9.

ISOMERISM

1. INTRODUCTION

Molecules with the same molecular formula, but different arrangements of atoms are called Isomers and the phenomenon is thus called Isomerism. They have different physical and chemical properties. They can be classified in the following manner.

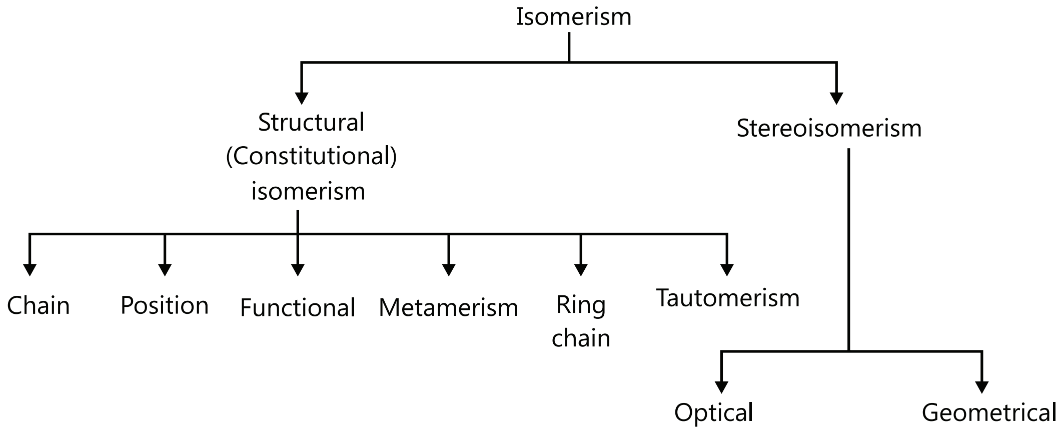


Figure 9.1: Types of isomerism – structural and stereoisomesrism

2. STRUCTURAL ISOMERISM

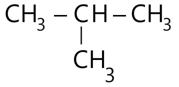
Compounds which have the same molecular formula but different structural formulas are called isomers and the phenomenon is known as isomerism.

Type of Structural Isomerism:

(a) **Chain Isomerism:** Chain isomers possess the same molecular formula, but different number of carbon in parent–chains (straight or branched).

(i) Butane: C_4H_{10}

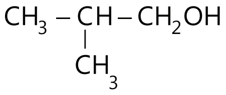
$CH_3-CH_2-CH_2-CH_3$ n – Butane



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

(ii) Butyl alcohol: C_4H_9OH

$CH_3-CH_2-CH_2-CH_2OH$ n – Butyl alcohol

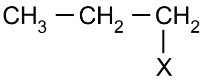


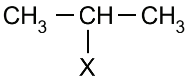
$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2OH$ Isobutyl alcohol

(b) Position Isomerism: Compounds having same molecular formula but the position of functional group, multiple bond or branches along the same chain length of carbon atoms varies.

(i) The same molecular formula
(ii) The same length of carbon chain
(iii) The same functional group

E.g. (i) Molecular formula; C_3H_7X(X=halogen, NH_2, OH or OR)

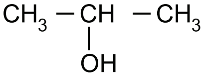

$CH_3-CH_2-\underset{X}{\underset{|}{CH_2}}$


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

In this structure three carbon atoms form a chain, and X is joined at the end in (I), while at the middle carbon in (II). To be specific.

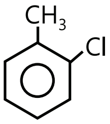
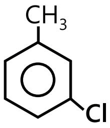
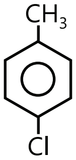
(ii) $CH_3-CH_2-CH_2OH$ and

1 — Propanol


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

2 — Propanol

Note: In di–substituted derivatives, position isomerism also exists because of the relative positions occupied by the substituents on the benzene ring. Thus, Chlorotoluene, $C_6H_4(CH_3)Cl$ exists in three isomeric forms–ortho, meta and para.

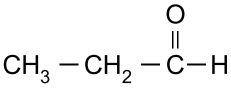
 o-Chlorotoluene	 m-Chlorotoluene	 p-Chlorotoluene

(c) Functional Group Isomerism: When isomers have the same molecular formula but different functional groups, these compounds are called functional group isomers. The following pairs of families show this isomerism.

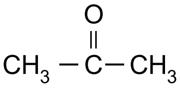
E.g. (i) Molecular formula: C_2H_6O

$CH_3–CH_2–OH$ and	$CH_3–O–CH_3$
Ethyl alchol	Dimethyl ether
(Alcohol)	(Ether)

(ii) Molecular formula: C_3H_6O


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$

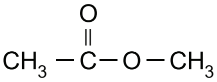
and


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Propanal	Propanone
(Aldehyde)	(Ketone)

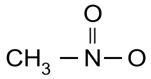
(iii) Molecular formula: $C_3H_6O_2$

CH_3-CH_2-COOH and


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

Propanoic acid	Methyl acetate
(Acid)	(Ester)

(iv) Molecular formula: CH_3NO_2



$CH_3-\overset{\overset{\displaystyle O}{\|}}{N}-O$ and $CH_3-O-N=O$

Nitromethane Methyl nitrite

(d) Metamerism: This type of Isomerism is due to different position of poly valency functional group (like S, N, O, and CO,) in molecule, with alkyl groups around it. Members belong to the same homologous series.

E.g. **(i)** Diethyl ether and methyl propyl ether

$CH_3CH_2OCH_2CH_3$	Diethyl ether
$CH_3OCH_2CH_2CH_3$	Methyl propyl ether

(ii) Diethyl amine and methyl propylamine

$CH_3CH_2–NH– CH_2CH_3$	Diethyl amine
$CH_3CH_2 CH_2–NH– CH_3$	Methyl propyl amine

(e) Ring chain Isomerism: Such isomerism arises due to difference of carbon–chain or ring. E.g. **(i)** Molecular formula: C_3H_6 $H_3C-CH=CH_2$ and

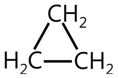
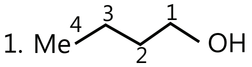


Illustration 1: Give various functional isomers of butanol and give their isomeric relations. **(JEE MAIN)**

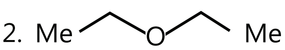
Sol: Functional Group Isomerism: These isomers have same molecular formula but different Functional groups. Alcohol show Functional group isomerism with ethers.

Alcohols:

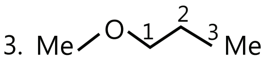


Butan-1-ol

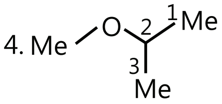
Ethers (R — O — R′)



Ethoxy ethane
(Diethyl ether)



1-Methoxy propane
(Methyl propyl ether)



2-Methoxy propane
(Isorophy methyl ether)

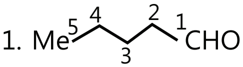
(1) and (2), (1) and (3), and (1) and (4) are functional isomers.

(2) and (3), and (2) and (4) are metamers.

(3) and (4) are positional isomers.

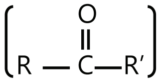
Illustration 2: Give various isomers of pentanal and give their isomeric relations. **(JEE MAIN)**

Sol: Aldehyde show Functional group isomerism with Ketone.

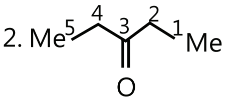


Pentanal

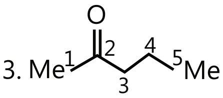
Ketones



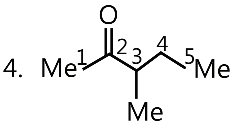
$\left(R-\overset{\overset{\displaystyle O}{\|}}{C}-R'\right)$



Pentan-3-one
(Diethyl ketone)



Pentan-2-one
(Methyl propyl ketone)



3-Methyl butan-2-one
(Isopropyl methyl ketone)

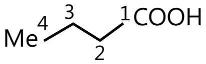
(1) and (2), (1) and (3), and (1) and (4) are functional isomers.

(2) and (3) are positional isomers.

(2) and (4) are position and chain isomers.

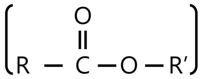
(3) and (4) are metamers.

Illustration 3: Give various isomers of butanoic acid and give their isomeric relations. **(JEE ADVANCED)**

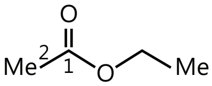
1. 
Butanoic acid

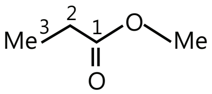
Sol: Acid show Functional group isomerism with Ester.

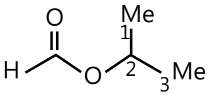
Acid:

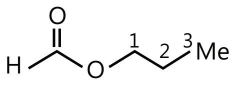
Esters 

$$\left(R - \overset{O}{\overset{\|}{C}} - O - R'\right)$$

2. 
Ethyl ethanoate
(Ethyl acetate)

3. 
Methyl propanoate
(Methyl proplonate)

5. 
Propyl-2-methanonate
(Isopropyl formate)

4. 
Propyl methanote
(Propyl formate)

(1) and (2), (1) and (3), (1) and (4), and (1) and (5) are functional isomers.

(2) and (3), (2) and (4), and (5) are metamers.

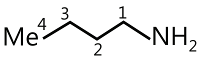
(3) and (4), and (3) and (5) are metamers.

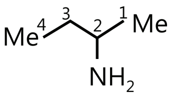
(4) and (5) are position isomers.

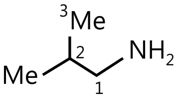
Illustration 4: Give various functional isomers of butan–1–amine and give their isomeric relations.

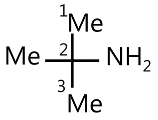
(JEE ADVANCED)

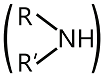
Sol: 1° amine (RNH$_2$)

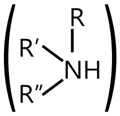
1. 
Butan-1-amine

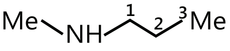
2. 
Butan-2-amine
(sec-Butyl amine)

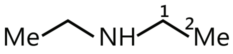
3. 
2-Methyl propan-1-amine
(Isobutyl amine)

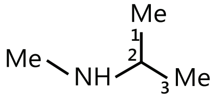
4. 
2-Methyl propan-2-amine
(t-Butyl amine)

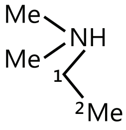
2° amine 

3° amine 

2. 
N-Methyl propan-1-amine
(Methyl propyl amine)

3. 
N-Ethyl ethan-1-amine
(Diethyl amine)

4. 
N-Methyl propan-2-amine
(Isopropyl methyl amine)

5. 
N,N-Dimethyl ethan-1-ami
(N,N-Dimethyl ethyl amin)

Note: (1° and 2° amine), (1° and 3° amine), and (2° and 3° amine) are functional isomers. 2° amine and other isomeric 2° amine are metamers. 3° amine and other isomeric 3° amine are metamers. But 1° amine and other isomeric 1° amine are position or chain isomers.

(2) and (2), (1) and (3), (1) and (4), and (1) and (5) as functional isomers.

(2) and (3), (2) and (4) and (4) are metamers.

(2) and (5), (3) and (5), and (4) and (5) are functional isomers.

Tautomerism: A phenomenon in which a single compound exists in two readily interconvertible structures that differ in the relative position of at least one atomic nucleus, generally hydrogen. Tautomeric structures are obtained by the simultaneous shift of H atom and a double bond (π–bond) at 1 and 3 positions. That is why it is also called 1, 3–shift, It is further called desmotropism (Greek: ⇒ desmosbond, troops ⇒ turn) or dynamic isomerism or kryptomerism or allelotropism or metrotropy or keto–enol tautomerism.

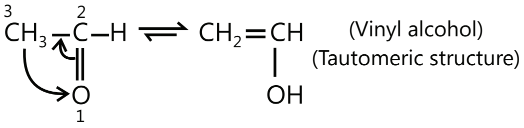
(a) Difference between resonance and tautomerism:

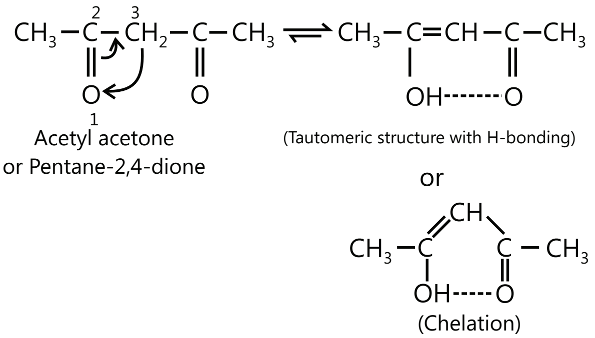
(i) Resonance is a hypothetical concept, whereas tautomerism is real.

(ii) Resonance–contributing structures (canonical structures) cannot be isolated, whereas tautomeric structures can be isolated.

(iii) In resonance, position of atoms or nuclei are fixed; while in tautomerism there is a simultaneous shift of an H atom and π–bond takes place at 1, 3–positions (1, 3–shift).

E.g.





Acetyl acetone or Pentane-2,4-dione

(Tautomeric structure with H-bonding)

(Chelation)

(iv) Tautomeric forms have different functional groups. Resonating structures have the same functional group.

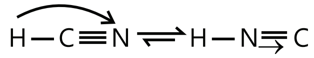
(v) Tautomeric forms have no effect on bond lengths, while resonance affects the bond length.

(vi) Resonance structures are obtained by the delocalisation of π or non–bonding e⁻'s or both, while tautomeric structures are obtained by delocalisation of σ–and π–bond.

(b) If the H atom oscillates between two polyvalent atoms linked together, the system is a dyad and if the H atom moves from the first to third atom in a chain, the system is a triad.

(c) Hydrocyanic acid is an example of dyad system in which the H atom oscillates between C and N atoms.

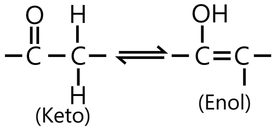
Therefore, (HCN) and ($HN \equiv C$) are the examples of tautomerism.



Hydrocyanic acid   Isohydrocyanic acid

(d) **Triad System**

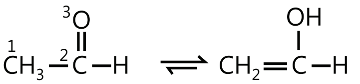
(i) Keto–enol system: Polyvalent atoms are O and two C atoms. It arises due to 1, 3–migration of a hydrogen atom from one polyvalent atom to the other within the same molecule. Isomers thus obtained exist in dynamic equilibrium with each other and are called tautomers and the phenomenon is called tautomerism.



(Keto)   (Enol)

There are several types of tautomerism but keto–enol tautomerism is most important. In this type of tautomerism, one form (tautomer) contains the keto group (>C=O) while the other contains the enolic (>C=C–OH) group. Two simplest examples of keto–enol tautomerism are acetaldehyde and acetone.

