B.Sc. I

Paper II Organic Chemistry

OPTICAL ISOMERISM

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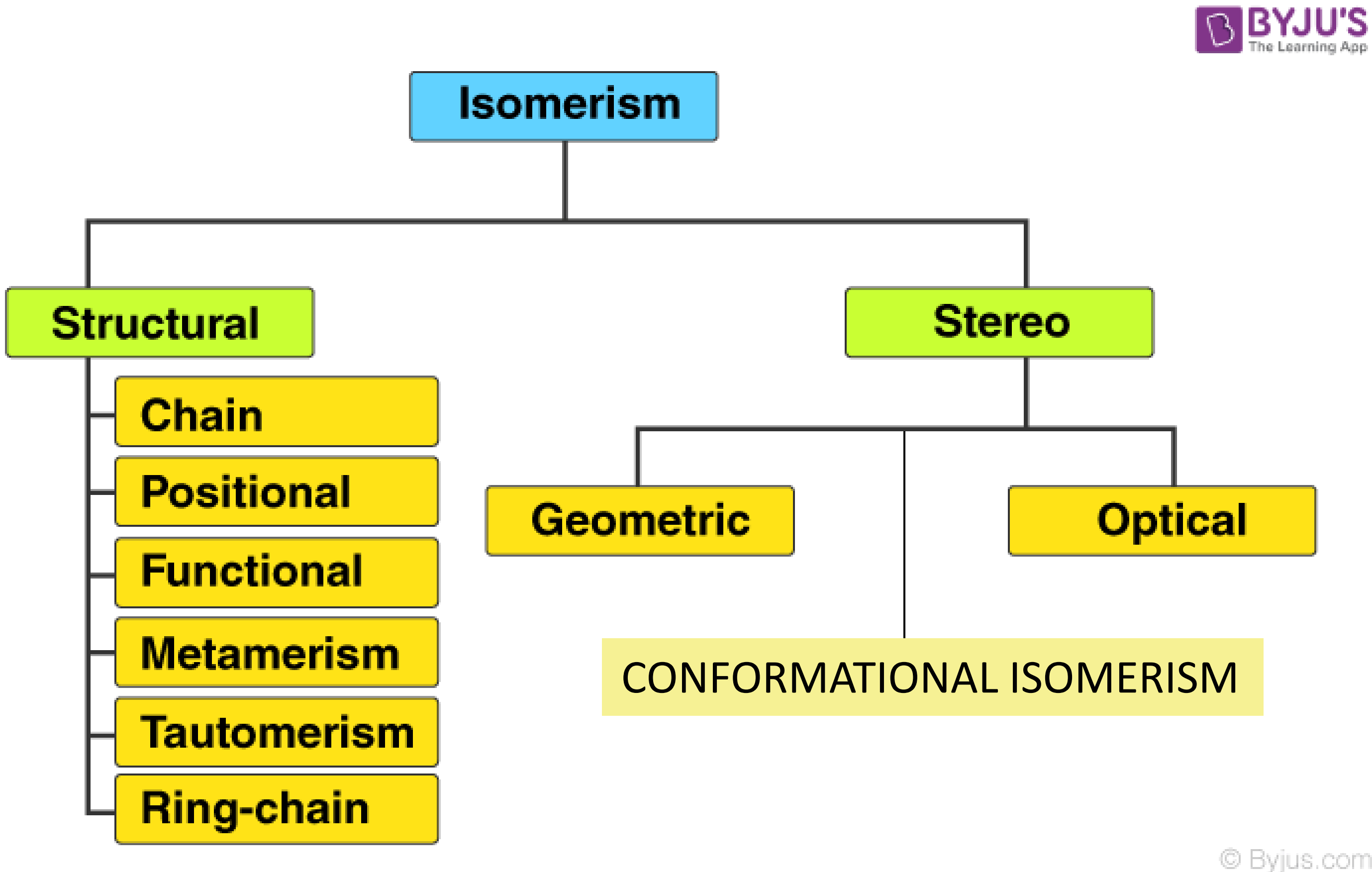
CONCEPT

The word “isomer” is derived from the Greek words “isos” and “meros”, which mean “equal parts”.
This term was coined by the Swedish chemist Jacob Berzelius in the year 1830.
Isomerism is the phenomenon in which more than one compounds have the same chemical formula but different chemical structures.
Isomers have same molecular formulae but different physical and chemical properties.
The arrangement of atoms in the molecule are also different
Therefore, the compounds that exhibit this property are known as isomers.

TYPES OF ISOMERISM

There are two primary types of isomerism, which can be further categorized into different subtypes. These primary types are

1. Structural Isomerism
2. Stereoisomerism.



TYPES OF ISOMERISM

Structural isomerism

This is commonly referred to as constitutional isomerism. The functional groups and the atoms in the molecules of these isomers are linked in different ways. Different structural isomers are assigned different IUPAC names since they may or may not contain the same functional group.

Stereoisomerism

This type of isomerism arises in compounds having the same molecular and structural formula but different orientations of the atoms belonging to the molecule in three-dimensional space. ‘Stereos’ means SPACE.The compounds that exhibit stereoisomerism are often referred to as stereoisomers.

STEREOISOMERS – OPTICAL ISOMERISM

Optical isomerism is a type of stereoisomerism.
Two or more than two compounds which have identical molecular formula but differ in their configuration in space (three dimensional view) – that is the arrangement of an atom or group of atoms is different within the molecules. Such compound groups are called Stereoisomers.

Isomers are those compounds which have the same molecular formula but different bonding arrangement/location and type of group of atoms.
In a stereoisomer, both molecular formula and bonding arrangement of atoms are the same. However, they have different spatial (three dimensional) arrangement of atoms.

The isomers display identical characteristics in terms of molecular weight as well as chemical and physical properties. However, they differ in their effect on the rotation of polarized light.
Alternatively, it can also be found in substances that have an asymmetric carbon atom.

