - CH_3$

Hexane

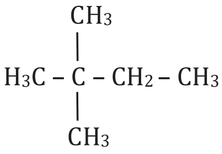
(d)



$CH_3 - \underset{\substack{|\\CH_3}}{CH} -\underset{\substack{|\\CH_3}}{CH} - CH_3$

2-Methyl pentane

(e)



$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

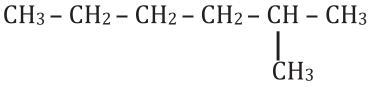
2,2-Dimethyl butane

- ➢ (a–b),(a–c),(a–d),(a–e)→ Chain Isomers (b–d),(b–e),(c–d),(c–e)
- ➢ b–c, d–e ⟶ Position Is b–c, d–e

Ex. How many structural isomers of C_7H_{16} are possible?

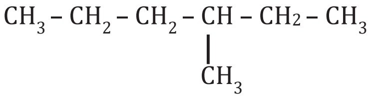
Ans. (9)

1. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ Heptane

2. 

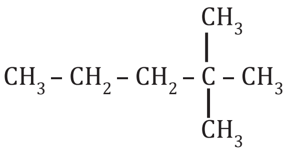
$CH_3-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2–Methyl hexane

3. 

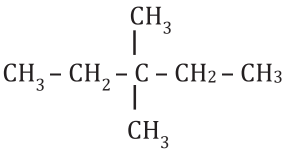
$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

3–Methyl hexane

4. 

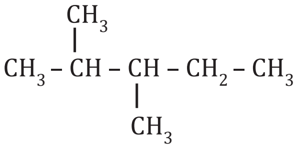
$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

2,2–Dimethyl pentane

5. 

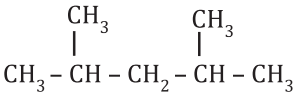
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

3,3–Dimethyl pentane

6. 

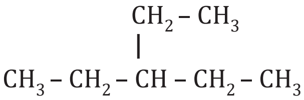
$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

2,3–Dimethyl pentane

7. 

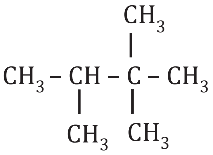
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$

2,4–Dimethyl pentane

8. 

$CH_3-CH_2-\overset{\overset{CH_2-CH_3}{|}}{CH}-CH_2-CH_3$

3–Ethyl pentane

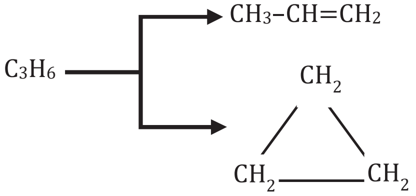
9. 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

2,2,3–Trimethyl butane
(Triptane)

(3) Ring chain isomerism (RCI)

Same molecular formula but different mode of linking (open chain & closed chain) of carbon atoms.



[Open Chain]

[closed Chain or ring]

- ➢ Alkenes with cycloalkane and alkynes and alkatrienes with cycloalkenes show Ring-chain Isomerism.
- ➢ Ring-chain Isomers are also Functional Isomers but priority must be given to Ring-chain Isomers.

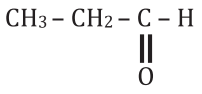
(4) Functional Isomerism

Same molecular formula but different functional groups.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

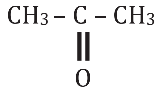
(i) Alcohol and Ether ⟶ CH_3-CH_2-OH and CH_3-O-CH_3

(ii) Aldehydes and Ketones ⟶



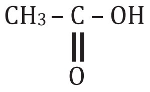
$CH_3-CH_2-\underset{\underset{O}{\Vert}}{C}-H$

and



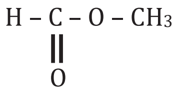
$CH_3-\underset{\underset{O}{\Vert}}{C}-CH_3$

(iii) Acids and Ester ⟶



$CH_3-\underset{\underset{O}{\Vert}}{C}-OH$

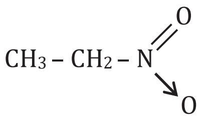
and



$H-\underset{\underset{O}{\Vert}}{C}-O-CH_3$

(iv) Cyanide and Isocyanide ⟶ $CH_3-CH_2-CH_2-CN$ and $CH_3-CH_2-CH_2-NC$

(v) Nitro and Nitrite ⟶

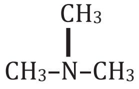


$CH_3-CH_2-N\begin{smallmatrix} \nearrow\!\!\!\!= O \\ \searrow O \end{smallmatrix}$

and $CH_3-CH_2-O-N=O$

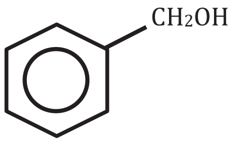
(vi) 1º,2º,3º Amines

(a) $CH_3-CH_2-CH_2-NH_2$ (b) $CH_3-NH-CH_2-CH_3$ (c)

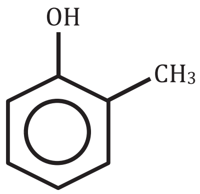


$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$

(vii) Alcoholic and Phenolic compounds



and

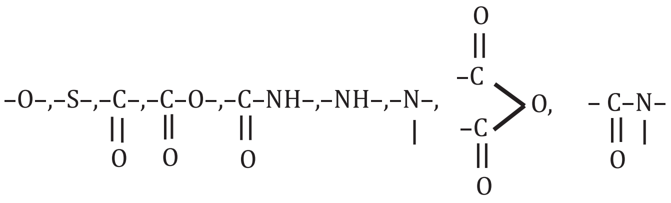


(viii) Alkyl halides do not show Functional isomerism.