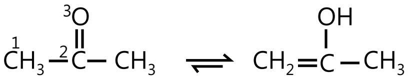
(ii)



(Acetaldehyde (Keto form)

Vinyl alcohol (Enolic form) Negligible amount)

(c)

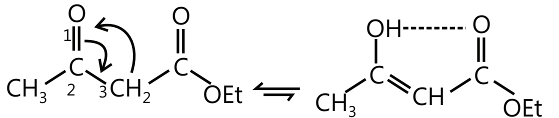


Acetone (Keto form)

Prop-1-en-2-ol (Enolic form) Negligible amount)

In simple aldehydes and ketones (i.e., acetaldehyde, acetone, etc.), the amount of enolic form is stabilised by the intramolecular hydrogen–bonding (chelation), such as in 1, 3–dicarbonyl compounds, the amount of the enolic form is much greater than in acetaldehyde or acetone. For example, in acetoacetic ester, the amount of enolic form is 7%.

(iii)

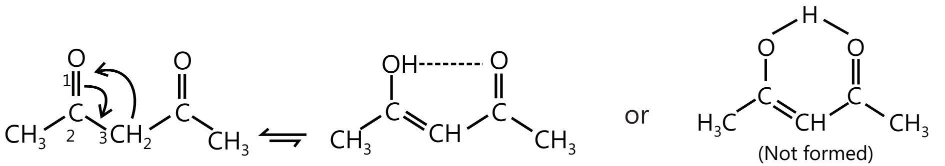


Acetoacetic ester
(Keto form 93%)

(Enolic form, 7%)

Similarly, acetyl acetone (i.e., a 1, 3–diketone) also exhibits keto–enol tautomerism but the amount of the enolic form here is much higher (76%) than even in acetoacetic ester. This is because the keto group is a much better electron–withdrawing group than the ester group.

(iv)



Acetyl acetone
(Keto form, 24%)

(Enolic form, 76%)
(More stable 5-membered ring)

(Not formed)
(Although 6-membered ring is more stable, H atomis so small that it dose not form a par of ring.)

Enol content of (I) is more stable because it has a conjugated (C=C–C=O) π–system and intramolecular H–bonding.

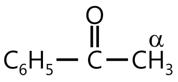
(v) Effect of solvent on enol content: Enol content of (I) is 15% in H_2O and 92% in hexane, since H_2O forms H–bonds with (C=O) of keto form, thereby inhibiting the intramolecular H–bonding of the enol form. Therefore, the enol content increases in the non–polar aprotic solvent (e.g., benzene or hexane) and decreases in polar protic or polar aprotic solvent (H_2O or acetone).

Order of enol content in different solvents:

Hexane> benzene> acetone > methanol> H_2O.

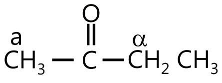
The enol content is more volatile and is separated by the careful distillation of the mixture in a fused quartz apparatus (eliminates base from glass).

(e) **Essential conditions:** In order for an aldehyde or a ketone to exhibit keto–enol tautomerism, it is essential that it must have at least one α–hydrogen atom. Thus, acetophenone, butan–2–one, Tpresence of , is essentialan



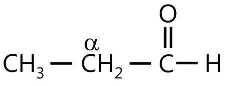
$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_3$

Acetopheone



$\overset{a}{C}H_3-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_2\ CH_3$

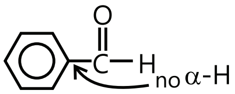
Butan-2-one



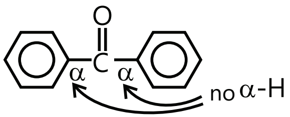
$CH_3-\overset{\alpha}{C}H_2-\overset{\overset{O}{\|}}{C}-H$

Propanal

In contrast, benzaldehyde, benzophenone, etc., do not show keto–enol tautomerism because of the absence of α–hydrogen atoms.



Benzaldehyde



Benzophenone

(i) Keto–form forms oximes, hydrazone, and gives DNP test which shows the presence of (C=O) group.

(ii) Enolic–form gives a colour with neutral $FeCl_3$ solution, a test of enolic $\left(-\underset{\text{OH}}{\underset{|}{\text{C}}}=\text{C}\langle\right)$ compounds

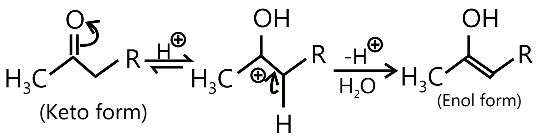
(iii) Enolic–form decolourises Br_2/CCl_4 solution –a test of unsaturation due to the presence of (C=C) bond.

(iv) Enolic–form also forms acetyl derivative, which shows the presence of (–OH) group.

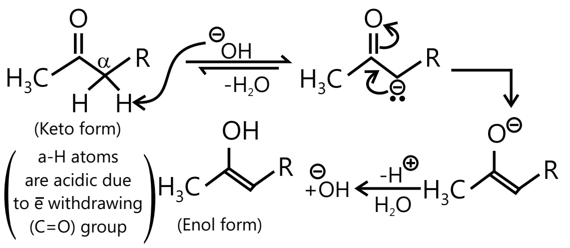
(v) Tautomerism occurs in both acidic and basic mediums.

(f) Mechanism of acid/base catalysed tautomerism:

(i) Acid–catalysed tautomerism:

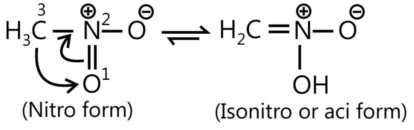


(ii) Base–catalysed tautomerism:

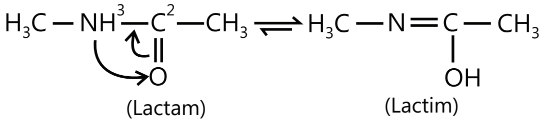


(b) Triad System Containing Nitrogen

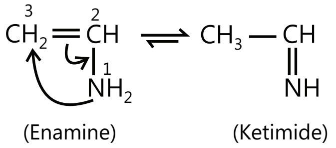
i) Nitro-isonitro tautomerism:



ii) Lactam-lactim tautomerism:

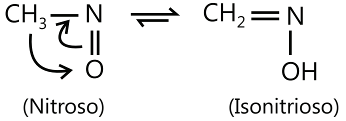


iii) Enamine-ketimide tautomerism:



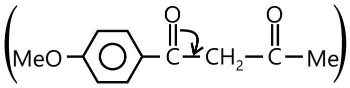
iv) Tautomerism of nitrous acid:

v)Nitroso-isonitroso tautomerism:

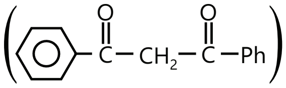


Increasing Order of Enol Content

Aldehyde (MeCHO) < ketone (MeCOMe) < ketoester ($CH_3COH_2COOC_2H_5$) < ketoester with (Ph) group ($PhCOCH_2COOC_2H_5$) < dial ($OHC–CH_2–CH_2–CHO$) < keto–aldehyde (CH_3COCH_2CHO) < diketone ($CH_3COCH_2COCH_3$) < (Ph) group containing e^- donating group with (C=O) group



< (Ph) group with (C=O)group



< (Ph) group containing e-withdrawing group with(C=O)group

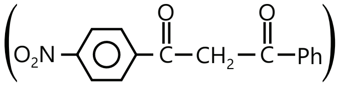


Illustration 5: Write more stable tautomerism structures of the following: **(JEE MAIN)**

(A) Phenol (B) Methyl–3–oxobutanoate (C) Cyclohexan–1, 3, 5–trione

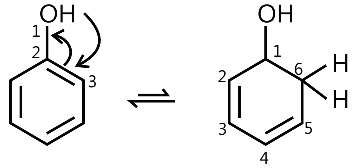
Sol:

(A) In case of phenol keto form is less stable due to loss of aromaticity.

(B) In case of Methyl–3–oxobutanoate Enol form is more stable as it involves hydrogen bonding between the OH group and carbonyl carbon.

(C) In case of Cyclohexan–1, 3, 5–trione Enol form is more due to gain of Aromatic structure.

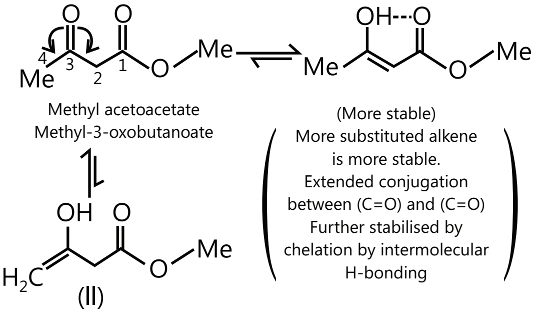
a.



Phenol
(More stable)
(Aromatic)

Cyclohexa-2,4-dine-1-one
(Less stable)
(non-aromatic)

b.

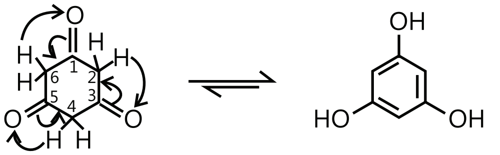


Methyl acetoacetate
Methyl-3-oxobutanoate

(More stable)
More substituted alkene
is more stable.
Extended conjugation
between (C=O) and (C=O)
Further stabilised by
chelation by intermolecular
H-bonding

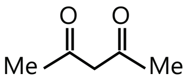
(II)
(Less stable)
Less substituted alkene
and no extended conjugation

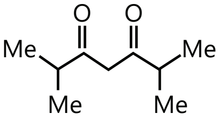
c.

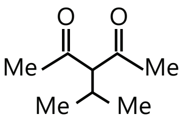


1,3,5-Trihydroxy benzene
(or) (Phloroglucinol)
(More stable due to aromatic character)

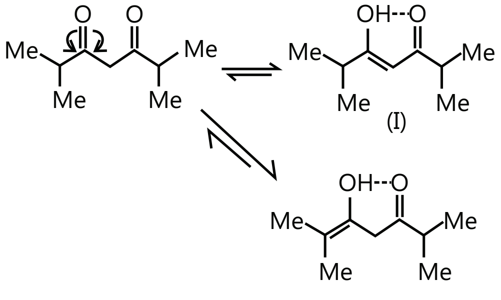
Illustration 6: Arrange the following in the decreasing order of enol content: **(JEE MAIN)**

a. 

b. 

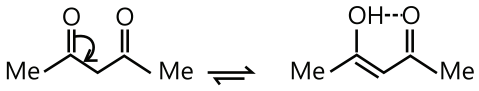
c. 

Sol: Both (B) and (A) are stabilised by intramolecular H–bonding. But (B) shows more enol content than (A) since (B) is more substituted alkene. In (C) there is only one α –H atom and its acidity is decreased by $\bar{e}$ donating (+I effect of) isopropyl group. It shows less enol form. b>a>c



(II)
(More substituted alkene; more stable)

(I) is more stable than (II), since (II) is more strained 5–membered ring joining the (C=C) bond.



Both (B) and (A) are stabilised by intramolecular H–bonding. But (B) shows more enol content than (A) since (B) is more substituted alkene.

In (C) there is only one α–H atom and its acidity is decreased by the e⁻ donating (+I effect of) isopropyl group. It shows a less enol form.

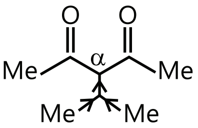
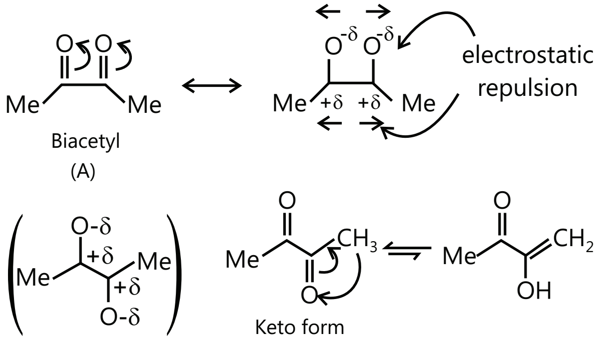
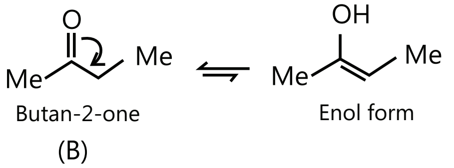
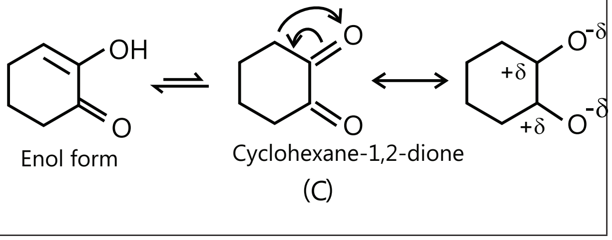
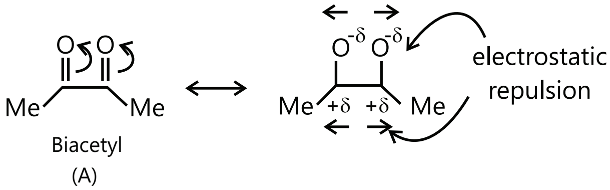


Illustration 7: Why is enol content of butane–2, 3–dione (biacetyl) (A) slightly higher than that of butan–2–one (B) and much less than that of cyclohexane–1, 2–dione (C)? **(JEE ADVANCED)**

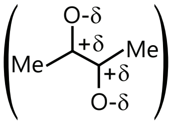
Sol:

(i)	In biacetyl (A), adjacent (C=O) groups destabilise the molecule due to the electrostatic repulsion of the similar charges on the O atom of (C=O), but the molecule relives some of this electrostatic repulsion by acquiring anti conformation. Some repulsion is further relieved in the enol form but enol content is still small because this relief occurs at the expenses of loss of (C=O) resonance energy.	
(ii)	In butan–2–one (B), no other factor except the loss of resonance energy occurs during enolisation.	
(iii)	In cyclohexane –1, 2–dione (C), the cyclohexane ring is rigid and the –σ charge on the adjacent (C=O) groups is in syn–position. Therefore, this molecule relieves its electrostatic repulsion only by the enolisation of one of the (C=O) groups.	