OPTICAL ACTIVITY IN OPTICAL ISOMERISM

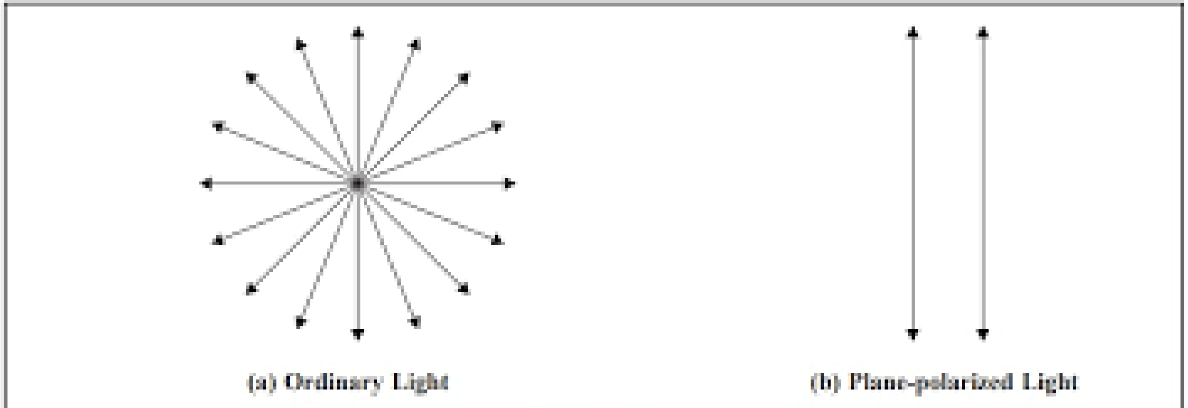
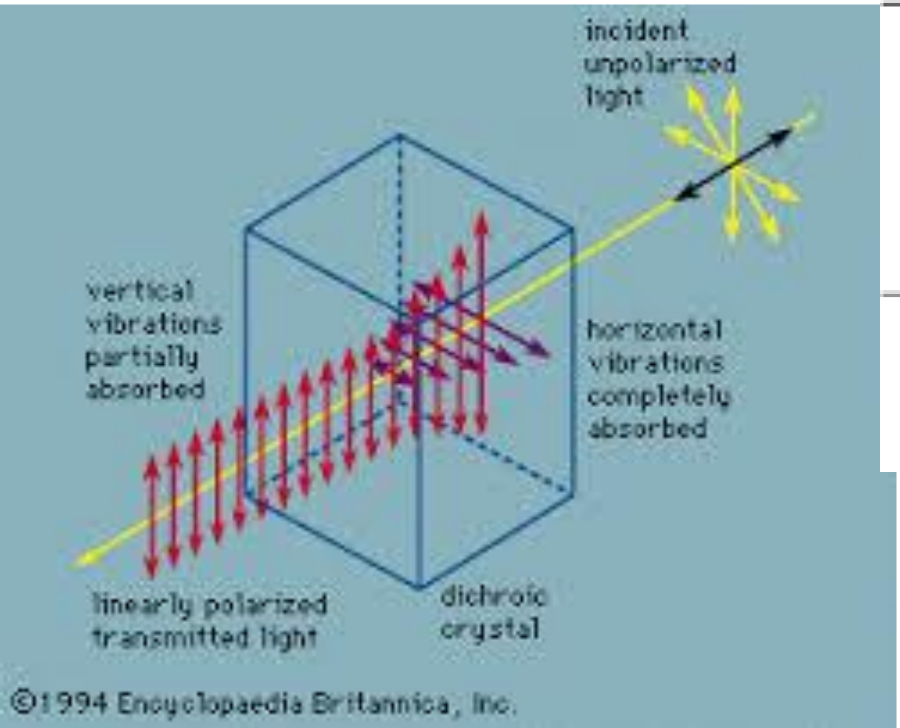
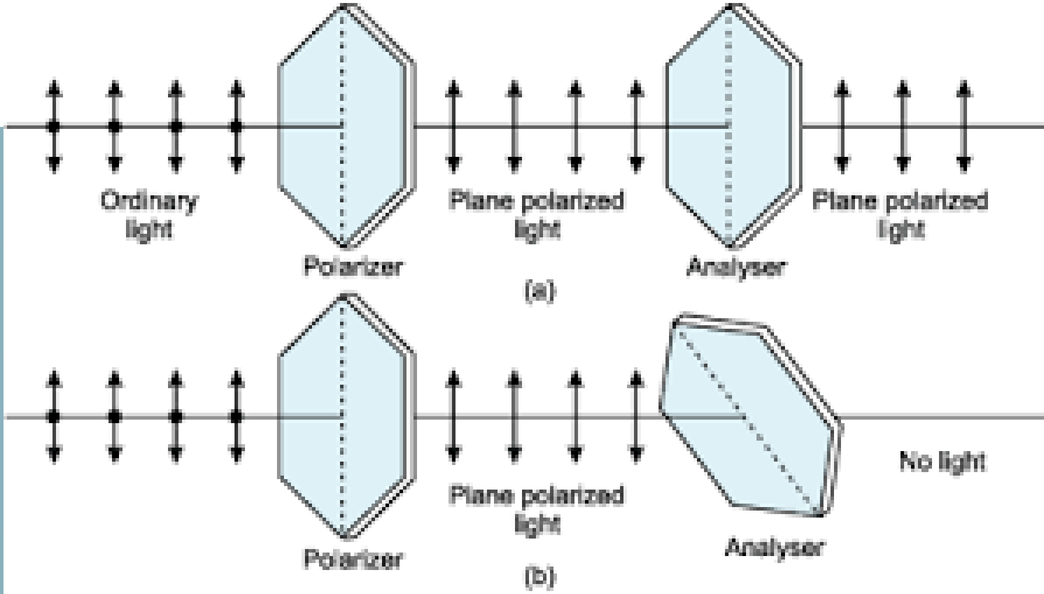