(ix) $CH_3-C\equiv CH$ propyne and $CH_2=CH=CH_2$

(5) Metamerism

Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group.



$-O-, -S-, -\underset{\underset{O}{\|}}{C}-, -\underset{\underset{O}{\|}}{C}-O-, -\underset{\underset{O}{\|}}{C}-NH-, -NH-, -\underset{|}{N}-, \overset{\overset{O}{\|}}{-C}\!>O\!<\underset{\underset{O}{\|}}{-C}, -\underset{\underset{O}{\|}}{C}-\underset{|}{N}-$

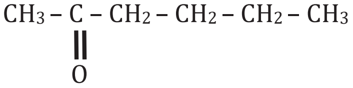
Polyvalent Functional group [Which have more than one valency] are:

Ex. $CH_3-O-CH_2-CH_2-CH_3$ $H_3C-CH_2-O-CH_2-CH_3$

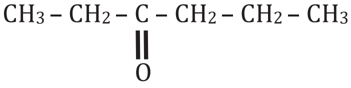
Ex. $CH_3-CH_2-NH-CH_2-CH_3$ $CH_3-NH-CH_2-CH_2-CH_3$

Ex. $CH_3-NH-CH_2-CH_2-CH_2-CH_3$ $H_3C-CH_2-NH-CH_2-CH_2-CH_3$

Ex.



$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$



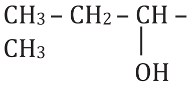
$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$

Examples Based on Structural Isomerism

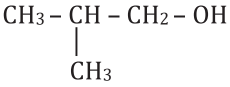
Ex.-1 $C_4H_{10}O$ Structural isomers

$\Rightarrow$ 7 [4 alcohol and 3 ethers] total 7 structural isomers are possible.

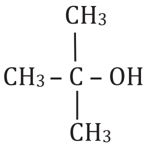
Alcohol: $CH_3-CH_2-CH_2-CH_2-OH$



$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$



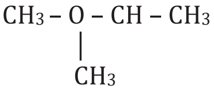
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

and

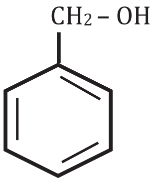
Ethers: $CH_3-O-CH_2-CH_2-CH_3$, $C_2H_5-O-C_2H_5$,



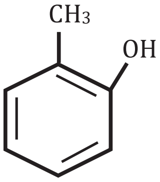
$CH_3-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$

Ex. 2 Aromatic isomers of C_7H_8O.

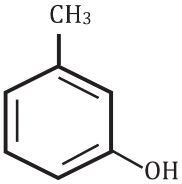
(a)



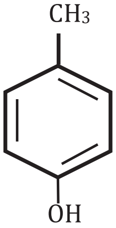
(b)



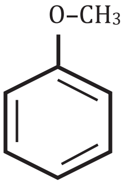
(C)



(d)



(e)



- a, b - Functional isomers
- b, c - Position isomers
- c, d - Position isomers
- a, d - Functional isomers

- a, e - Functional isomers
- a, c - Functional isomers

Note: Alcoholic and phenolic groups are Functional isomers.

(6) Tautomerism

In the occurrence of tautomerism, dynamic equilibrium is established between two or more compounds with distinct constitutional structures. This equilibrium is induced by the movement of an atom, commonly a proton, from one position to another within a molecule. The phenomenon is identified as tautomerism, and the different constitutional isomers involved in this equilibrium state are recognized as tautomer.

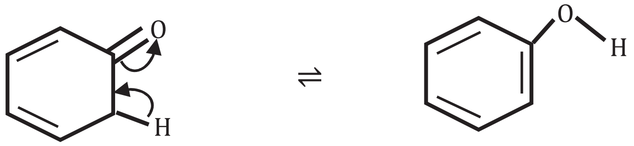
Types of Tautomerism

There are several types of tautomerism, each characterized by distinct structural changes. These include:

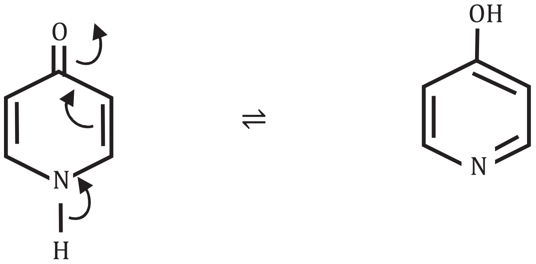
(a)	Die none Phenol Tautomerism	(b)	Nitroso-oxime Tautomerism
(c)	Nitro-aci Tautomerism	(d)	Imine-enamine Tautomerism
(e)	Keto-Enol Tautomerism		

Each type represents a specific category of tautomerism, showcasing unique transformations and shifts in molecular structure within the given compounds.