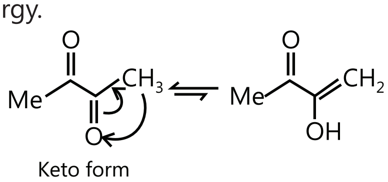


In biacetyl (A), adjacent (C=O) groups destabilise the molecule due to the electrostatic repulsion of the similar charges on the O atom of (C=O), but the molecule relives some of this electrostatic repulsion by acquiring

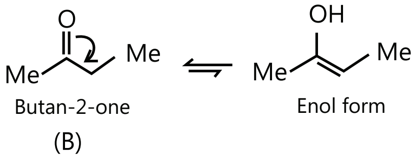
anti–conformation,

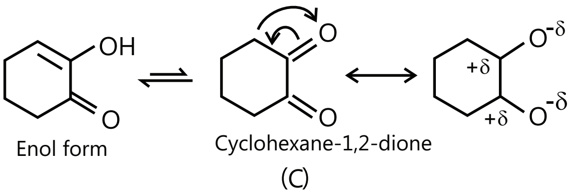


Some repulsion is further relieved in the enol form but enol content is still small because this relief occurs at the expenses of loss of (C=O) resonance energy.



In butan–2–one (B), no other factor except the loss of resonance energy occurs during enolisation.





In cyclohexane –1, 2–dione (C), the cyclohexane ring is rigid and the–σ charge on the adjacent (C=O) groups is in syn–position. Therefore, this molecule relieves its electrostatic repulsion only by the enolisation of one of the (C=O) groups.

Thus, the enol content of (A) is slightly higher than that of (B) but much less than (C).

Illustration 8: Give the decreasing order of enol of ethyl acetoacetate in the following solvents: **(JEE ADVANCED)**

(A) Water (B) Methanol (C) Benzene (D) Acetone

Sol: Enol content increases in non–polar aprotic solvent (e.g., benzene or hexane) and decreases in polar protic or polar aprotic solvent.

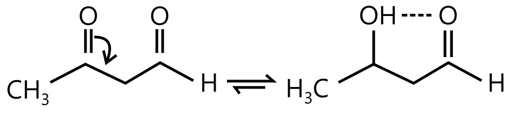
Effect of solvent on enol content c>d>b>a. Benzene (non–polar)>acetone (slightly polar)> methanol (polar, protic solvent)> H_2O (higher polar, protic solvent)

Illustration 9: Arrange the following in the decreasing order of enol content:

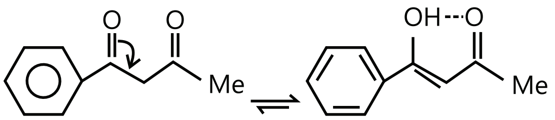
(A) $CH_2(COOEt)_2$ (Diethyl malonate) (B) CH_3COCH_2COOEt (EAA)

(C) $CH_3COCH_2COCH_3$ (D) $PhCOCH_2COCH_3$ **(JEE ADVANCED)**

Sol: d>c>b>a (89%>7.7%>1%) (diketone with (ph) group > diketone > keto ester> diester)

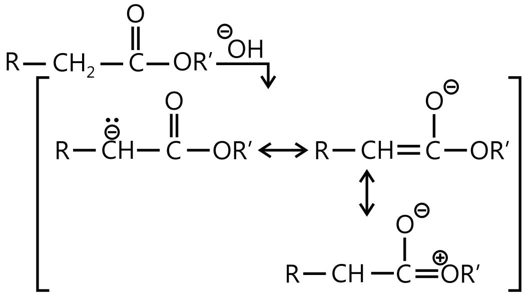


Enol is stabilised by intra-molecular H-bonding (Chelation)



(Ph group stabilises the enol by extending conjugation by p-bond delocalisation and also by chelation)

Esters do not show tautomerism due to the cross–conjugated resonance structures, which decreases the ability of (C=O) group of ester in stabilizing the enol from.



So, diethyl malonate does not show tautomerism.

3. STEREOISOMERISM

Those compounds having same molecular and structural formula but a different arrangement of group or atom in space is called stereo and phenomenon is termed as stereo isomerism.

It is divided into two parts:

(i) Configuration isomerism (ii) Conformational isomerism

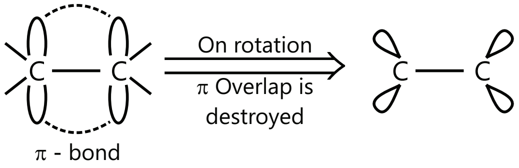
Configurational isomerism is further divided into two parts:

(i) Geometrical isomerism (ii) Optional isomerism

4. GEOMETRICAL ISOMERISM

The main criteria for geometrical isomerism is the restriction in rotation:

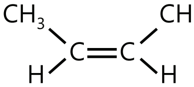
In alkenes, (C=C) bond is made of σ–and π–bonds. A π–bond is made by the sideways overlap of the un–hybridised π–orbitals of two C atoms above and below the plane of two C atoms. If one of the atoms is rotated through 90°, orbitals will no longer overlap and π–bond would break, which requires 25kJ/mol of energy. Hence, the rotation around (C=C) bond is not free but restricted. Due to this restricted rotation, the relative position of atoms or groups attached to the C atoms of the double bond gets fixed, which results in the formation of two distinct forms called geometrical isomers.



Types of geometrical isomerism: There are 3 types of geometrical isomerism on the basis of groups attached to double bond or the site of restricted rotation. They are mentioned below:

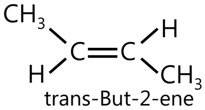
4.1 Cis–Trans Isomers

This kind of isomerism is used when there is at least a common group on both sides of the double bond or the site of restricted rotation (especially cycloalkane)



cis-But-2-ene

(I)

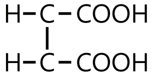


trans-But-2-ene

(II)

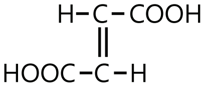
The isomer (I) in which similar groups or atoms lie on the same side of the double bond is called cis–isomer, whereas the isomer (II) in which the similar atoms or groups lie on the opposite side of the double bond is called the trans–isomer.

E.g. (I)



$\begin{array}{l}\mathrm{H-C-COOH}\\ \quad | \\ \mathrm{H-C-COOH}\end{array}$

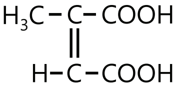
Maleric acid (cis)



$\begin{array}{r}\mathrm{H-C-COOH}\\ \| \quad\quad\\ \mathrm{HOOC-C-H}\end{array}$

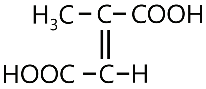
Fumatic acid (trans)

(II)



$\begin{array}{r}\mathrm{H_3C-C-COOH}\\ \| \quad\quad\\ \mathrm{H-C-COOH}\end{array}$

Crotonic acid (cis-isomer)



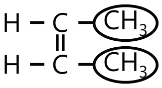
$\begin{array}{r}\mathrm{H_3C-C-COOH}\\ \| \quad\quad\\ \mathrm{HOOC-C-H}\end{array}$

Mesaconic acid (tran-isomer)

Properties of cis–trans isomer

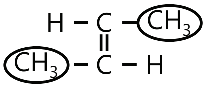
(i) Stability: Cis < Trans

Cis forms is less stable then trans because of the mutual repulsion between the same group e.g.



$\begin{array}{l}\mathrm{H-C-CH_3}\\ \quad \| \\ \mathrm{H-C-CH_3}\end{array}$

Cis form
(more repulsion)



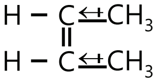
$\begin{array}{r}\mathrm{H-C-CH_3}\\ \| \quad\quad\\ \mathrm{CH_3-C-H}\end{array}$

Trans form
(less repulsion)

(ii) Dipole moment: Asymmetrical trans molecule has zero dipole moment, even if trans molecule is not symmetrical than its dipole moment is less than that of the cis isomer.

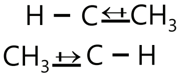
μ(Sym trans)=0

(unsym trans) μ < cis isomer



$\begin{array}{l}\mathrm{H-C\overset{\leftarrow\!+}{}CH_3}\\ \quad \| \\ \mathrm{H-C\overset{\leftarrow\!+}{}CH_3}\end{array}$

Cis form
μ=+ve



$\begin{array}{r}\mathrm{H-C\overset{\leftarrow\!+}{}CH_3}\\ \mathrm{CH_3\overset{+\!\rightarrow}{}C-H}\end{array}$

Trans form
μ=0

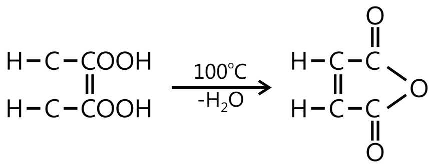
(iii) Polarity: Cis > Trans

(iv) Solubility: Soluble in a polar solvent. Cis > Trans

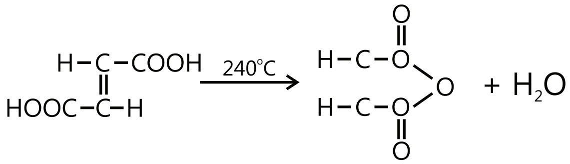
(v) Boiling point: Cis >Trans (due to high polarity)

(vi) Melting point: Cis < Trans. It is due to better packing in crystal due to symmetry. But heat of hydrogenation, heat of combination, density refractive index is higher in cis isomer than trans.

(vii) Heating effect: Maleic acid from anhydride at 100°C but fumaric acid forms anhydride at 250°C

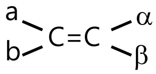


Maleic Acid



Fumaric Acid

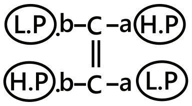
4.2 E–Z Isomerism



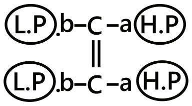
A better system E–Z, is applicable for those type of compounds which cannot be express by cis trans nomenclature.

E → Entegen (opposite)   Z → Zusamann (same)

E–form: When two same priority groups present on the opposite side of the double bonded is known E–form and when the same priority group present on same side of the double bond is called Z–form.



E-Form



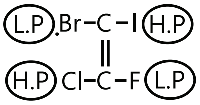
Z-Form

L.P=Low Priority group or atom

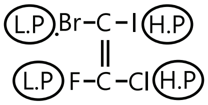
H.P.= High Priority group or atom

Priority rule: Chann, ingold & prelong proposed a sequence rule:

Rule 1: When an atom or group of atoms which are directly attached to the stereo genic centre have a higher atomic number, they will have higher priority. For example

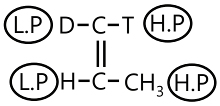


E-Form

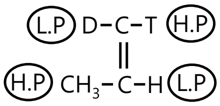


Z-Form

Rule 2: When the atomic number will be same, then higher atomic weight or group of atom have higher priority

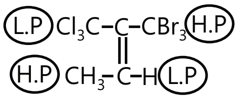


Z-Form

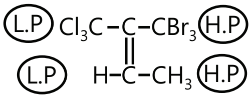


E-Form

Rule 3: When both atomic number and atomic weight are the same, then priority will be decided by the next joining atom.

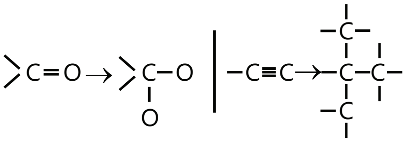


E-Form

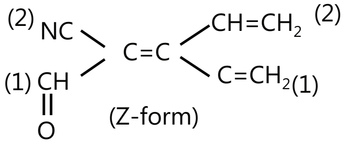


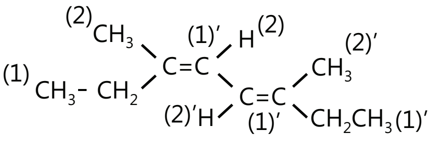
Z-Form

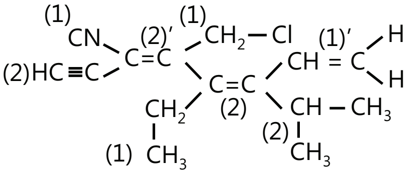
Rule 4: If multiple bonded group attach to the double bonded carbon, then they are considered in the following manner.



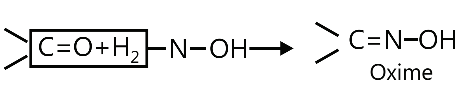
Some E–Z configuration of following compounds


(Z-form)


(3Z,5E)

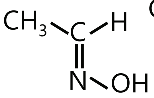

(2Z, 4E)'

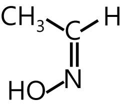
4.3 Syn–Anti Isomerism



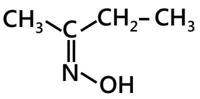
Oxime of aldehyde
and oxime of unsymmetrical
ketone also show
Geometrical Isomerism

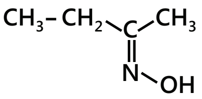
Aldoximes


Syn form


Anti form

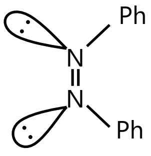
When the –OH group and H atom is on the same side of the double of C and N, then it is the syn form otherwise anti form

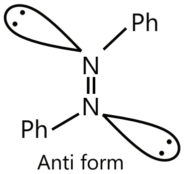

Syn form


Anti form

In unsymmetrical Ketoxime, if –OH and the alphabetically alkyl present on the same side of double bond, then it is syn form and other isomer is anti form.

Geometrical isomerism in AZO compounds:

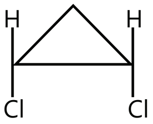

Syn form


Anti form

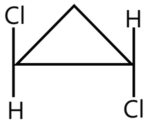
4.4 Geometrical Isomerism in Cyclic Compounds

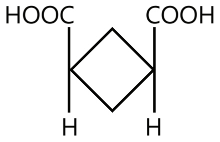
There is a restriction in rotation about the bonds in geometrical isomerism which is also seen in cycloalkanes.

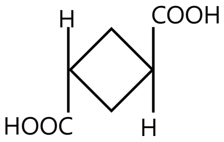
cycloalkanes


Cis form

cycloalkanes


Trans form


Cis form


Trans form

MASTERJEE CONCEPTS

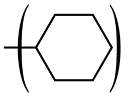
- In E–Z nomenclature, According to CIP rules priority is to be given to atomic numbers but in case they have same atomic number, i.e., isotopes, then priority is to be given to molecular weights.
- Misconception– it is not necessary that a compound having double bond must have geometrical isomers. In case if the 2 substituents on 1 side are the same, geometrical isomers are not possible.
- Geometrical isomers are diastereomers
- Misconception– in compounds having cumulative double bonds geometrical isomerism need not be defined. Those having an even number of double bonds can be optically active but doesn't have geometrical isomers while those having an odd number of double bonds cannot be chiral (unless chiral substituents) but can have geometrical isomers.
- Misconception– geometrical isomerism is not only restricted to double bonds but it can be extended to cyclic compounds and spiranes.