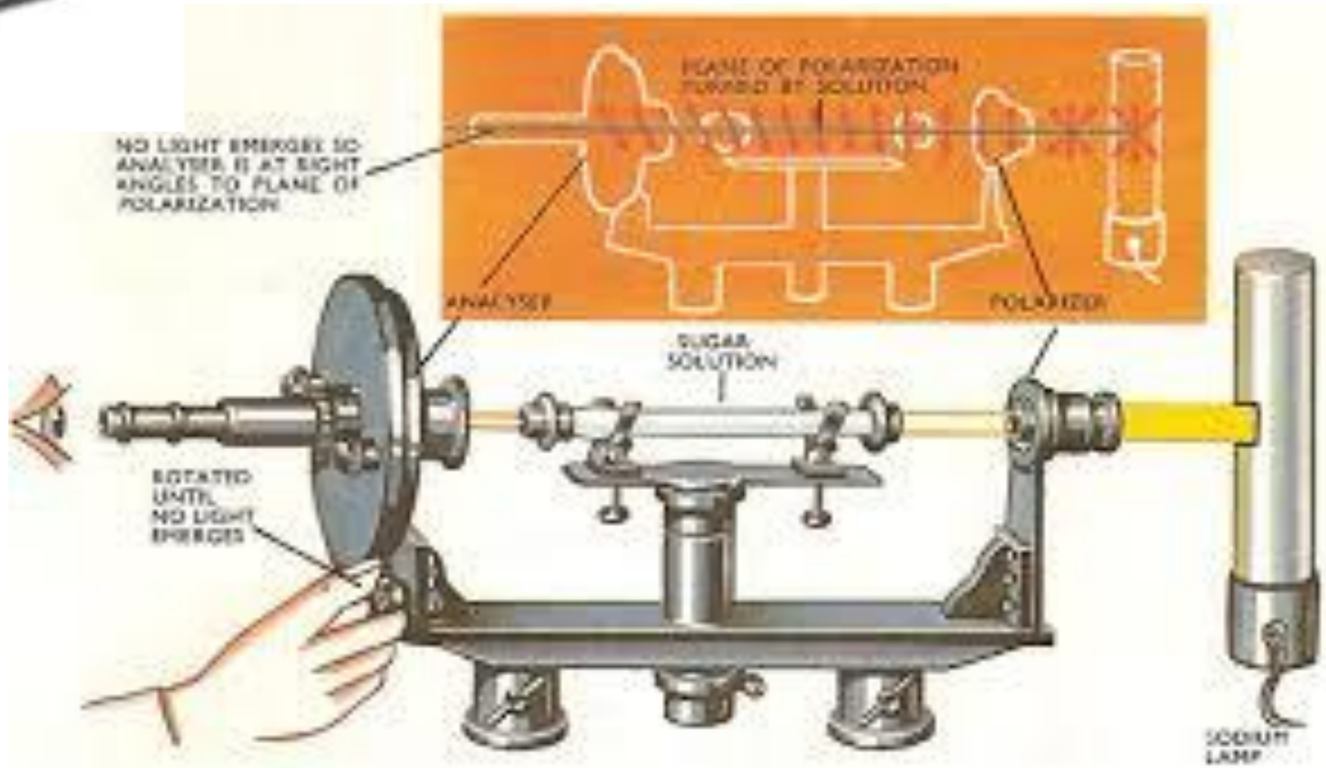
Figure 19.1



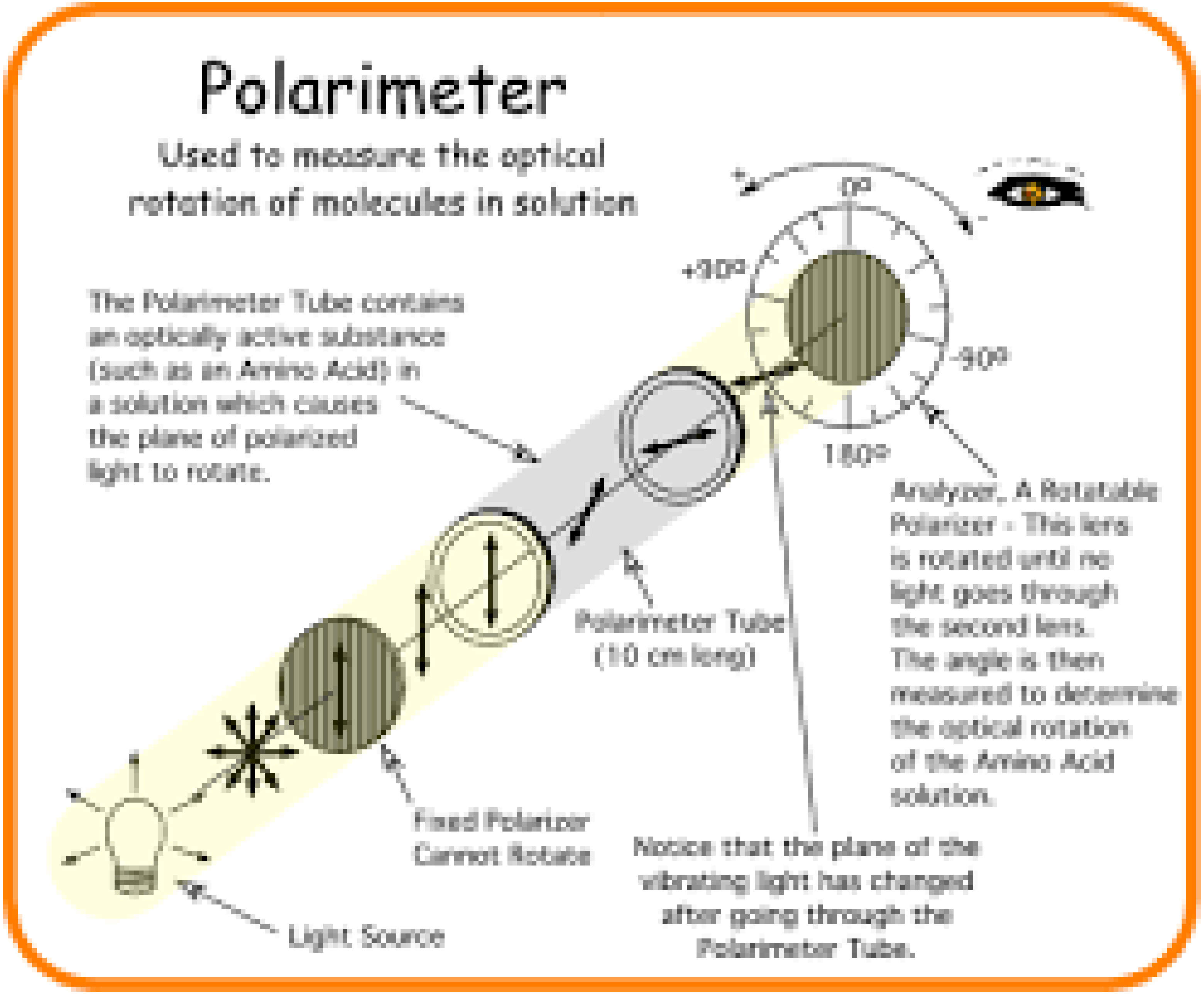


OPTICAL ACTIVITY IN POLARIMETER

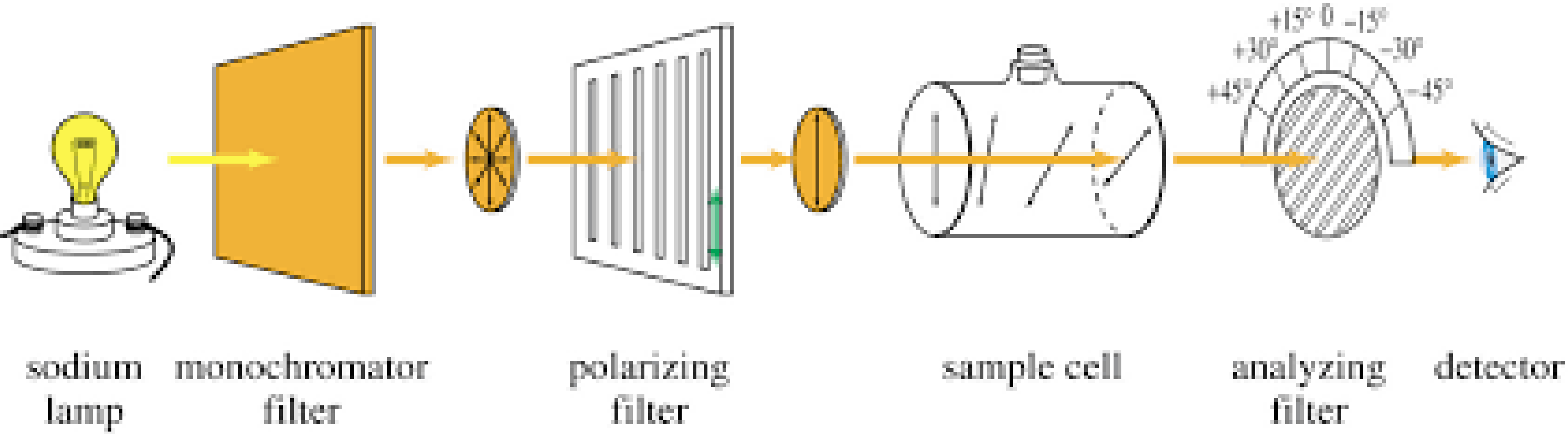
SODIUM LAMP POLARIMETER



OPTICAL ACTIVITY IN POLARIMETER



OPTICAL ACTIVITY IN POLARIMETER



MAGNITUDE OF ROTATION DEPENDS UPON

1. Concentration of solution
2. Nature of solvent
3. Nature of compound
4. Length of sample cell
5. Wavelength of light used
6. Temperature of the solution

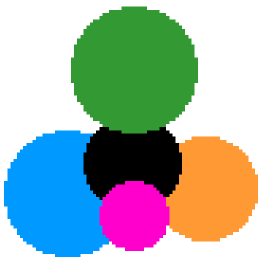
The substances which rotate the plane polarized light are called optically active compounds.

The substance which rotates the PPL towards Right is DEXTRO rotatory.

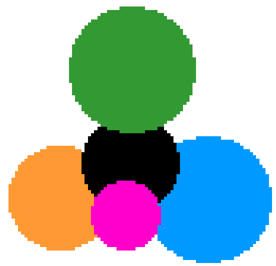
The substance which rotates the PPL towards Left is LEAVO rotatory.

CAUSE OF COPTICAL ACTIVITY

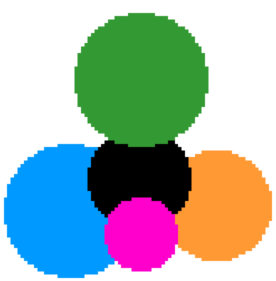
To determine whether the compound is optically active or not, we have to first see whether the carbon is attached to four different groups or not.