(a) Die none Phenol Tautomerism

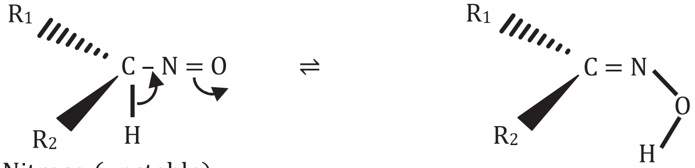


Non-aromatic Aromatic



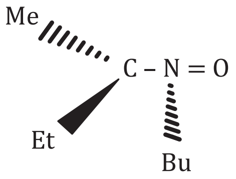
In the majority of phenols, the equilibrium strongly favors the side featuring the phenolic form.

(b) Nitroso- Oxime Tautomerism

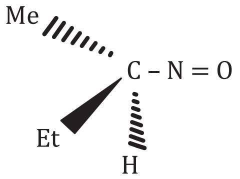


Nitroso (unstable) Oxime (stable)

The equilibrium in nitroso compounds significantly leans towards the right, and generally, these compounds exhibit stability only in the absence of alpha-hydrogens.

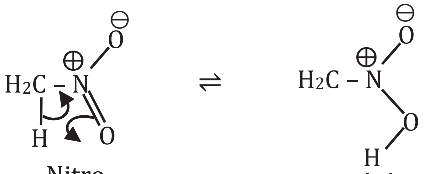


Nitroso compound
capable of resolution.



Non -Resolvable due to
the increased stability

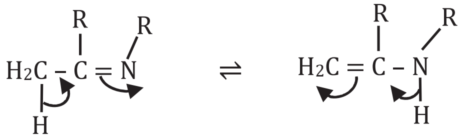
(c) Nitro-aci Tautomerism



Nitro

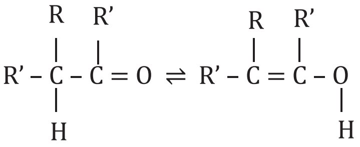
Aci

(d) Imine-enamine Tautomerism



(e) Keto-Enol Tautomerism

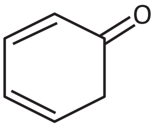
Keto-enol tautomerism refers to a chemical equilibrium occurring within organic chemistry, specifically between a keto form, in straightforward carbonyl compounds, the equilibrium predominantly favors the keto form, signifying a substantial bias in that direction.



$$R'-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-\overset{\overset{R'}{|}}{C}=O \rightleftharpoons R'-\overset{\overset{R}{|}}{C}=\overset{\overset{R'}{|}}{C}-\underset{\underset{H}{|}}{O}$$

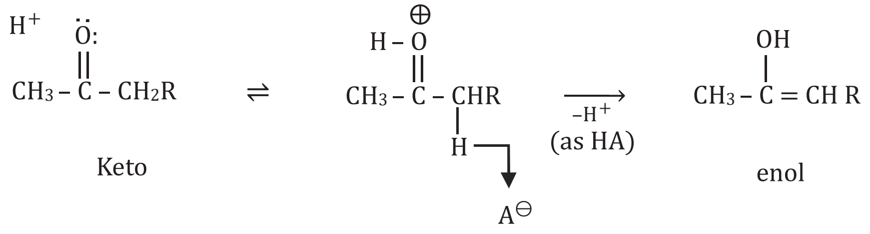
keto Enol

This inclination is attributed to the heightened stability exhibited by the keto form, which is directly associated with the bond dissociation energy within the molecule. However, distinctive structural features, like the existence of hydrogen bonding, extended conjugation, or aromaticity, possess the capability to exert influence on the equilibrium, thereby increasing the relative abundance of the enol form.

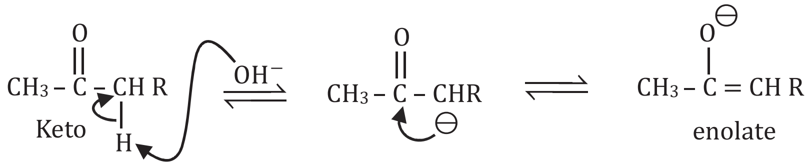
Compound	% of enol content
CH_3CHO	6×10^{-5}
Butanal	5.5×10^{-4}
	99.99%
$Ph_2CH - CHO$	9.1
CH_3COCH_2COOEt	8.4

General Mechanism of Tautomerism

Acid Catalysed Tautomerism



Base Catalysed Tautomerism



Unsaturation Number

The molecular formula of an organic compound offers detailed information about the occurrence of rings and multiple bonds, including double or triple bonds, in the compound. The unsaturation number of a hydrocarbon functions as a quantitative measure, disclosing the presence of rings or double bonds in the molecular arrangement. This numerical value is essential for gaining insights into the comprehensive structural features of the organic compound.

$$U = (C + 1) - \left(\frac{H-N}{2}\right)$$

Where:

C → Total number of tetravalent atoms
H → Total number of monovalent atoms
N → Total number of trivalent atoms

Note: The unsaturation number, alternatively referred to as the index of hydrogen deficiency or degree of unsaturation, carries important implications in organic chemistry.

- Each instance of a single ring within a molecule corresponds to an increment of 1 in the unsaturation number.
- Similarly, the presence of a double bond is reflected by an increase of 1 in the unsaturation number.
- Notably, a triple bond contributes a value of two to the unsaturation number, indicating a more significant impact on the overall unsaturation of the molecule.

(B) Stereoisomerism

Two or more than two compounds having same molecular formula, same structural formula but different arrangement of atoms or groups in space.

(i) Configurational Isomerism

Stereo isomers which have following characteristics.