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 10: Arrange the following ligands in the decreasing order of priority. **(JEE MAIN)**

(i) $-CH\left(CH_3\right)_2$

(ii)



Cyclohexyl

Sol: In cyclohexyl, (–CH) is joined to two (CH_2) groups and is further joined to another ring C atom. In (i), (–CH) is joined to two (CH_3) groups each having three H atoms.

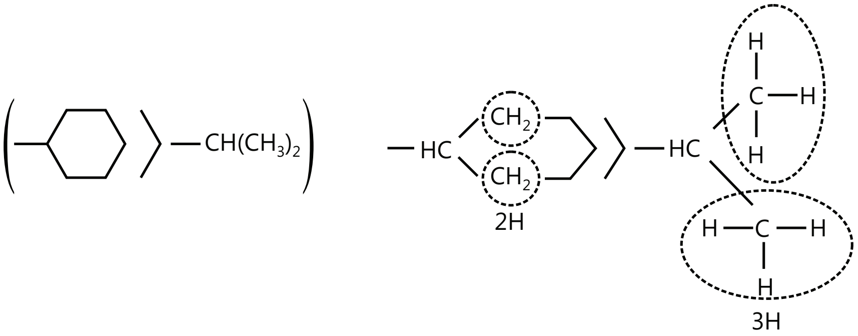
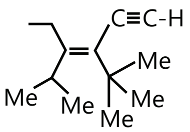
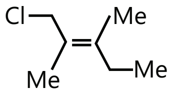


Illustration 11: Assign E–Z configuration to each of the following: **(JEE MAIN)**

a.



b.



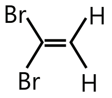
Sol: If two higher priority groups are on same side we assign it Z–configuration.

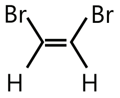
If two higher priority groups are on opposite sides we assign it E–configuration.

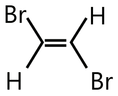
(i) (Z) Priority of $HC\equiv C- > -CMe_3$ and priority of $CH_2 = CH- > -CHMe_2$. So two higher priority groups on same side, hence Z–configuration.

(ii) (E) Priority of $-CH_2Cl > Me$, and $CH_3\ CH_2- > Me$. So two higher priority groups on opposite sides, hence E–configuration.

Illustration 12: Give the decreasing order of net dipole moments of the following **(JEE ADVANCED)**

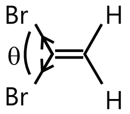
(I)


(II)


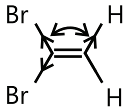
(III)


Sol: I>II>III

(I) has a smaller angle of separation between two Br atoms than in (II) and (III). Resulting in more net dipole moment (μ).



(II) Has a large angle of separation between two Br atoms; therefore, net (μ) is less than (I).



In (III), two Br atoms and two H atoms have equal and opposite bond moments; therefore, net μ is zero.

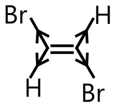
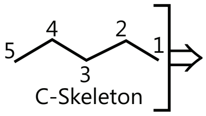
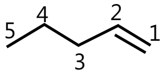


Illustration 13: Give the structural and diastereomers of pent–1–ene. **(JEE ADVANCED)**

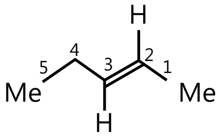
Sol: Write the C–skeletons and introduce double bond. The possible structures are: (In Image II double bond is missing)





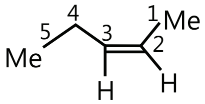
Pent-1-ene

(I)



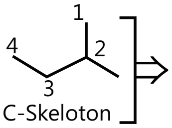
(E)-Pent-2-ene

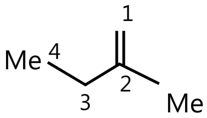
(II)



(Z)-Pent-2-ene

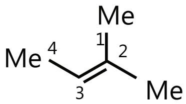
(III)





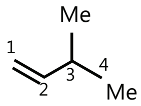
(IV)

2-Methyl but-1-ene



(V)

2-Methyl but-2-ene

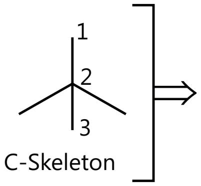


(VI)

3-Methyl
but-1-ene

(II) and (III) are diastereomers (geometrical isomers).

C–2 is 4° C atom and cannot form a double bond to give an alkene.



5. OPTICAL ISOMERISM

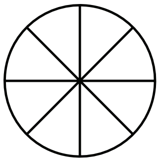
Compounds which can rotate plane polarised light, are called optically active compounds and this phenomenon is called optical activity. Plane polarised light can obtained by passing ordinary light through Nicol prism. Solution of an Optical active compound can rotate plane polarised light either left or to the right through the angle α. This property of a substance of rotating plane polarized light is called optical activity and the substance passing through it, is said to be optically active.

The observed rotation of the plane of polarised light produced by a solution depends upon–

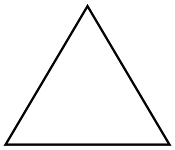
(i) The amounts of the substance in tube.

(ii) On the strength of the solution examined.

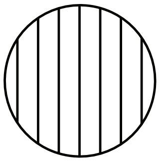
(iii) The temperature of the experiment and the wavelength of the light used.



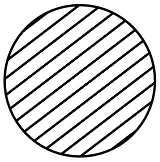
Ordinary light waves vibrating in all direction



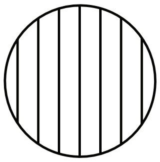
Nicol prism



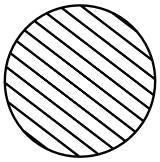
Plane polarizes waves vibrating in one direction



Plane Rotated to the right



Plane polarizes light



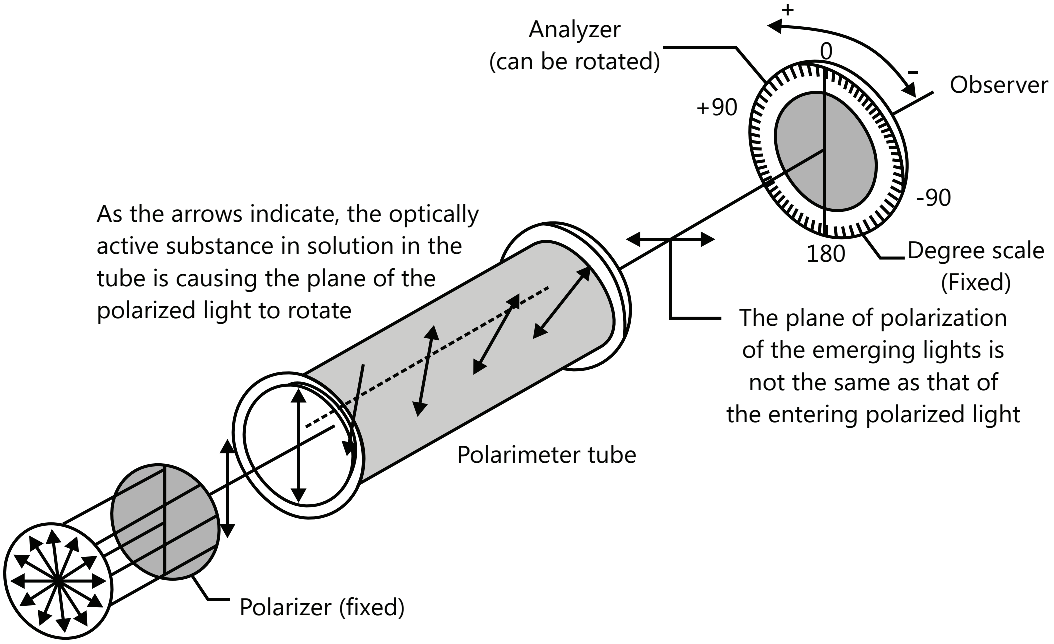
Plane Rotated to the left

All these substance are known to exist in three stages.

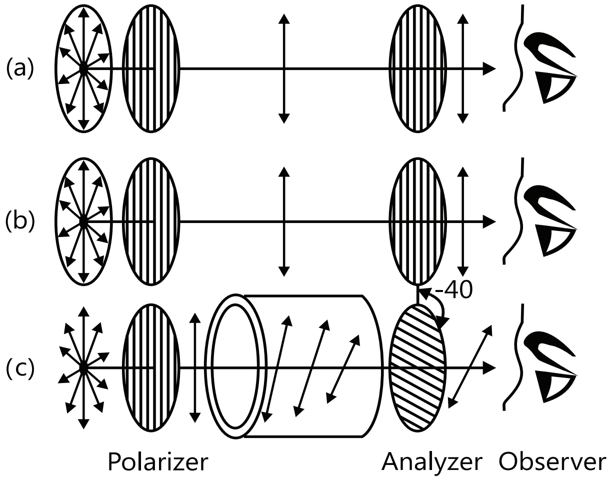
(i) One rotating the plane of polarised light to the left this forms is named laevorotatory.

(ii) One rotating the plane of polarized light exactly to the some extent but to the right. This form is named dextrorotatory.

(iii) An inactive form which does not rotate plane polarized light at all this is mixture of equal amounts of (+) and (–) forms and hence it is optical inactive. It is named (±)–mixture or Racemic mixture. (Latin, Racemic–mixture of equal compounds)



The principal working parts of a polar meter and the measurement of optical rotation.



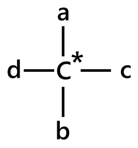
Polarizer and analyser are parallel. No optically active substance is present. Polarized light can get through the analyser.

- Polarizer and analyser are crossed.
- No optically active substance is present.
- No polarized light can emerge from the analyser.
- The substance between polarizer and analyser is optically active.
- Analyser has been rotated to the left (from observer's point of view) to permit rotated polarized light through (substance is levorotatory).
- Clockwise direction is also said to be dextrorotatory, and one that rotates plane–polarized light in a counterclockwise direction is said to be levorotatory (Latin: dexter, right, and leavus, left).

5.1 Specific Rotation

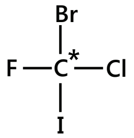
The number of degrees that the plane of polarization is rotated as the light passes through a solution of an enantiomer depends on the number of chiral molecules that it encounters. This, of course, depends on the length of the tube and the concentration of the enantiomer. In order to place measured rotations on a standard basis, chemicals calculate a quantity called the specific rotation, $[\alpha]$, by the following equation: $[\alpha] = \frac{\alpha}{c.l}$ where $[\alpha]$= The specific rotation α = The observed rotation

Asymmetric carbon (or) Chiral Carbon: If all the four bonds of carbon are bounded by four different atoms / groups, it is chiral. Chiral carbon is denoted by star.



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

Optical isomerism in bromochlorofluoroiodo methane: The structural formula of bromo chloroiodomethane is

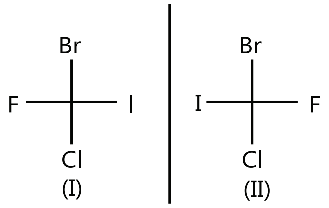


$$\begin{array}{c} Br \\ | \\ F - \overset{*}{C} - Cl \\ | \\ I \end{array}$$

The molecule has one chiral carbon as designated by star. So, the molecule is chiral and is non–super imposable on its mirror image.

According to Van't Hoff rule, Total number of optical isomers should be = 2^n, where n is number of chiral centre(s).

The fischer projections of the two isomers are



These are optically active, which are non–super imposable mirror images of each other and can rotate the plane of polarized light.

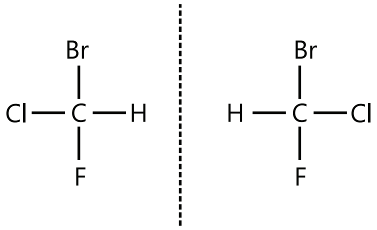
Stereoisomers which are mirror–images of each other can called enantiomers (or) Enantiomorphs. (i) and (ii) are enantiomers. All the physical and chemical properties of enantiomers are the same except two: They rotate PPL to the same extent but in opposite directions. One which rotates PPL in clockwise direction is called dextro–rotatory (dextro is Latin word meaning thereby right) and is designated by d (or) (+). One which rotates PPL in anti–clockwise direction is called laevo rotatory (means towards left) and designate by ℓ (or) (–).

5.2 Chirality

This term is been used to describe molecules without any elements of symmetry, thus unsymmetrical molecules are also called chiral molecules and optical activity is attributed to certain chiral centres in them. An asymmetrical carbon is a chiral center. Chirality is lost when two atoms bonded to an asymmetric carbon become similar, thus lactic acid is optically active but propionic acid is inactive.

Conditions for optical activity

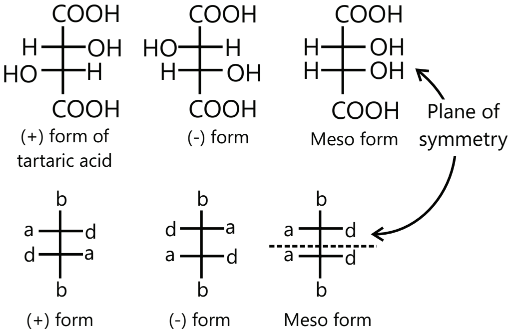
(i) It must have an asymmetric C atom or the chiral C atom. C atom which is attached to four different atoms or groups is called an asymmetric C atom or the chiral centre or stereo genic or stereo centre.



(ii) It must have a non–superimposable mirror image.

(iii) It should not contain any element of symmetry, i.e.,

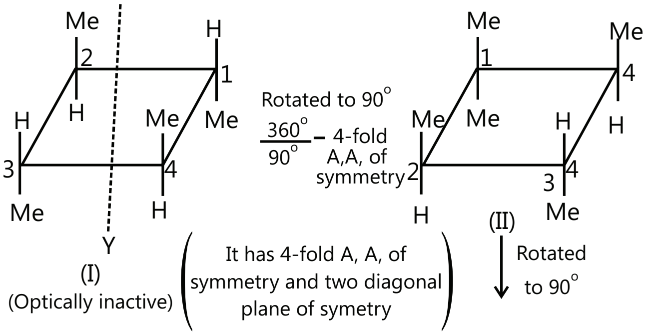
- Plane of symmetry or (mirror plane or σ –plane).
- Alternating axis of symmetry.
- Centre of symmetry or centre of inversion.



(i) **Plane of symmetry or mirror plane or σ –plane:** It is defined as an imaginary plane which divides the molecule into two equal parts such that one part of the molecule is a mirror image of the other part. For example:

(ii) **Alternating axis of symmetry:** A molecule possesses an n–fold alternating axis (A.A) of symmetry. When rotated through an angle of $360^o/n$ about this axis, followed by the reflection in a plane perpendicular to this axis, the molecule is identical to the original molecule. For example, 1,2,3,4–tetramethyl cyclobutane (I) contains four–fold alternating axis of symmetry. Rotation of (I) through 90^o about axis XY, which passes through the centre of the ring perpendicular to its plane, gives (II) and reflection of (II) in the plane of the ring gives (I).