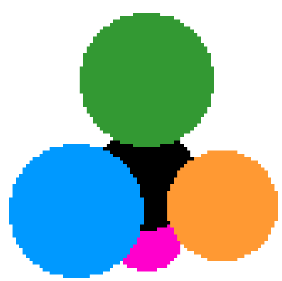
A



B



A

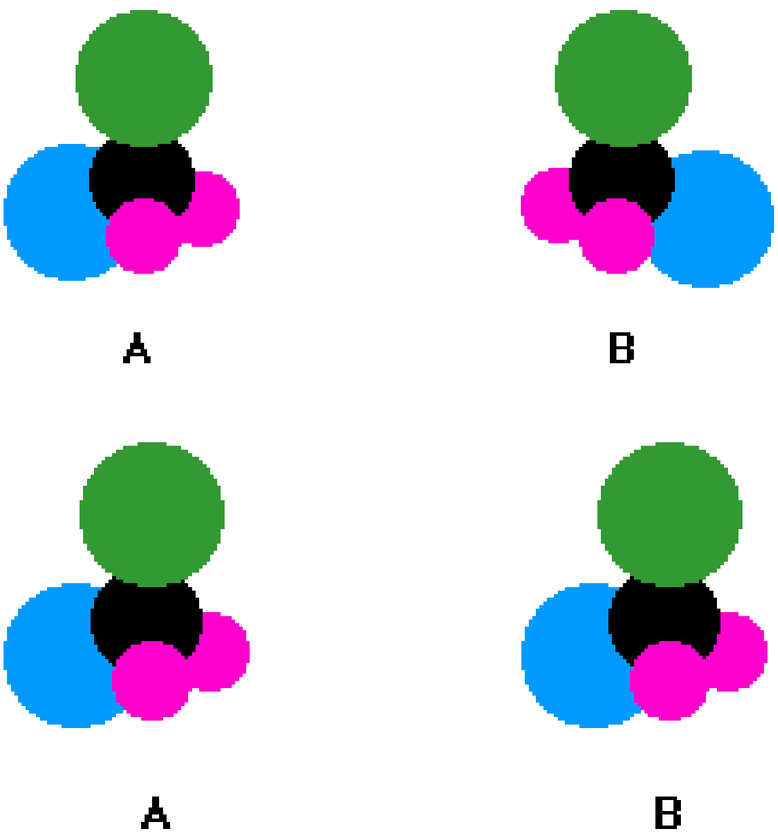


B

These two models have the same bonding arrangement of the atom but a different spatial arrangement. From the above model of A and B, it is clear that the arrangement of the blue and orange group in space is different. Is it possible to align model A exactly like model B by rotating it? The answer is no. The reason for that is if we rotate A the arrangement of other group gets disturbed as shown below.

CAUSE OF COPTICAL ACTIVITY

below-We cannot make the spatial arrangement of A and B exactly the same by rotating them in any direction. A and B is said to be non-superimposable because we cannot make them look exactly.



If a molecule containing two same groups attached to a central carbon atom is rotated as shown in the figure below. Rotating molecule A by 180 degrees will give the same arrangement of the atom as that of B as shown below.

From the above explanation, we can conclude that the compound will be optically active only if all the group attached to the central carbon atom are different.

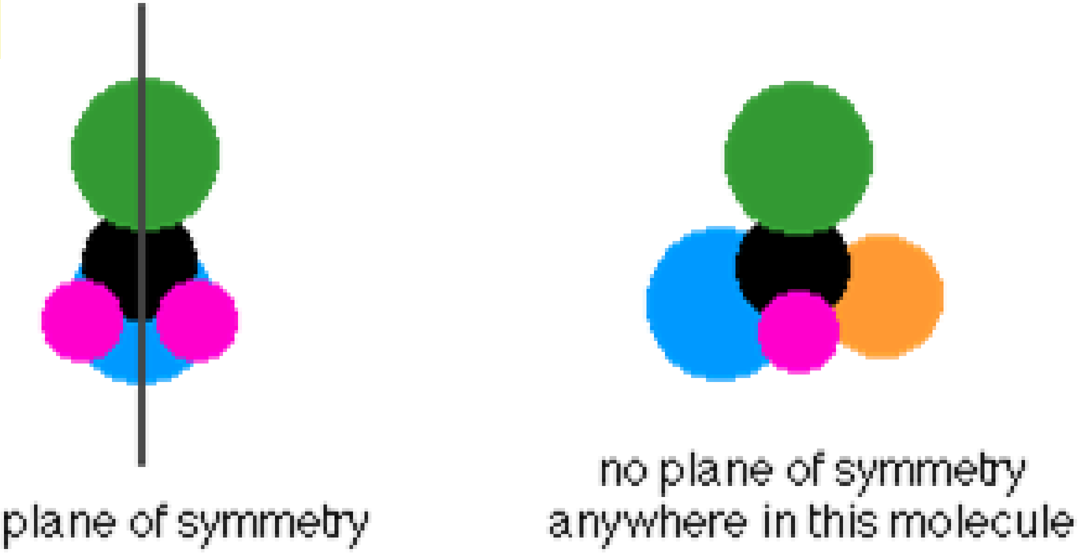
ELEMENT OF SYMMETRY

<u>Chiral And Achiral Molecules</u>

The difference between chiral and achiral molecules can be explained on the basis of the plane of symmetry. If all the attached group to the central carbon atom are different then there is no plane of symmetry. Such a molecule is known as a chiral molecule.

If all the group attached to the central carbon atom are not different then there exist plane of symmetry. Such molecules are called achiral molecules.

It is mandatory that only molecule having chiral centre will show optical isomerism.