(a) Stereo isomer which cannot interconvert at room temperature due to restricted rotation known as Geometrical isomerism.

(b) Stereo isomers which have different behavior towards plane polarized light are known as optical isomers.

(a) Geometrical isomerism (G.I)

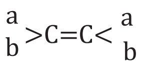
(i) Alkenes (>C=C<), oximes (>C=N–OH) and azo compounds [–N=N–] ets., show G.I. due to restricted rotation about double bond

(ii) cycloalkanes show G.I. due to restricted rotation about single bond in ring.

G.I. in Alkenes
Reason: Restricted rotation about double bond

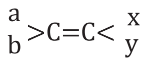
Condition for Geometrical isomerism

Only those alkenes show G. I. in which "Each sp^2 carbon individually have different atoms or groups"



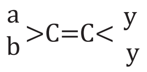
$${}^{a}_{b}\!>\!C{=}C\!<\!{}^{a}_{b}$$

Geometrical isomerism possible



$${}^{a}_{b}\!>\!C{=}C\!<\!{}^{x}_{y}$$

Geometrical isomerism possible



$${}^{a}_{b}\!>\!C{=}C\!<\!{}^{y}_{y}$$

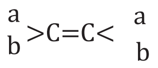
Geometrical isomerism not possible

Geometrical isomerism not possible

Nomenclature Systems of Geometrical isomers

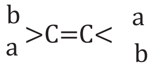
(a) Cis-Trans System

If same groups are at same side, then cis and if same groups are at different side, then



$${}^{a}_{b}\!>\!C{=}C\!<\!{}^{a}_{b}$$

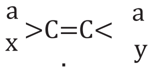
trans. [Same groups, same side cis]



$${}^{b}_{a}\!>\!C{=}C\!<\!{}^{a}_{b}$$

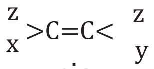
[Same groups different side cis]

Ex.



$${}^{a}_{x}\!>\!C{=}C\!<\!{}^{a}_{y}$$

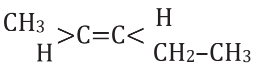
cis



$${}^{z}_{x}\!>\!C{=}C\!<\!{}^{z}_{y}$$

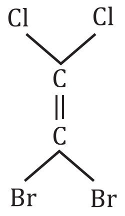
cis

Ex.



$${}^{CH_3}_{H}\!>\!C{=}C\!<\!{}^{H}_{CH_2-CH_3}$$

Trans-2-pentene



It does not show Geometrical isomers
So, no cis-trans

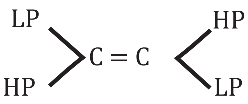
(b) E-Z System

E (Ent Gegen)

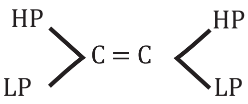
When high priority groups are at opposite side.

Z (Zu Samman)

When high priority groups are at same side.



'E'

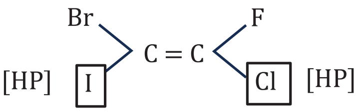


'Z'

HP-High priority and LP-Low priority

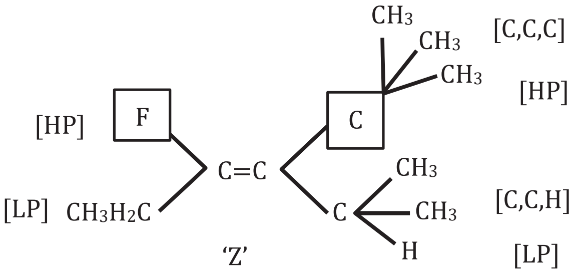
Priority Rules [CIP Sequence Rule)

Rule I: Priority is proportional to atomic number of atoms which is directly attached to sp^2 carbon.



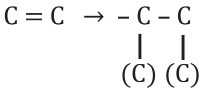
'Z'

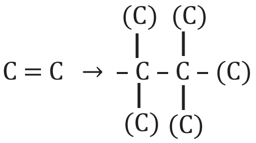
Rule II: If rule-I is failed then consider the atomic number of next atom and so on.

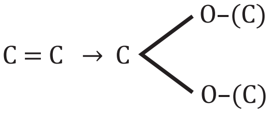


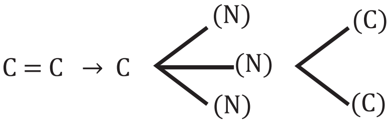
'Z'

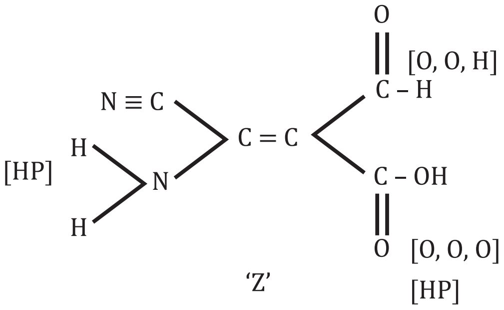
Rule III: If multiple bonds is present then consider them as:





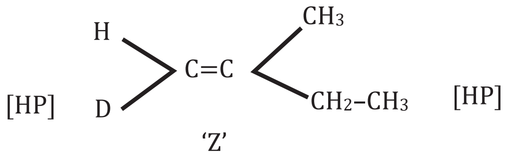






'Z'

Rule IV: If isotopes are present then consider atomic weight.