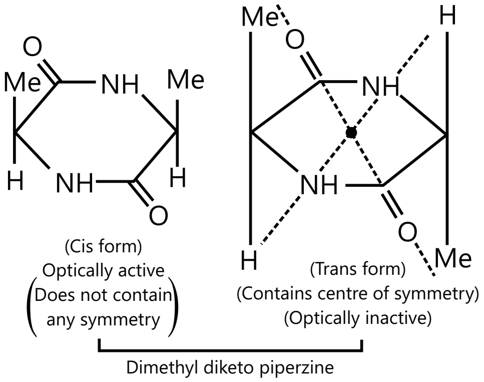
This situation arises n times in the molecule: (I) has two diagonal planes of symmetry.



(I)
(Optically inactive)

(It has 4-fold A, A, of symmetry and two diagonal plane of symetry)

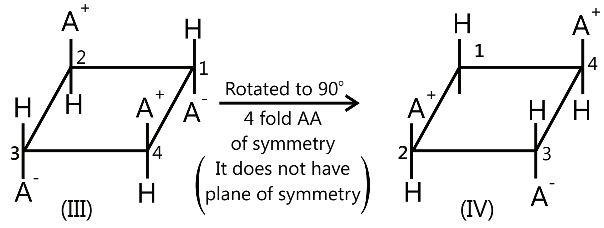
(II)



(Cis form)
Optically active
(Does not contain any symmetry)

(Trans form)
(Contains centre of symmetry)
(Optically inactive)

Dimethyl diketo piperzine



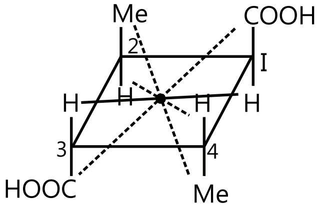
(III)
(Optically inactive)

(IV)

(iii) Centre of symmetry (or centre of inversion): It is defined as a point from which lines when drawn on one side and produced to an equal distance on the other side will meet identical points in the molecule. For example: (It possesses a centre of symmetry, which is the centre of the ring and is therefore optical inactive)

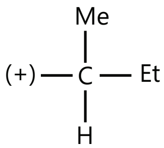
Fig. – Dimethyl cyclobutane–1.3 – dicarboxylic acid (It possess a centre of symmetry, which is the centre of the ring and is therefore optical inactive.

It may be noted that only an even–membered ring can possibly possess a centre of symmetry.

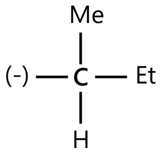


2,4–Dimethyl cyclobutane–1,3–dicarboxylic acid

A^+ and A^- are chiral group, e.g., $A^+ \Rightarrow$ $A^- \Rightarrow$

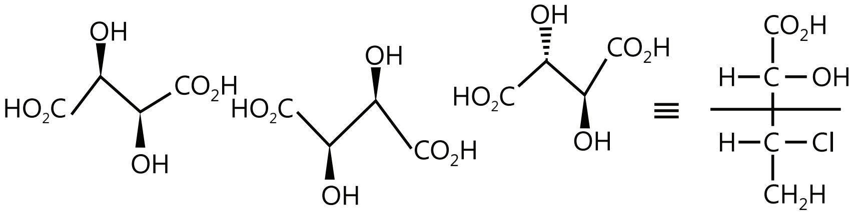


$$(+)-\overset{\displaystyle Me}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Et$$



$$(-)-\overset{\displaystyle Me}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-Et$$

Stereoisomerism in Tartaric acid: Compounds which contain two asymmetric carbon atoms and are of the type Cabc–Cabc exist in only three isomeric forms. Two of these are non–superimposable mirror images of each other and are optically active and the third, a diastereomer of the first two, contains a plane of symmetry, is super imposable on its mirror image, and is not optically active.



I(-) tartaric acid   d(-) tartaric acid   Mesotartaric acid

The inactive diastereomer is usually described as a meso form. As with other examples of diastereomers, the properties of meso forms are different from those of the isomeric mirror–image pairs; for example, mesotartaric acid melts at a lower temperature [140° C] than the d and ℓ isomers [170° C], and is less dense, less soluble in water, and a weaker acid.

5.3 R–S System (Absolute Configuration)

R→ Rectus (Right) S→Sinister (Left)

R→ S nomenclature is assigned as follow:

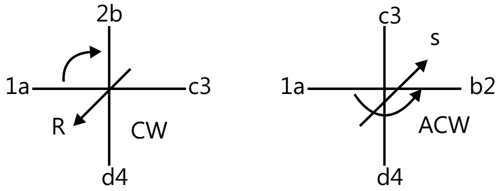
Step I: By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

Step II: If atom/group of minimum priority is present on the vertical line, then

Movement of eyes in clockwise direction = R

Movement of eyes in anticlockwise =S

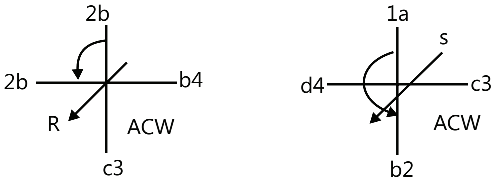
Movement of eyes taken from $1 \rightarrow 2 \rightarrow 3$ through low molecular weight group (if needed)



Step III: If minimum priority group present on the horizontal line, then

clockwise rotation ⇒ S

anticlockwise rotation ⇒ R



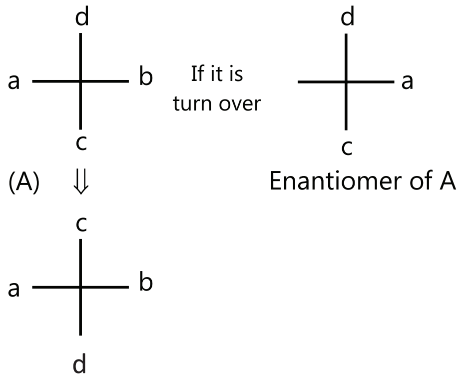
5.4 ENANTIOMERS

Those compounds which are nor superimposable on their mirror image, is called enantiomeric pairs.

Condition → same molecular formu, same structure formul, different configuration.

Some important facts about the fisher projection formulae.

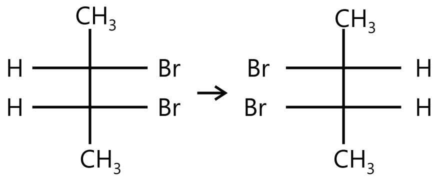
(a) If the fisher projection of stereoisomers is lifted from the plane of paper & turned over, then such an operation will be result in enantiomers of the original compound.



Enantiomer of A

i.e. if either vertical or Horizontal line groups are inverted, then enantiomers of the original compound result.

(b) If more than one chiral centre is present molecule have plane of symmetry



(A) Same as A

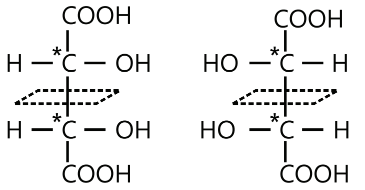
Properties of enantiomers:

(i) Enantiomers have a chiral molecule

(ii) Enantiomers have identical physical properties like b.p.,m.p., refractive index, density etc. They rotate the ppl in opposite direction but to equal extent.

(iii) They have identical chemical properties, However, their reactivity i.e. rate of reaction will be differ if they combine with other optically active reagents.

- All the optically active compounds exist in two or more isomeric forms, which differ from one another in the relative spatial arrangement of atoms or groups.
- These stereoisomers which resemble one another in their chemical reactions and most of the physical properties but differ only in their behaviour towards plane–polarised light are called optical isomers and the phenomenon is called optical isomerism.
- Optical isomers which are non–superimposable mirror images of each other are called enantiomers and the phenomenon is called enantiomerism. The enantiomers have identical physical and chemical properties but rotate the plane of polarised light in opposite directions but to the same extent.
- It may be noted that the necessary and sufficient condition for a molecule to exhibit enantiomerism (and hence optical activity) is chirality or dissymmetry of molecules, i.e., the molecule and its mirror image must be non–superimposable. It may or may not contain chiral or asymmetric carbon atoms.
- Usually, the presence of one or more chiral carbon atoms causes the molecule to show enantiomerism and hence the optical activity but certainly it is not the necessary and sufficient condition. For example, meso–tartaric acid contains two chiral carbon atoms (marked by asterisks) but does not show enantiomerism and is actually optically inactive.



Meso-tartaric acid Optically inactive

Plane of Symmetry (contains a plane of symmetry and hence does not show enantiomerism)

This is because it contains a plane of symmetry which divides the molecule into two equal halves so that one half of the molecule is a mirror image of the other. As a result, meso–tartaric acid and its mirror image are superimposable. In other words, meso–tartaric acid is an achiral or non–dissymmetric or symmetric molecule and hence it does not show enantiomerism or optical activity. Thus, the optical inactivity of meso–tartaric acid is due to internal compensation, i.e., the rotation caused by one half of the molecule is exactly cancelled by an equal and opposite rotation caused by the other half of the molecule.

5.5 Diastereomers

Those compounds which are neither mirror images nor are superimposable on each other, are called as diastereoisomers.

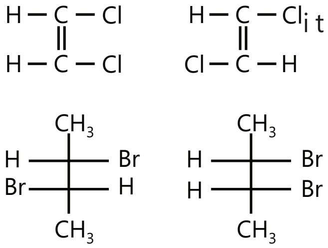
Ex: Cis–trans isomer are configurational isomers but they are not mirror images and are thus, they are said to be diastereomers.

Characterstic of Diastereomers

- Generally optical active, however geometrical isomers are an exception.
- Their physical properties are different like mpt, bpt, density, solubilities & values of specific rotation.
- They can be separated by fractional distillation, fractional crystallization & chromatography etc.
- They exhibit similar but not identical chemical behaviour.

5.6 Meso Compounds

A meso compound is superimposed on its mirror image. It is optically inactive although contains two or more stereocenters. All meso compounds are achiral due to internal compensation.



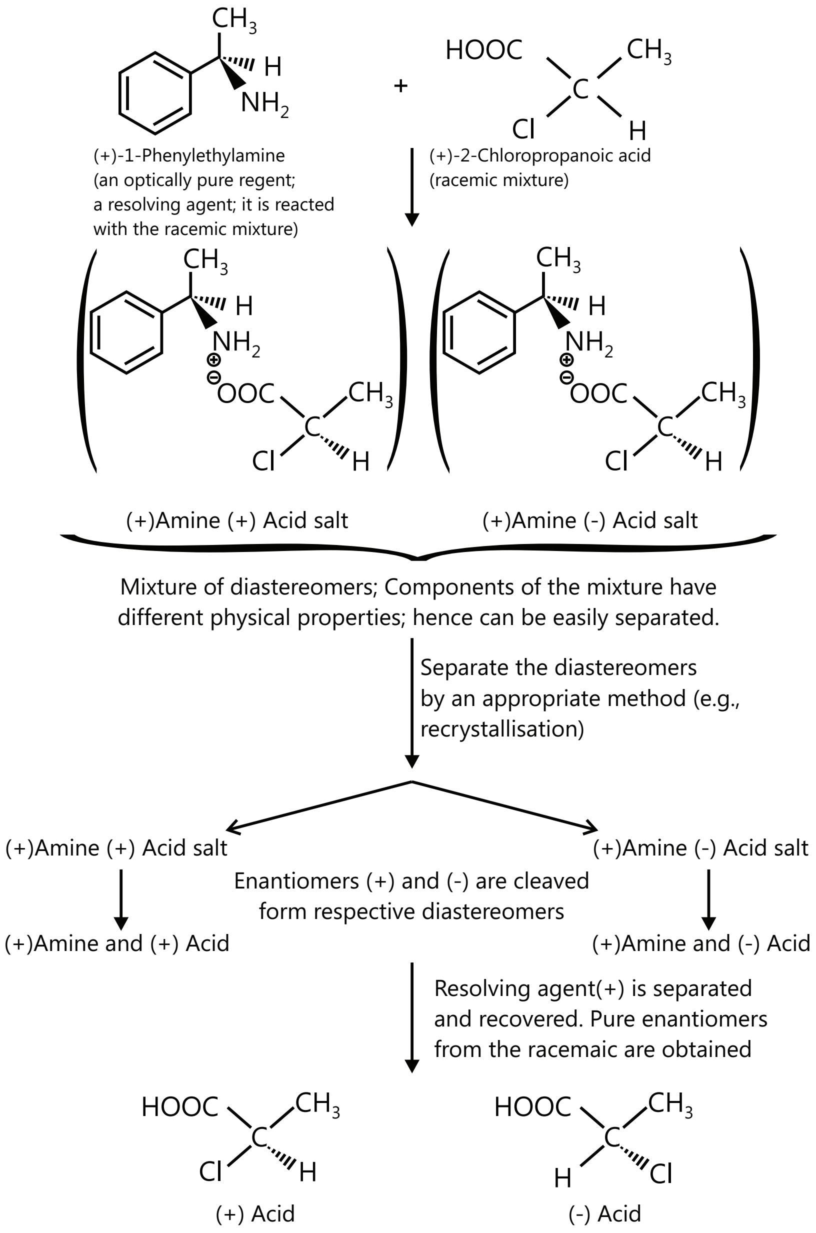
5.7 Racemic Mixture and Optical Resolution

When equal amounts of two enantiomers are mixed together, it gives an optically inactive form called racemic mixture or modification. It is denoted by using the prefix $\pm \text{or} \, \text{dl}$ before the name of compound. For example, if equal amounts of (+) lactic acid and (–) lactic acid are mixed together, we get the racemic or $(\pm)$ lactic acid, which is optically inactive. Evidently, the optical inactivity of a racemic mixture is due to external compensation i.e. the rotation caused by molecules of one enantiomer is exactly cancelled by an equal and opposite rotation caused by the same number of molecules of the other enantiomer.

A racemic mixture can also be obtained chemically. The process by which one enantiomer (+or–) of an optically active compound is converted into a racemic mixture is called racemization. Racemisation can be carried out by heat, light, or chemical reagents. For example, lactic acid and tartaric acid undergo racemisation in the presence of a base.