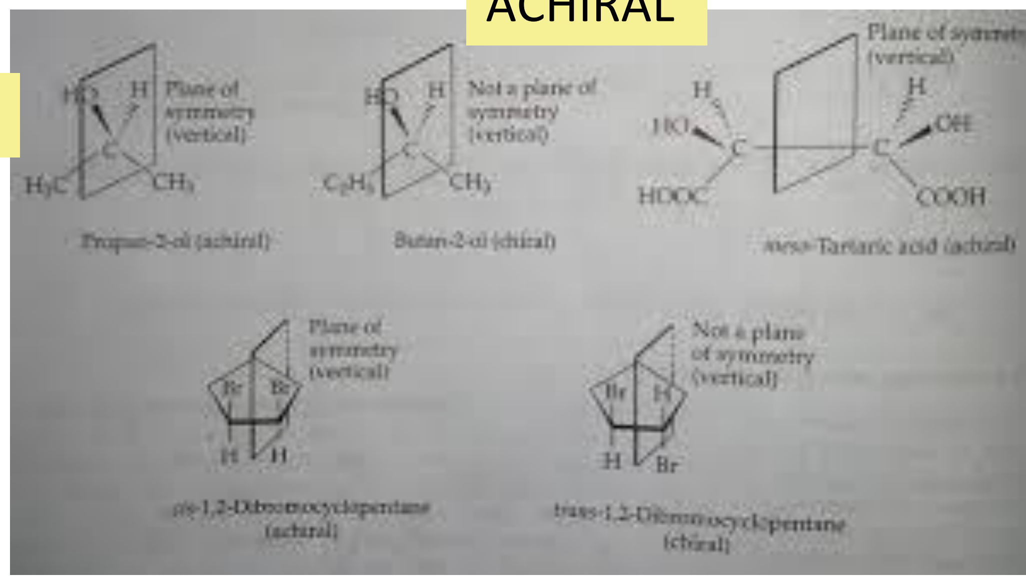


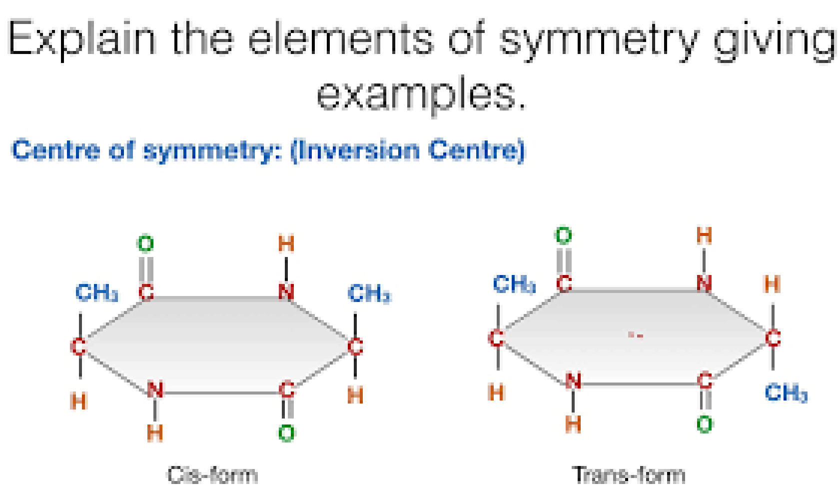
ELEMENT OF SYMMETRY

If there are two groups the same attached to the central carbon atom, the molecule has a plane of symmetry. If you imagine slicing through the molecule, the left-hand side is an exact reflection of the right-hand side. A molecule which has no plane of symmetry is described as chiral