(b) Optical Isomerism

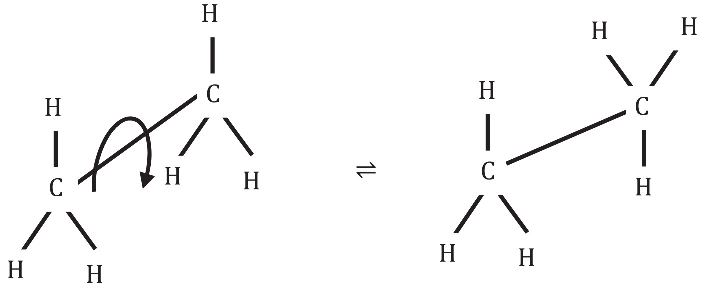
Optical isomerism emerges when molecules possess non-superimposable mirror images, known as enantiomers. This phenomenon is characterized by the presence of chiral centers, resulting in distinct optical activities for each isomer.

(ii) Conformational Isomerism

Conformational isomerism involves variations in the three-dimensional arrangement of atoms or groups within a molecule, primarily occurring due to the unrestricted rotation around single bonds. These isomers can easily transition between different forms through rotations of these bonds.

The symmetric distribution of electrons around the internucleon axis of the carbon-carbon bond remains undisturbed during the free rotation of the carbon-carbon single bond. This rotation leads to diverse spatial arrangements of atoms in space, and these arrangements, interchangeable through free rotation, are referred to as conformations.

Conformations represent distinct three-dimensional configurations of atoms within a molecule that can be transformed into one another by free rotation around the axis of the carbon-carbon single bond. These dynamic configurations, known as conformers, are rapidly interconvertible and no separable, earning them the labels "Conformational isomers" or "rotamers."



In the context of alkanes, the ability for rotation around the carbon-carbon single bonds allows for an infinite number of conformations. However, this rotational freedom is not entirely unhindered, as a small energy barrier of 1-20 kJ mol arises due to weak repulsive interactions between adjacent bonds. This repulsive interaction is identified as torsional strain.

Conformations of ethane

Ethane, a simple hydrocarbon with the molecular formula C_2H_6, primarily exists in the form of free rotation around its carbon-carbon (C-C) single bond. This rotational freedom leads to different spatial arrangements known as conformations. The two main conformations of ethane are the eclipsed conformation and the staggered conformation.

(a) Eclipse Conformation

In this conformation, hydrogen atoms attached to two carbons are positioned as closely together as possible, resulting in an arrangement termed "eclipsed."

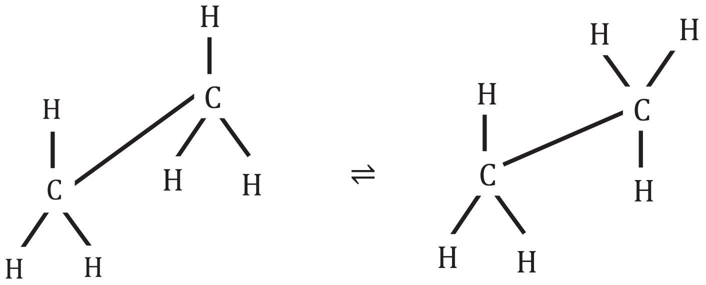
(b) Staggered Conformation

In contrast, the staggered conformation involves positioning hydrogen atoms attached to two carbons as far apart as possible. The staggered conformation is notably more stable than the eclipse conformation, primarily due to minimized repulsive forces and energy, stemming from increased separation between the electron clouds of C-H bonds.

Conformation of ethane [CH_3–CH_3]

Sawhorse Projections

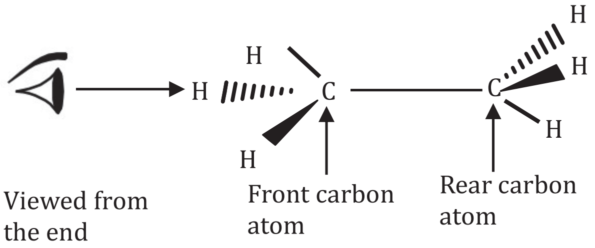
The carbon-carbon bond is visually represented as a lengthy straight line. The lower terminus of this line signifies the front carbon atom, while the upper end represents the rear carbon atom. Given that each carbon atom within ethane forms bonds with three hydrogen atoms, three lines extend from each carbon atom, symbolizing the C-H bonds. These lines are inclined at an angle of 120° to each other, reflecting the geometric arrangement of the hydrogen atoms around the carbon atoms in the molecule.



(Saw horse projection)

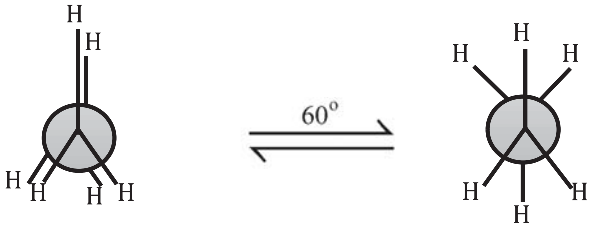
Newman Projections

This method involves illustrating a molecule by looking directly down the bond that connects two carbon atoms, giving the impression of a head-on view of the carbon-carbon bond. The carbon atom closer to the observer is symbolized by a point. Three lines, forming a Y shape and inclined at 120° to each other, represent the three hydrogen atoms attached to the front carbon atom. Conversely, the rear carbon atom (located away from the observer) is depicted by a circle. This circle features three bonds extending from it, each shorter in length and oriented at an angle of 120° to one another.