Resolution of a Racemic Mixture

1. Since a racemic mixture contains equal amounts of two enantiomers, so they can be separated into (+) or (–) enantiomers by a number of methods. The process of separation of a racemic mixture into its (+) and (–) enantiomers is called resolution. Since, the enantiomers have identical physical and chemical properties except towards optically active reagents, they cannot be separated by the usual techniques such as fractional crystallization, fractional distillation, chromatography, etc. Therefore, special methods are used to achieve their separation. Some of these are listed below:
    - Mechanical method.
    - Biological method using enzymes.
    - Chemical methods (by making their diastereomers).
    - Chromatographic separation by using special adsorbents.
2. Diastereomeric method: One of the most common methods is to allow a racemic mixture to react with an enantiomer of some other compound. This changes a racemic form into a mixture of diastereomers which have different solubilitys as well as melting and boiling points. These can be separated from one another by conventional methods of separation of compounds. The separated diastereoisomer is then broken down to give pure enantiomers.



5.8 Racemic Forms and 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 enantiomerically pure sample of (S)–(+)–2–butanol shows a specific rotation of $+13.52^{o}\left[\alpha\right]_{D}^{25} = +13.52^{o}$). On the other hand, a sample of (S)–(+)–2–butanol that contains less than an equimolar amount of (R)–(–)–2–butanol will show a specific rotation that is less than +13.52° but greater than 0°. Such a sample is said to have an enantiomeric excess less than 100%. The enantiomeric excess (ee) is defined as follows:

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

The enantiomeric excess can be calculated from optical rotations:

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

Let us suppose, for example, that a mixture of the 2–butanol enantiomers showed a specific rotation of +6.76°. We would then say that the enantiomeric excess of the (S)–(+)–2–butanol is 50%:

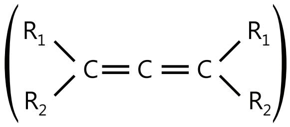
$$\text{Enantiomeric excess } = \frac{+6.76^{o}}{+13.52^{o}} \times 100 = 50\%$$

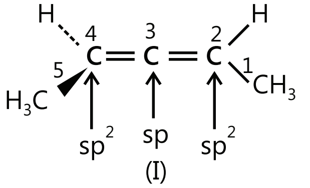
When we say that the enantiomeric excess of this mixture is 50%, we mean that 50% of the mixture consists of the (+) enantiomer (the excess) and the other 50% consists of the racemic form. Since for the 50% that is racemic the optical rotations cancel one another out, only the 50% of the mixture that consists of the (+) enantiomer contributes to the observed optical rotation. The observed rotation is, therefore, 50% (or one–half) of what it would have been if the mixture had consisted only of the (+) enantiomer.

5.9 Chirality in Compounds with No Optical Centres

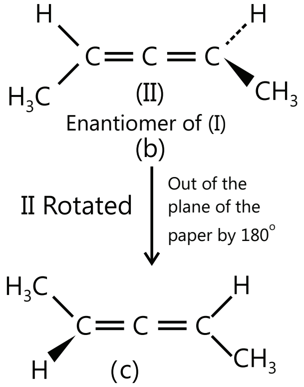
Stereochemistry of C Compounds Not Containing an Asymmetric C Atom (Allenes)

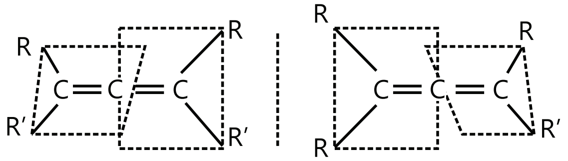
The presence of an asymmetric C atom is not essential for optical activity. The essential requirement is the asymmetry of a molecule as a whole.

Allenes of the type are  Asymmetric and are resolvable, e.g., penta–2,3–diene (I) has no chiral C atoms, yet it is a chiral molecule and has two enantiomers.



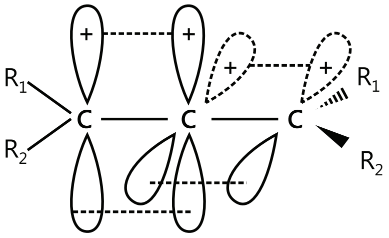
(I)
(Penta-2-3-diene)
(a)

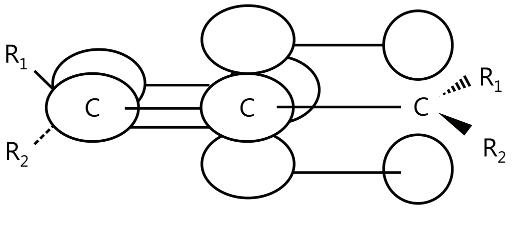




Non-superimposable minor images show cnantiomerism
(d)

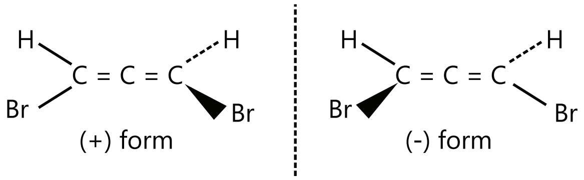
The planes of π– bonds of alkenes are perpendicular to each other. This geometry of π– bonds causes the groups attached to the end C atoms to lie in perpendicular planes. The allenes with different substituents on the end C atoms are chiral. Such allenes do not show cis–trans isomerism. This is an example of a chiral molecule which has two stereocentres at (C^2 and C^4) but no chiral centres.





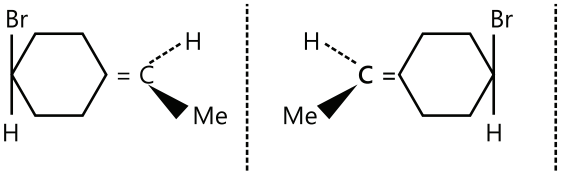
C^3 is sp–hybridised and has one p–orbital overlapping in the xy plane with the p–orbital of C^4, and the other p–orbital overlapping in the xz plane with the p–orbital of C^2 to form two double bonds. The two groups H and CH_3 attached to C^4 are, therefore, in the plane at right angles to the plane of two groups H and CH_3 attached to C^2. The mirror images are not identical as can be shown by rotating one of the structures, (II), 180° out of the plane of paper in order to superpose the H and Me groups in the plane of paper. The groups extending in the front and back of the plane of paper will not match.

(A) 1,3–Dibromo allene also shows optical activity.


(+) form

(-) form

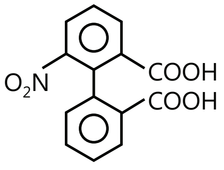
(B) 4–Bromoethenyl cyclohexane also shows enantiomers by considering the ring to be flat.

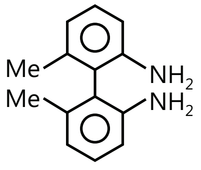


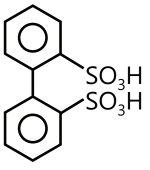
(C) Penta–1,2–diene does not show enantiomers, since terminal C has two H atoms.

$\overset{5}{H_3C}-\overset{4}{H_2C}-\overset{3}{HC}=\overset{2}{C}=\overset{1}{CH_2}$

5.9.1 Optical Activity of Biphenyl Compounds


(I)


(II)

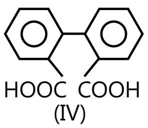

(III)

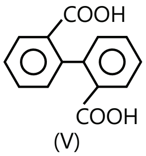
When at least three of the 2,2′,6, and 6′ positions are occupied by sufficiently large groups, free rotation about the single bond joining the two phenyl groups is no longer possible, provided each ring has no vertical plane of symmetry. This restricted rotation gives rise to optical activity due to the molecule being asymmetrical as a whole. Hence, 6–nitrobiphenyl–2, 2′–dicarboxylic acid (I) and 6, 6′–diamino–2, 2′–dimethyl biphenyl (II) have been resolved.

If the substituent groups are large enough, only two groups in the o and o′–positions will cause restricted rotation, e.g. biphenyl–2, 2′–disulphonic acid (III) has been shown to be optically active. So I, II, and III are resolvable.

The cause of restricted rotation is mainly due to the steric effects of groups in the o– and o′ positions (not at m and m′, and p and p′). This type of stereoisomerism arising from restricted rotation about a single bond (and where the stereoisomers can be isolated) is called ATROP ISOMERISM and the isomers are called ATROP ISOMERS.

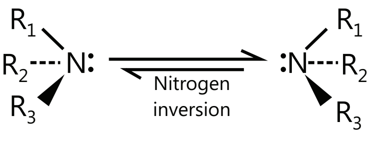
Diphenic acid is not optically active. In configuration (IV), the molecule has a plane of symmetry, and in configuration (V), it has a centre of symmetry. Further, IV is less stable than (V) because of the repulsion between two (–COOH) groups.

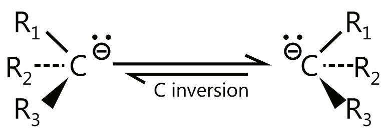

(IV)

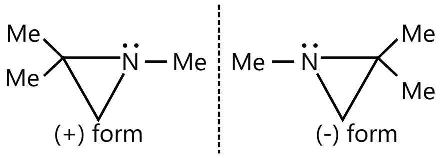

(V)

5.9.2 Optical Activity of t–Amines and t–Carbanion of the type ($R_1R_2R_3N$) and ($R_1R_2R_3C$)

Such an amine and carbanion with a lone pair of e^-s (being considered a fourth different group) are chiral because of their pyramidal geometry, but they are optically inactive. A rapid" Umbrella" type inversion converts either of the enantiomers to a racemic mixture. The energy required for this inversion is very low bond breaking and bond formation. Thus, racemization occurs and enantiomers cannot be isolated. However amine salts are optically active. Nitrogen inversion is not possible e.r $R_1R_2R_3N^{\oplus}H]Cl^{\oplus}$






(+) form

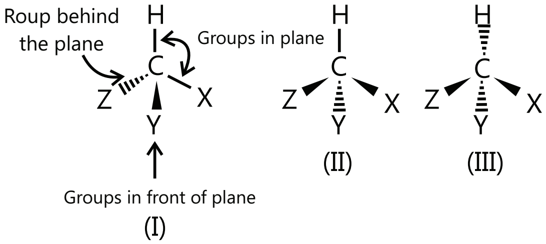
(-) form

1,2,2-Trimethyl aziridine

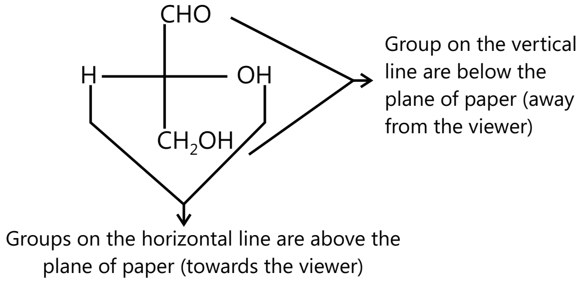
5.9.3 Projection Formulae

(a) Wedge–Dash formula: The configuration of organic molecules can be visualised by three–dimensional (3D) structures, which may be depicted by any of the following representations:

The thick solid (solid wedge) line indicates the bonds lying above the plane of paper (Projecting towards the viewer): thin lines indicate the bonds lying within the plane of paper; while the dotted lines indicate the bonds lying below the plane of paper. Such a representation is called Wedge–Dash formula.

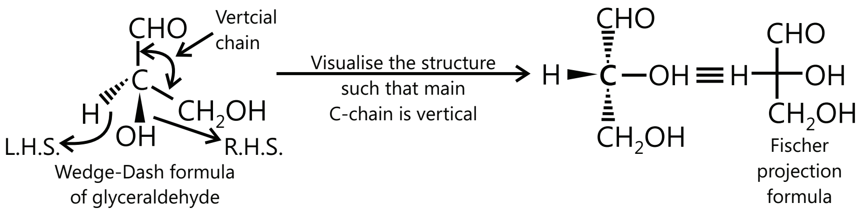


(b) Fischer projection formula: This formula is a standard way of depicting 3D structures in two dimensions (2D). It is useful for simpler representation of the stereochemistry of compounds that contain one or more chiral C atoms. In this formula, the molecule is drawn in the form of a cross with the chiral C atom at the intersection of the horizontal and vertical lines. The horizontal lines represent the bonds directed towards the viewer and the vertical lines away from the viewer. As far as possible, the vertical part of the projection formula thus obtained represents the longest chain of C atoms with the most–oxidised C atoms (mainly the principal functional group) at the top. For example, (–CHO) group in glyceraldehyde, (–COOH) group in lactic acid, etc. The C atoms are then numbered according to the IUPAC nomenclature.



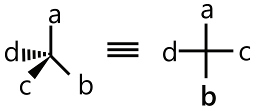
(c) Interconversion of Wedge–Dash formula to Fischer formula: For molecules containing several C atoms; it is customary to orient the molecule in such a way that the C–chain is vertical. Substituents which are at left and right of the viewer are written at left and right, respectively, and other two substituents which appear above and below are written at top and bottom positions.

E.g.



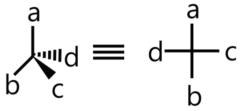
Although the Fischer projections are planar structures, these can be rotated end–for–end on the plane of paper only in multiples of 180° but not 90° at a time. Also, a Fischer projection formula may not be taken out of the plane of paper and flipped over.

(i)



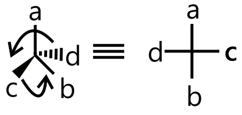
(d on L.H.S.) and (c on R.H.S.)

(ii)



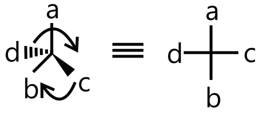
(d on L.H.S.) and (c on R.H.S.)

(iii)



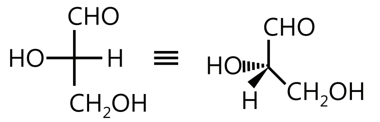
(d on L.H.S.) and (c on R.H.S.)

(iv)



(d on L.H.S.) and (c on R.H.S.)

(d) Interconversion of Fischer formula to Wedge–Dash formula

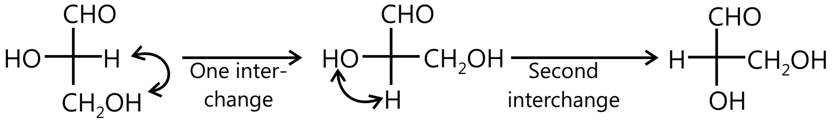


Fischer formula Wegde-Dash formula

When drawing the 3D formulae from the corresponding Fischer formula, it is better to draw the group at the lower end of the vertical line towards R.H.S.