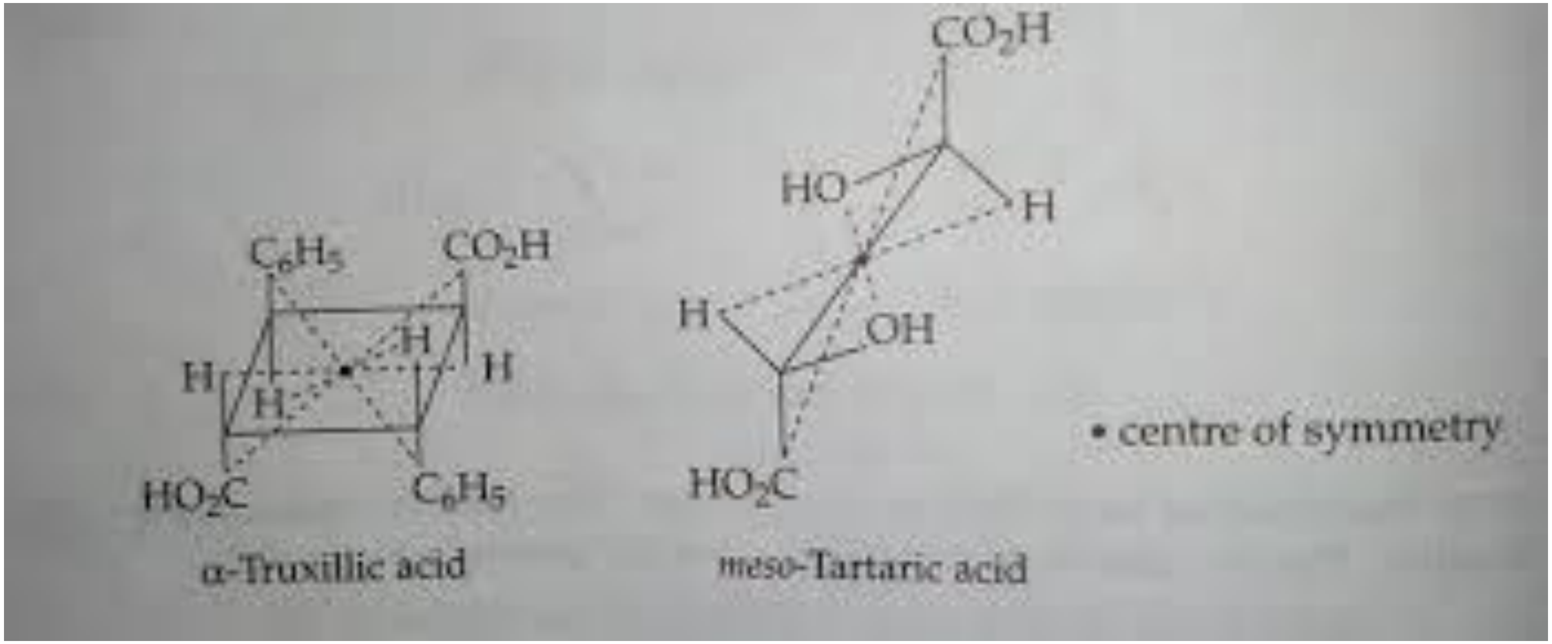
ACHIRAL

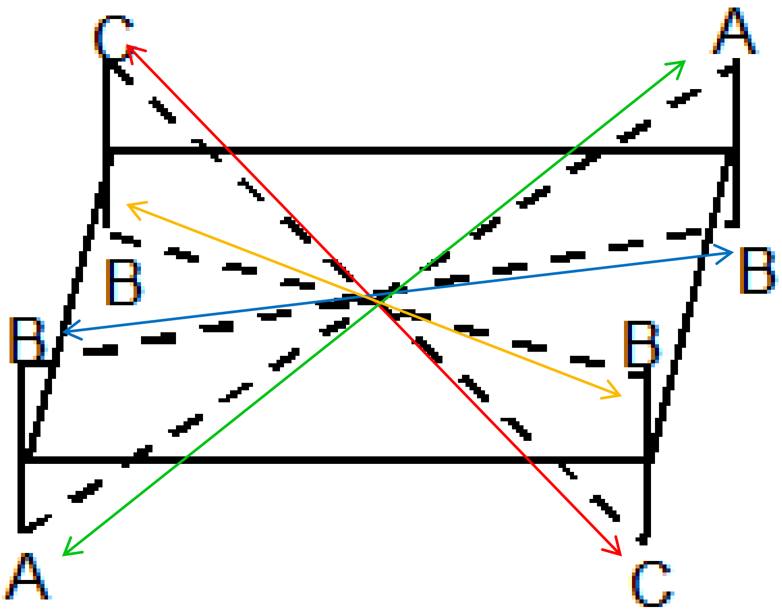
CHIRAL





ELEMENT OF SYMMETRY





ELEMENT OF SYMMETRY

(a)

$$\begin{array}{c} CHCOOH \\ \| \\ CHCOOH \end{array}$$

maleic acid
(no chiral centre,
so, optically
inactive

(b)

$$\begin{array}{c} R-\overset{*}{C}H-COOH \\ | \\ NH_2 \end{array}$$

α-amino acids
(one chiral centre,
so, optically active)

(c)

$$CH_3\overset{*}{C}H(OH)COOH$$

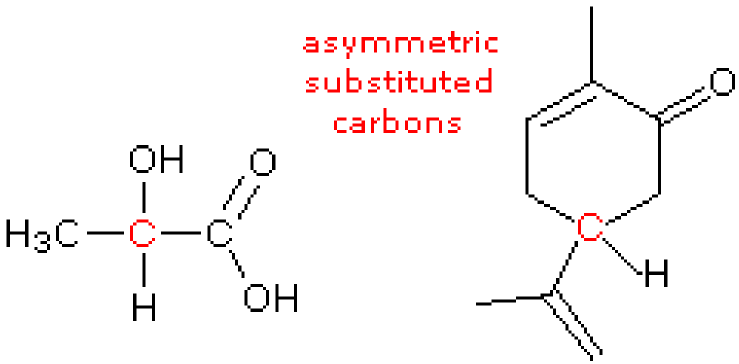
lactic acid
(one chiral centre,
so optically active)

(d)

$$\begin{array}{l} {}^{*}CH(OH)COOH \\ | \\ {}^{*}CH(OH)COOH \end{array}$$

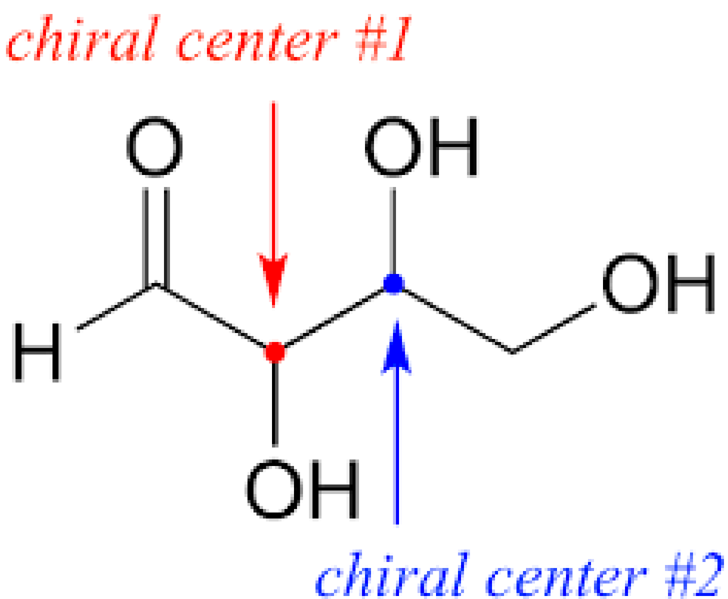
tartaric acid
(two chiral carbon,
so optically active)