Perspective drawing

Below, you can find illustrations of Newman's projections.



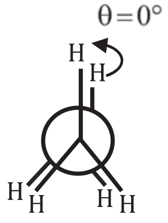
(Newman projection)

Relative Stability of Conformations

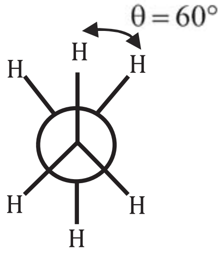
The relative stability of conformations in ethane is determined by their structural arrangements. In the staggered form, the electron clouds in the C-H bonds are maximally separated, leading to minimal repulsive forces, lower energy, and heightened stability of the molecule. Conversely, when the staggered form transitions into the eclipsed form, the electron clouds of the carbon-hydrogen bonds draw closer, resulting in increased electron cloud repulsion. To counteract these heightened repulsive forces, the molecule must possess more energy, thereby exhibiting lower stability.

As ethane undergoes rotation towards the eclipsed conformation, its potential energy increases, imposing restrictions on its rotation. This resistance to twisting, which impacts the stability of a conformation, is termed torsional strain. The energy required to restrict this rotation is referred to as torsional energy. The magnitude of torsional strain is contingent upon the angle of rotation around the C-C bond, denoted as the dihedral angle or torsional angle (θ).

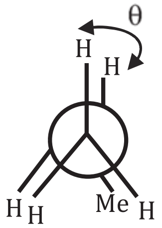
Among the various conformations of ethane, the staggered form experiences the least torsional strain, while the eclipsed form encounters the maximum torsional strain. Consequently, it can be inferred that rotation around the C-C bond is not entirely free. Despite the relatively small energy difference between the two forms, approximately 12.5 kJ mol^{-1}, ethane molecules easily overcome this barrier, even at ordinary temperatures, by gaining thermal or kinetic energy through intermolecular collisions. Consequently, it remains challenging to isolate or separate different conformational isomers of ethane.



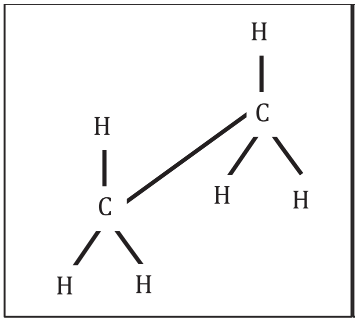
Eclipsed



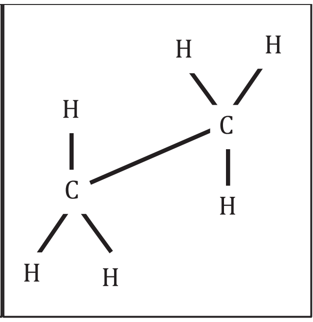
Staggered



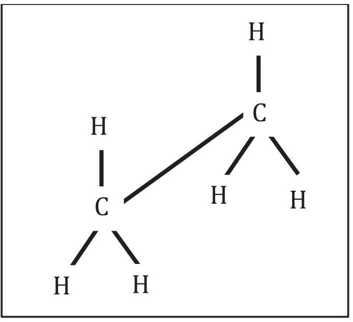
Skew



Eclipsed,θ = 0°

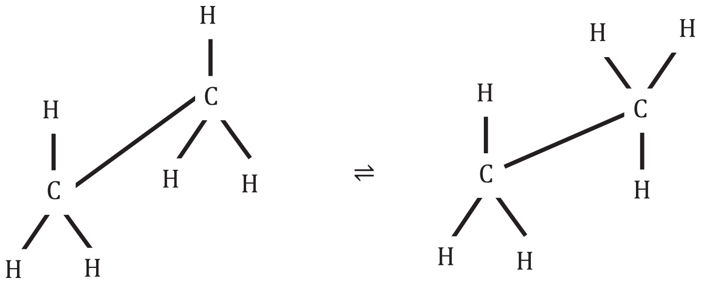


Staggered,θ = 60°

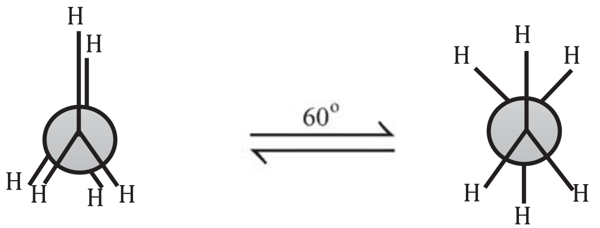


Skew,θ = anything else

Conformation of ethane [$CH_3–CH_3$]



(Saw horse projection)



Eclipsed

Staggered

(Newman projection)

[Stability order: Staggered > Eclipsed]

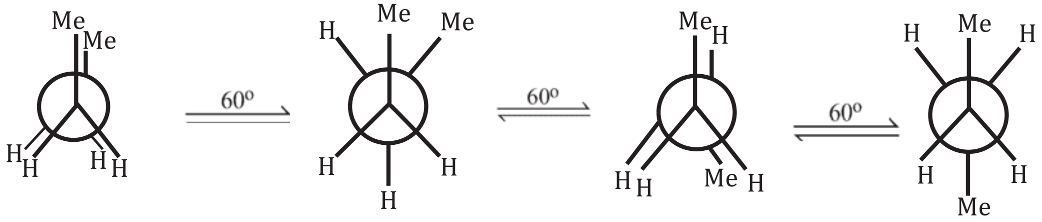
Dihedral Angle

Dihedral angle in eclipsed form of ethane is 0º.