Several Fischer projections can be drawn depending on the bonds drawn in the horizontal and vertical positions, respectively. It is, therefore, necessary to compare two different formulae to check whether they represent the same or different compounds. The following rules must be observed:

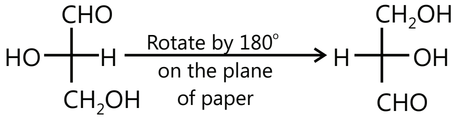
(i) A Fischer projection should not be taken out of the plane of paper and turned over. It would lead to the Fischer projection of the enantiomer, since it changes the configuration at the chiral centre.



(I) (II) (III)

(ii) Even number of interchanges clockwise or anti–clockwise leads to the same stereoisomer, while odd number of interchanges results in an enantiomer. (I) and (III) are equivalent Fischer projections.

(iii) Rotation of Fischer projection by 180° on the plane of paper results in the equivalent Fischer projection.

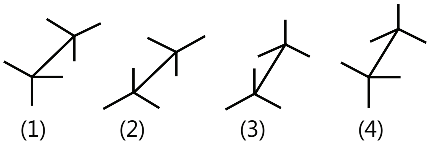


(I) (II)

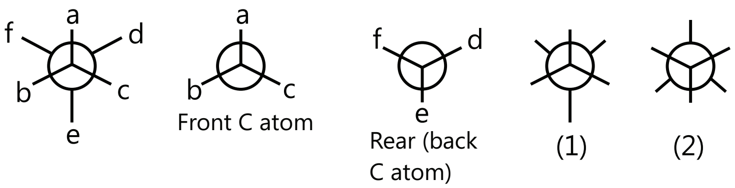
(I) and (II) are equivalent Fischer projections.

E.g. Sawhorse and Newman projection formulae.

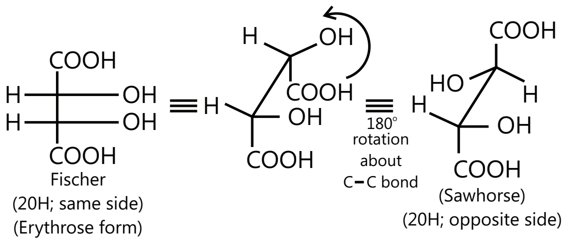
- **Sawhorse projection formula:** This is a simple method of representing three–dimensional formula on paper. The molecule is viewed slightly from above and from the right and projected on the paper. The bond between the two carbon atoms is drawn diagonally and is slightly elongated for clarity. The lower left–hand carbon is considered to be towards the front and the upper right–hand carbon towards the back. It can be represented in various ways as shown, but structure (4) is the most convenient way of representing the Sawhorse projection formula.



- **Newman projection formula:** Newman devised a simple and highly useful method of representing three–dimensional formula on paper. These are called Newman projections after his name. These projection formulae are obtained by viewing the molecule along the bonds joining two carbon atoms. The carbon atom near the eye is represented by a point and the three atoms or groups attached to it by three equally spaced (120o) radii. The carbon atom farther from the eye is designated by a circle and the three atoms or groups attached to it by three equally spaced radial extensions. It can be represented as shown in (1) or (2).

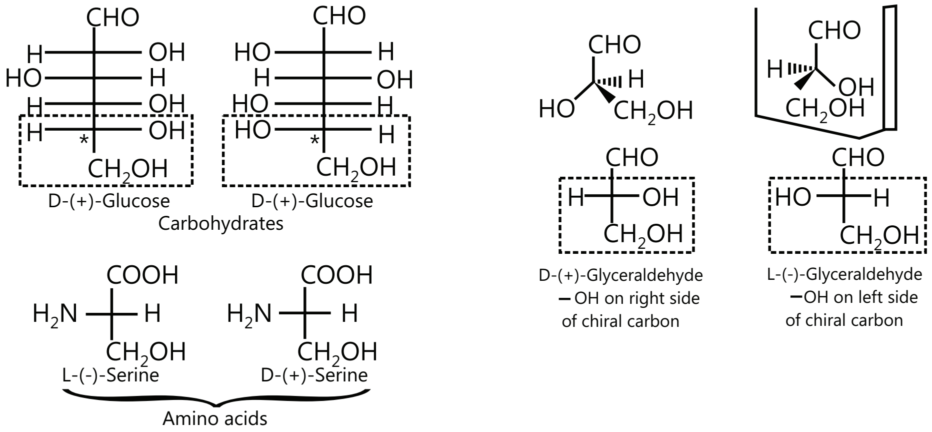


Conversion of Sawhorse and Newman projection formulae in Fischer and vice versa: Groups on the horizontal line in Fischer projection are below the plane of paper and groups on the horizontal lines are above the plane of paper.



5.10 D–L Configuration (Relative Configuration)

D and L: Symbols D and L refer to the relative configuration of the (–OH) group at the penultimate carbon w.r.t. glyceraldehyde taken as a standard. D refers to the (–OH) group which lies on the right hand side and L refers to the (–OH) group which lies on the left hand side.



All molecules which can be chemically related to D–glyceraldehyde are assigned the D configuration and those related to L–glyceraldehyde are all designated the L configuration. It may be noted that there is no direct relation between D and L configurations with d and l or (+) or (–) notations.

The DL system is commonly used in assigning the stereochemistry to carbohydrates and amino acids. For amino acid, (–)–serine has been used as a configurational reference compound, because there is a configurational similarity between L–glyceraldehyde and (–)–serine.

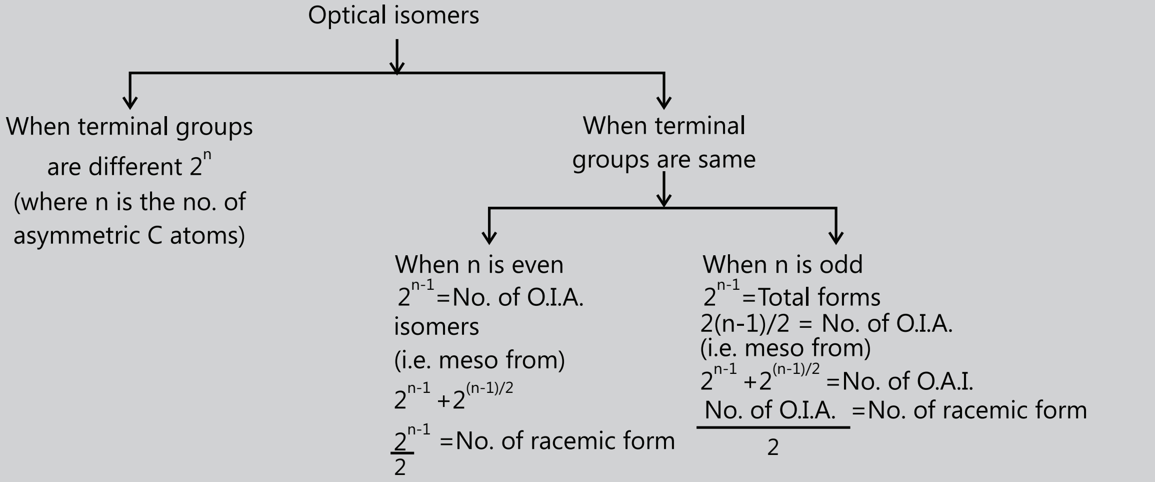
In drawing the Fischer projections while assigning D, L configuration, the Fischer projection of the molecule is drawn in such a way that the main longest chain becomes vertical with carbon–1, the most highly oxidised carbon at the top. For α –amino acids, the configurational arrangement of $–NH_2$, –COOH , R and H groups at the C_a atom is related to that of –OH, –CHO, $–CH_2OH$ and H groups, respectively, of glyceraldehyde (2,3–dihydroxy propanal). Thus, L–glyceraldehyde and $L-\alpha-$ amino acids are said to have the same relative configurations.

MASTERJEE CONCEPTS

- The basic of deciding diastereomers is that the two compounds should be non–superimposable and non–mirror images of each other.
- Mesomers are optically inactive due to internal compensation while diastereomers are inactive due to external compensation.
- Generally anti conformation is the most stable conformation but if intramolecular hydrogen bonding is possible than in some cases the gauche form becomes the most stable.
- Diastereomers have different physical and chemical properties.
- In optical resolution of enantiomers, it is first converted to different diastereomers and then it is separated on the basis of difference in physical and chemical properties.
- If Sawhorse or Newman projection of two molecules are given and a relation is asked then convert it into fisher projection, assign R–S nomenclature and then compare the relation.

MASTERJEE CONCEPTS

Formula for the number of optical isomers



Optical isomers

When terminal groups are different 2^n (where n is the no. of asymmetric C atoms)

When terminal groups are same

When n is even
2^{n-1}=No. of O.I.A. isomers
(i.e. meso from)
$2^{n-1}+2^{(n-1)/2}$
$\frac{2^{n-1}}{2}$ =No. of racemic form

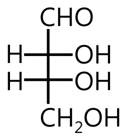
When n is odd
2^{n-1}=Total forms
2(n-1)/2 = No. of O.I.A.
(i.e. meso from)
$2^{n-1}+2^{(n-1)/2}$=No. of O.A.I.
$\frac{\text{No. of O.I.A.}}{2}$ =No. of racemic form

(O.A.I. ⇒ Optically active isomers. O.I.A. ⇒ Optically inactive isomers)

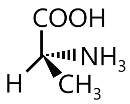
Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 14: Specify the configuration of following compounds in D or L. **(JEE MAIN)**

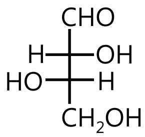
(i)



(ii)



(iii)



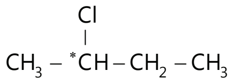
Sol: (a) D configuration, OH is at right.: (b) L– (Convert to fischer),–NH_2 is on the left) (c) L configuration (–OH on C–3 is on the left side).

Illustration 15: b. Which of the following are optically active compounds and why?

(i) Butan–1–ol (ii) 2–Chlorobutane (iii) Lactic acid (iv) 3–Chloropentane **(JEE MAIN)**

Sol: Compound containing chiral carbon (carbon bearing four different group is referred as chiral carbon) shows optical activity and are said to be optically active compound. From the given name write down the chemical structure of the compound and check whether the compound contains any chiral carbon and accordingly write down the answer.

The structural formulas of the given compounds are as under:

Butan–1–ol is not optically active since it does not contain any asymmetric carbon atom. Hence, the molecule is achiral.	$CH_3CH_2CH_2CH_2OH$ (Butan–1–ol)
Is a chiral molecule, since it contains an asymmetric carbon atom marked with an asterisk. Hence, it is optically active.	 $CH_3-\overset{\overset{\displaystyle Cl}{|}}{^{*}CH}-CH_2-CH_3$

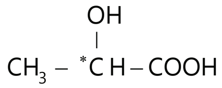
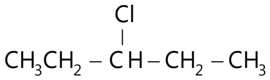
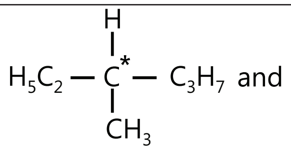
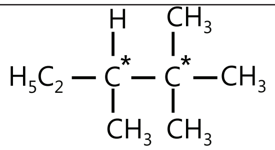
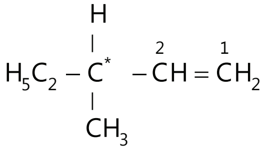
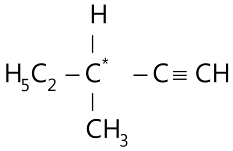
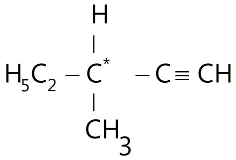
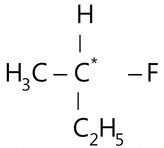
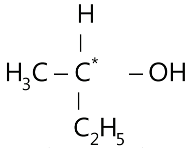
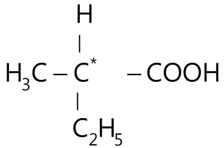
Contains one asymmetric carbon atom and its molecule is chiral. Thus, it shows optical activity.	 $\overset{\text{OH}}{\underset{\vert}{}}$ $CH_3-{}^{*}\overset{\vert}{C}H-COOH$
Is a symmetrical molecule since it does not contain an asymmetric carbon atom. Hence, it does not show optical activity.	 $CH_3CH_2-\overset{Cl}{\overset{\vert}{C}}H-CH_2-CH_3$

Illustration 16: Write the name and structure of the following optically active compounds with lowest molecular weight.

(i) alkane (ii) alkene (iii) alkyne (iv) unsaturated hydrocarbon

(v) alkyl halide (vi) alcohol (vii) acid (viii) amine **(JEE ADVANCED)**

Sol:

i.	Optically active alkane with the lowest molecular weight:	 $H_5C_2-\overset{H}{\underset{CH_3}{C^*}}-C_3H_7$ and  $H_5C_2-\overset{H}{\underset{CH_3}{C^*}}-\overset{CH_3}{\underset{CH_3}{C^*}}-CH_3$ 3-Methyl hexna 2,3-Dimethyl pentane
ii.	Optically active alkene with lowest molecular weight:	 $H_5C_2-\overset{H}{\underset{CH_3}{C^*}}-\overset{2}{C}H=\overset{1}{C}H_2$ 3–Methyl hexane
iii.	Optically active alkyne with the lowest molecular weight:	 $H_5C_2-\overset{H}{\underset{CH_3}{C^*}}-C\equiv CH$ 3–Methyl hexane
iv.	Optically active unsaturated hydrocarbon with the lowest molecular weight:	 $H_5C_2-\overset{H}{\underset{CH_3}{C^*}}-C\equiv CH$ 3–Methyl hexane
v	Optically active alkyl halide with the lowest molecular weight:	 $H_3C-\overset{H}{\underset{C_2H_5}{C^*}}-F$ (2–Flurobutane)
vi	Optically active alcohol with the lowest molecular weight:	 $H_3C-\overset{H}{\underset{C_2H_5}{C^*}}-OH$ (Butan–2–ol)
vii	Optically active acid with the lowest molecular weight:	 $H_3C-\overset{H}{\underset{C_2H_5}{C^*}}-COOH$ (2–Methyl butanoic acid)

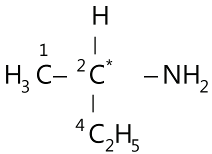
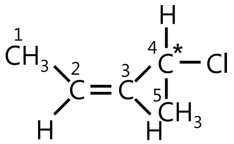
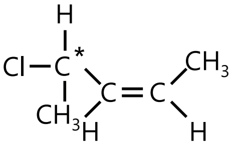
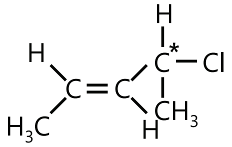
viii	Optically active amine with the lowest molecular weight:	 $\overset{1}{H_3C}-\overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle {}^{4}C_2H_5}{\mid}}{{}^{2}C^{*}}}-NH_2$ (Butan–2–amine)

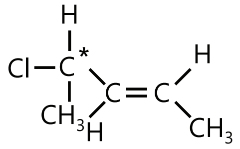
Illustration 17: How many stereoisomers are possible for the compound $CH_3CH = CHCHClCH_3$? **(JEE ADVANCED)**

Sol: One double bond, two GI, and one asymmetric C atom, two optical isomers, total four.