Dihedral angle in staggered form of ethane is 60º.

Conformation of Butane

[$CH_3–CH_2–CH_2–CH_3$]



(i) (Fully eclipsed)

(ii) (Gauche)

(iii) (Partially eclipsed)

(iv) Anti (Staggered)

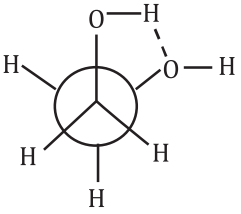
I (Fully eclipsed form): In this form distance between 2 methyl groups is minimum so maximum repulsion or minimum stable.

IV (Anti or staggered): In this form distance between 2 methyl groups is maximum so minimum repulsion or maximum stable.

Stability order: IV > II > III > I

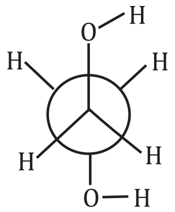
The energy profile illustrating the conformers of n-butane through rotation around the C_2-C_3 bond reveals a nuanced relationship between stability and conformation. While the conventional understanding suggests that the anti or staggered conformation is typically more stable than the skew or gauche conformation, there are instances where this rule does not universally apply.

In certain cases, the skew or gauche conformer can exhibit greater stability than the anti-conformer due to the presence of intramolecular hydrogen bonding, which serves to stabilize the skew form. This phenomenon is observed in molecules such as ethylene glycol and 2-chloro ethanol, where the unique influence of intramolecular hydrogen bonding contributes to the overall stability of the skew or gauche conformation, challenging the conventional expectation of anti or staggered conformers always being more stable.

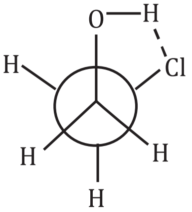


Skew form of ethylene glycol

>

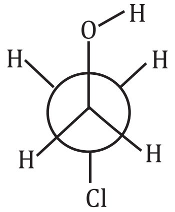


Staggered form of ethylene glycol



Skew form of 2-chloroethanol

>



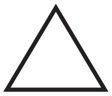
Staggered form of 2-chloroethanol

Cyclo Alkanes

Cycloalkanes are a category of alkanes characterized by the presence of carbon atoms arranged in ring structures. Although the synthesis of simple cycloalkanes, extending up to approximately C_{30}, has been achieved, those with 5 or 6 carbon atoms in the ring are the most prevalent.

The exploration of the relative stabilities of cyclic molecules began with Adolf von Baeyer. He sought to elucidate the factors influencing the stability of cyclic molecules compared to their acyclic counterparts. One of the primary reasons for the relative instability of cyclic molecules, specifically cyclic alkanes, is the deviation from the ideal tetrahedral angle.

When a cycloalkane is formed, it necessitates bond angles that differ from the standard 109°28'. This deviation means that the orbitals of its carbon-carbon (C-C) bonds cannot attain maximum overlap, leading to the introduction of angle strain. This phenomenon is commonly referred to as Baeyer strain. For example, in the case of cyclobutene, the bond angle is 90°, resulting in reduced stability compared to cyclopentane, where the bond angle is 108°. The presence of angle strain, a consequence of non-ideal bond angles, is a pivotal factor influencing the stability of cycloalkanes.



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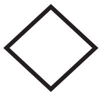

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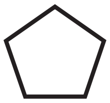


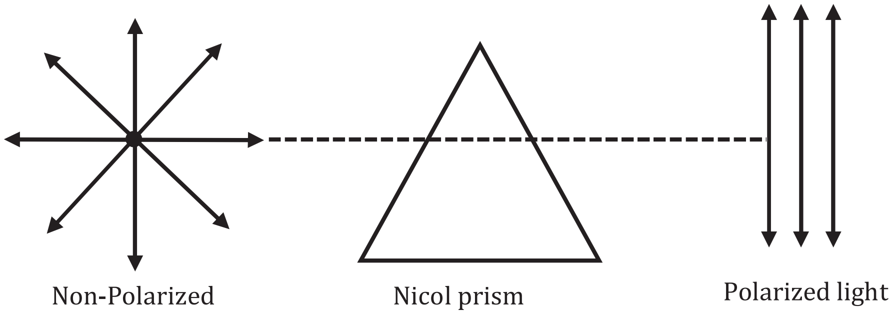
→ increasing stability

Stability Sequence: Cyclopropane < Cyclobutene < Cyclopentane < Cyclohexane

Within the realm of cycloalkanes, a distinct order of stability is observed, with cyclopropane being the least stable, followed by cyclobutene, cyclopentane, and finally, the most stable being cyclohexane.