(I) (+) cis-4-Chloro-pent-2-ene


(II) (-) cis-4-Chloro-pent-2-ene

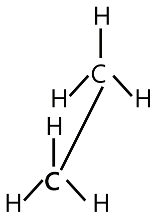

(III) (+) trans-4-Chloro-pent-2-ene

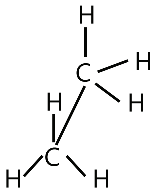

(IV) (-) trans-4-Chloro-pent-2-ene

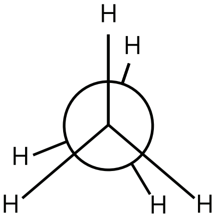
(I) and (II), and (III) and (IV) are enantiomers; (I) and (III), (II) and (IV), (I) and (IV), and (II) and (III) are diastereomers.

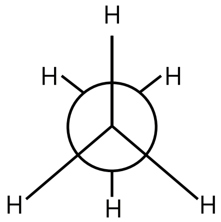
6. CONFORMATIONAL ISOMERISM

Different non–identical arrangement of atoms or group in a molecule that result by the rotation about a single bond and that can easily be reconverted at room temperature are known as conformational stereoisomers of conformers

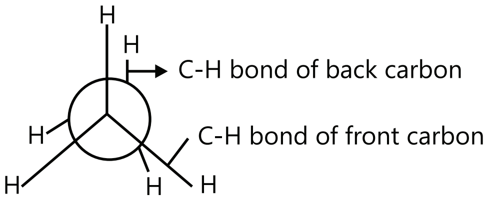

Eclipsed Sawhorse projection


Staggered Sawhorse projection

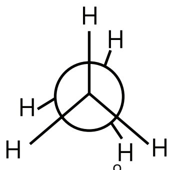

Eclipsed conformation

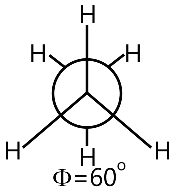

Staggered conformation

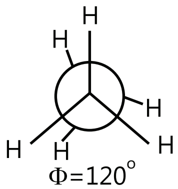
Note: In Newman projection of ethane both carbon atoms represented by circle but one behind the other so that only the front carbon is seen the C–H bond of the front carbon are depicted from the centre of the circle while C–H bonds of back carbon are drawn from the circumference of circle as

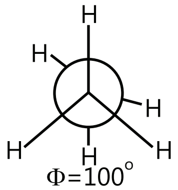


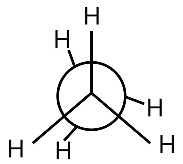
Conformation of ethane:


$\Phi=0^\circ$
(I)

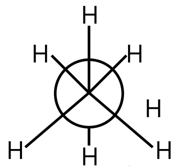

$\Phi=60^\circ$
(II)


$\Phi=120^\circ$
(III)

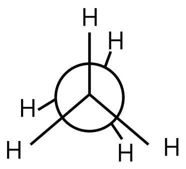

$\Phi=100^\circ$
(IV)



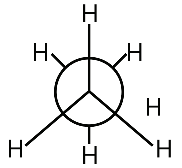
$\Phi=240^{\circ}$
(V)



$\Phi=300^{\circ}$
(VI)



Eclipsed conformation



Staggered conformation

(i) Ethane molecule contains an infinite number of conformers.

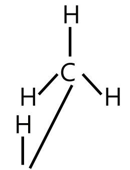
(ii) The extreme conformation of ethane molecules are staggered and eclipsed.

(iii) The energy of staggered conformation is lower than eclipsed conformation by 2.8kcal/mole(11.7kJ/mole).

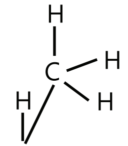
(iv) Staggered conformation is more stable than the eclipsed conformation.

(v) The mixture contains 99% staggered conformation and 1% eclipsed conformation.

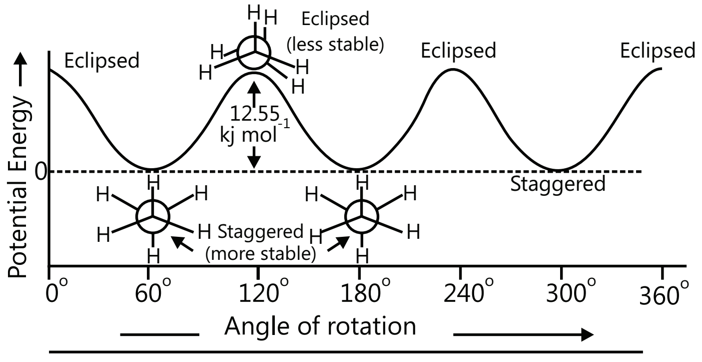
(vi) Eclipsed and staggered conformations are not isolated from the mixture.



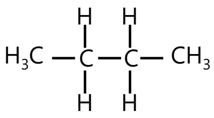
Eclipsed Sawhorse projection



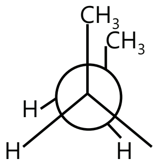
Staggered Sawhorse projection



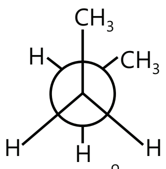
Conformation of Butane:



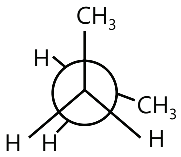
$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-CH_3$$



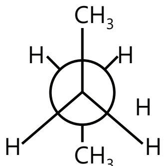
$\Phi=0^{\circ}$
(I)



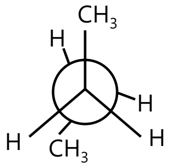
$\Phi=60^{\circ}$
(II)



$\Phi=120^{\circ}$
(III)



$\Phi=180^{\circ}$
(VI)



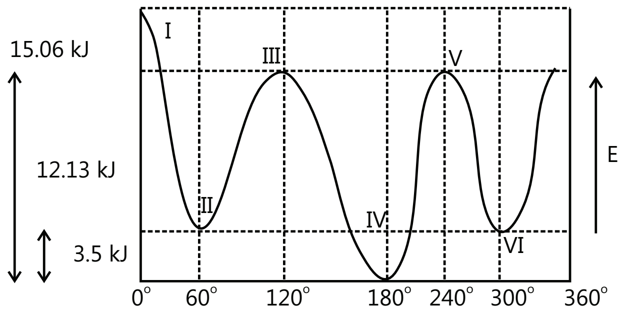
$\Phi=240^{\circ}$
(V)

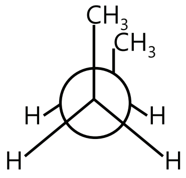
(I) = Fully eclipsed (CH, group eclipsed by CH, group)

(II) = (IV) = Gauche (Staggered)

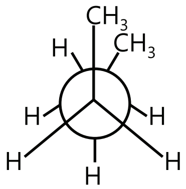
(IV) = Anti or trans (Staggered)

(V) = (V) = Partial eclipsed (CH, group eclipsed by H)

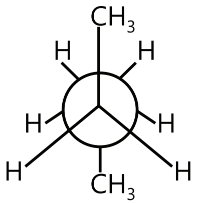




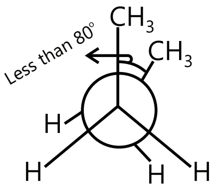
Eclipsed
(A)



Gauche
(B)



Staggered (anti)
(C)



Staggered (anti)
(D)

If the dihedral angle is less than 60, it is known as skew. Here stability of (C)>(B)>(D)>(A).

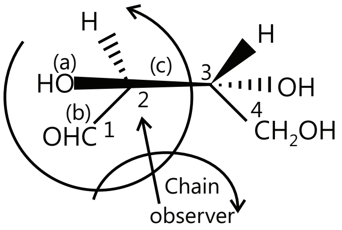
Partial eclipsed stability > Fully eclipsed stability.

MASTERJEE CONCEPTS

- Two important factors that determine the stability of the conformers are– Torsional strain and Van der Waals strain.
- Generally, anti– conformation is the most stable conformation but if intramolecular hydrogen bonding is possible than in some cases the gauche form becomes the most stable.

Rohit Kumar (JEE 2012, AIR 79)

Illustration 18: Assign R and S configuration of the following compound.

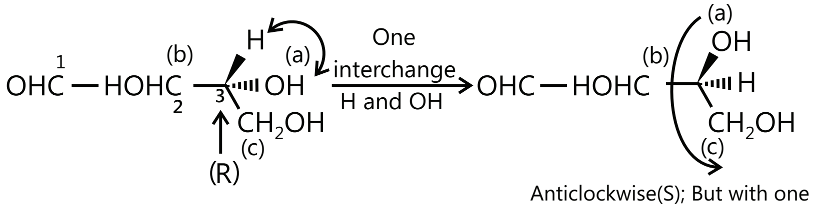


Sol: Priority order at C–2:

$$\underset{\substack{\downarrow\\ a}}{-OH} > \underset{\substack{\downarrow\\ b}}{CHO} > -\underset{\substack{\downarrow\\ c}}{CH(OH)CH_2OH} > -\underset{\substack{\downarrow\\ d}}{H}$$

First assign R/S at C–2, here, the lowest ligand is in the plane (i.e. on the dotted line). Priority sequence is anticlockwise, hence the configuration at C–2 is S.

Priority order at C – 3: –OH > –CHOHCHO. Here, H is not on the dotted line, so make one interchange of H and –OH so that –OH is projected away from the observer.



Anticlockwise(S); But with one interchange, the configuration changes from (S) to (R)

Illustration 19: Give the effect of the configuration of (S)–2–bromo butane on performing the following operations:

a. Exchanging ligands across the horizontal bond.

b. Exchanging ligands across the vertical bond.

c. Making both switches (A) and (B).

d. Exchanging a horizontal and vertical ligand.

e. A 180° vertical or horizontal rotation outside the plane of paper.

f. A 90° rotation on the plane of paper. **(JEE ADVANCED)**

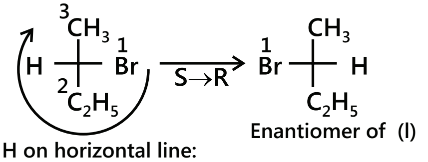
Sol: a. Priority order $-Br > -C_2H_5 > -CH_3 > -H$.

c. Thus, there is no change in the configuration when both switches (A) and (B) are made.

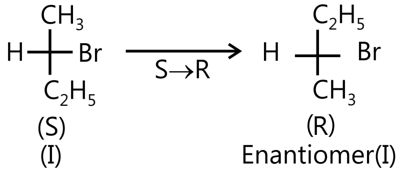
e. This type of operation is not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer.

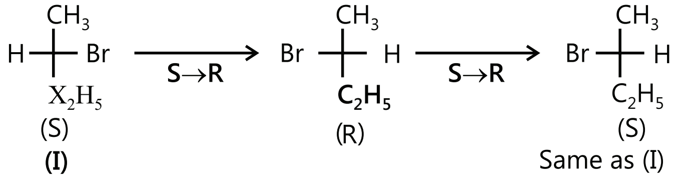
f. Those ligands formerly pointing towards the observer would change to behind the paper.

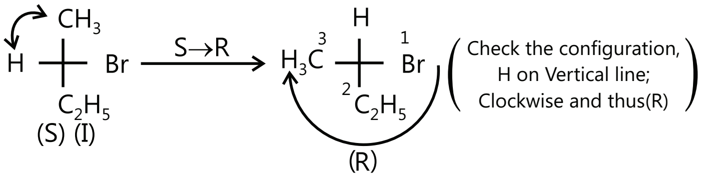
Priority order : $— Br > — C_2H_5 > — CH_3 > — H$.



H on horizontal line:
Clockwise (R);
Change (R) to (S);
(S)-2-Bromobutane (I)





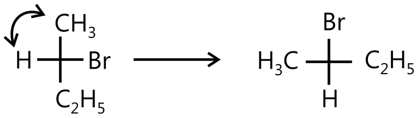


(Check the configuration, H on Vertical line; Clockwise and thus(R))

e. This type of operation is also not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer.

Those ligands formerly pointing of paper to projecting towards the observer would change to behind the paper.

f. This type of operation is also not allowed in Fischer projection. F



(I) (I′)

POINTS TO REMEMBER

- **Chain Isomerism:** Chain isomers possess same but different number of carbon chains (straight or branched).
- **Position Isomerism:** Compounds having same molecular formula but the position of functional group, multiple bond or branches along the same chain length of carbon atoms varies.
- **Functional Group Isomerism:** These isomers have same molecular formula but different Functional groups. Such compounds are called functional group isomers.
- **Metamerism:** This type of Isomerism is due to different position of poly valency functional group in molecule Members belong to the same homologous series.
- **Ring chain Isomerism:** Such isomerism arises due to difference of carbon–chain or ring.
- **Cis–Trans Isomers:** The isomer (I) in which similar groups or atoms lie on the same side of the double bond is called cis–isomer, whereas the isomer (II) in which the similar atoms or groups lie on the opposite side of the double bond is called the trans–isomer.
- **E–Z Isomerism: E–Form:** When two same priority group present on the opposite side of double bonded is known Z–form and when same priority group present same side of double bond is called Z–form.
- **Racemic Forms and Enantiomeric Excess:**

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

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

$$\text{Specific Rotation, } \left[\alpha\right]_{D} = \frac{\theta}{I \times C}$$

- **Optical activity in Allenes:** The planes of π–bonds of allenes are perpendicular to each other. This geometry of π–bonds causes the groups attached to the end C atoms to lie in perpendicular planes. The allenes with different substituents on the end C atoms are chiral.
- **Optical Activity of Biphenyl Compounds:** When at least three of the 2,2′,6, and 6′ positions are occupied by sufficiently large groups, free rotation about the single bond joining the two phenyl groups is no longer possible, provided each ring has no vertical plane of symmetry.

  This restricted rotation gives rise to optical activity due to the molecule being asymmetrical as a whole.

  If the substituent groups are large enough, only two groups in the o and o′–positions will cause restricted rotation.