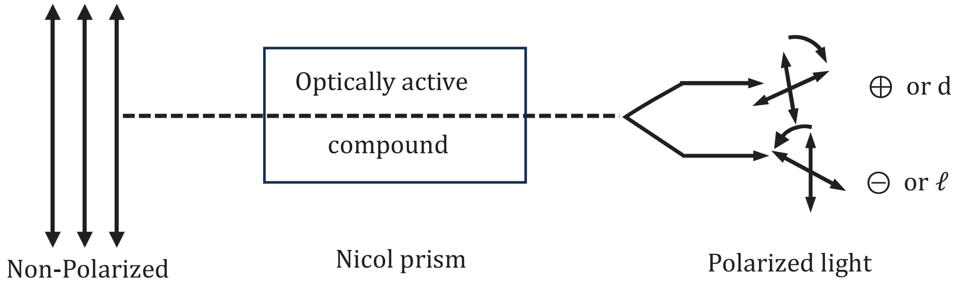
Optical Isomerism

Two or more than two compound have same molecular formula, same structural formula but different behaviour towards PPL (plane polarized light).



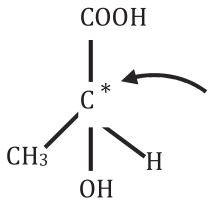
Optical activity

Tendency to rotate plane of PPL in a particular direction. If a compound rotates plane of PPL in clockwise direction, then it will be dextrorotatory or d or (+) and if a compound rotates plane of PPL in anticlockwise direction, then it will be levorotatory or λ or (–).



Chiral carbon

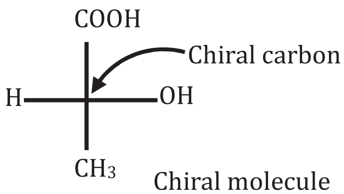
Carbon which is bonded to four different atoms or groups.



Chiral carbon or asymmetric carbon.

Chiral molecule

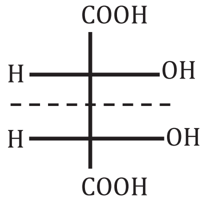
(i) A molecule having only one chiral centre then it will be always chiral.
Except flipping



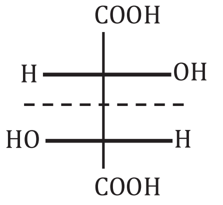
Chiral carbon

Chiral molecule

(ii) A molecule having at least two chiral carbons and no symmetry then it will be chiral molecule.



Plane of symmetry
(Achiral molecular)



No symmetry
(Chiral molecular)

Essential and sufficient condition for optical activity is "Molecule should be **chiral**" or "Molecule should be **unsymmetrical**" or "**Nonsuperimposable** mirror images"

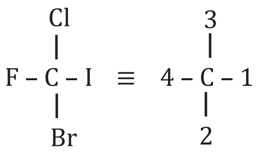
Absolute Configuration (R, S configuration)

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

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

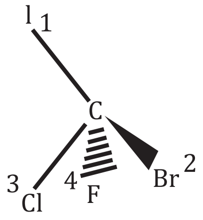
1. Each group attached to stereocenter is assigned a priority on the basis of CIP sequence rule.

Example:



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

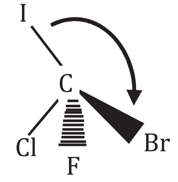
2. After assigning priorities, the least priority group is written at remotest valency (going away).



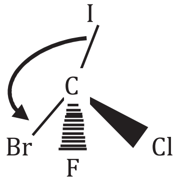
Note that priority order is: I>Br>Cl>F

➢ Now the order from top priority to second priority and then to the third priority is determined. If it gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration.

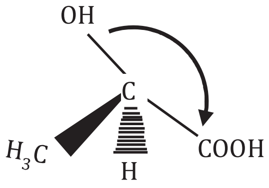
For example.



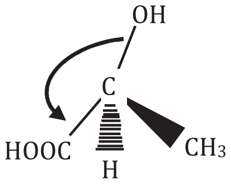
R–Configuration
(Clockwise from top priority)



S–Configuration
(Anti clockwise from top priority)



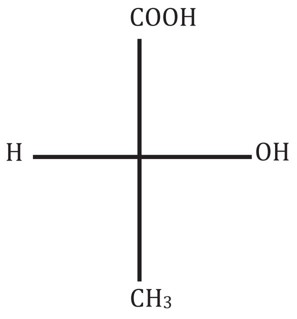
R–Configuration
(Clockwise from top priority)



S–Configuration
(Anti clockwise from top priority)

Enantiomers

Stereoisomers which are mirror images to each other and not superimpose to each other. Nonsuperimposable mirror images are called as enantiomers.



Object (I)

mirror

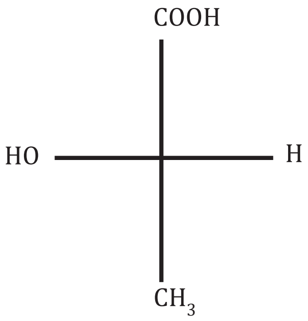


Image (II)

I and II are nonsuperimposable mirror images, so I and II are enantiomers.

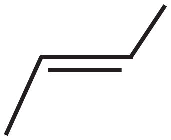
(i) Enantiomers have chiral structures.

(ii) Enantiomers are optically active substance. They rotate the plane polarized light in opposite directions but to the equal extent.

Diastereomers

Stereoisomers which are not mirror images of each other's.

Cis–2 butene
(I)



Cis–2 butene
(II)

I and II are not mirror images, so I and II are diastereomers.