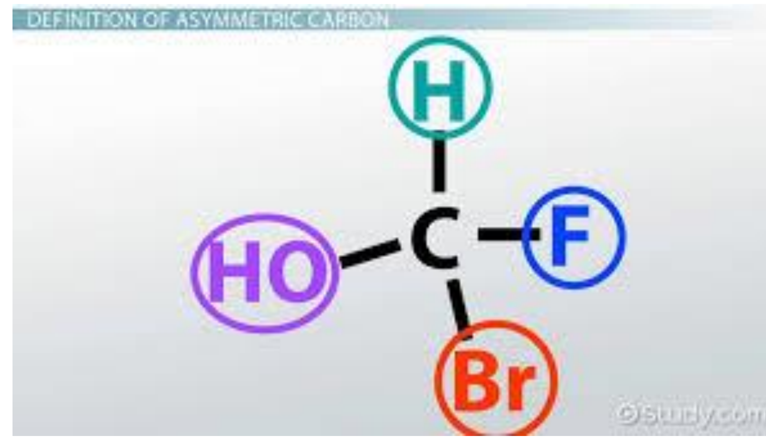
Achiral/Asymmetric carbon atom



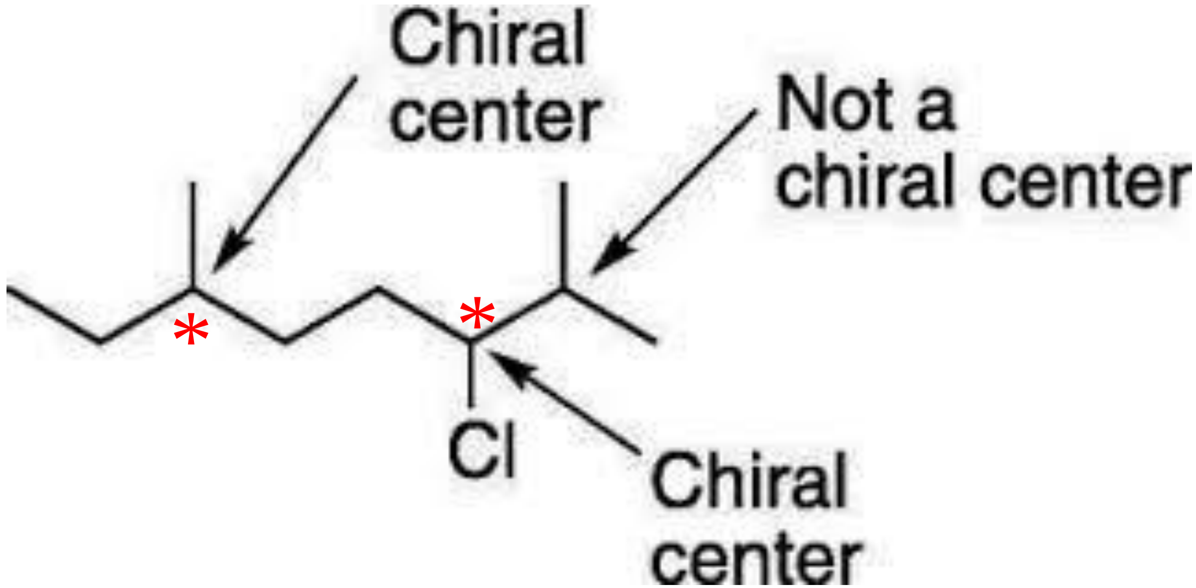
Lactic Acid

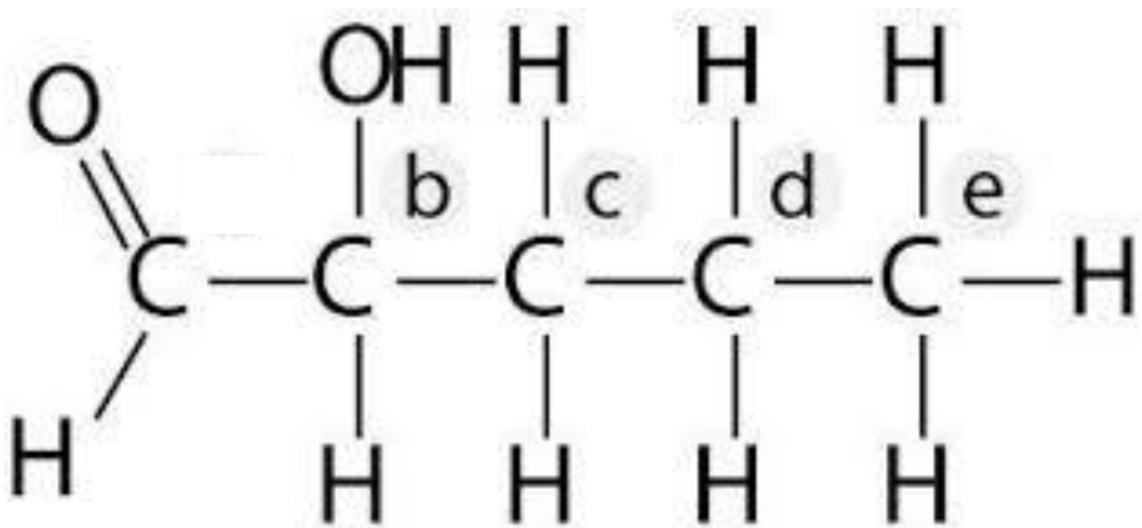
Carvone



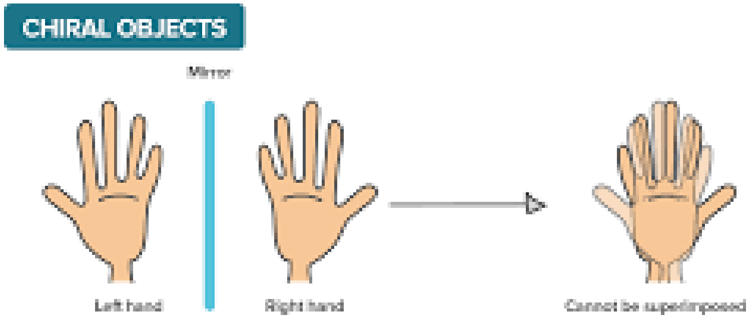


Achiral/Asymmetric carbon atom

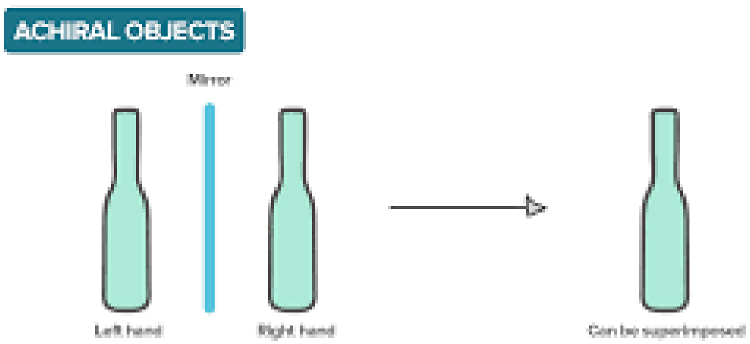




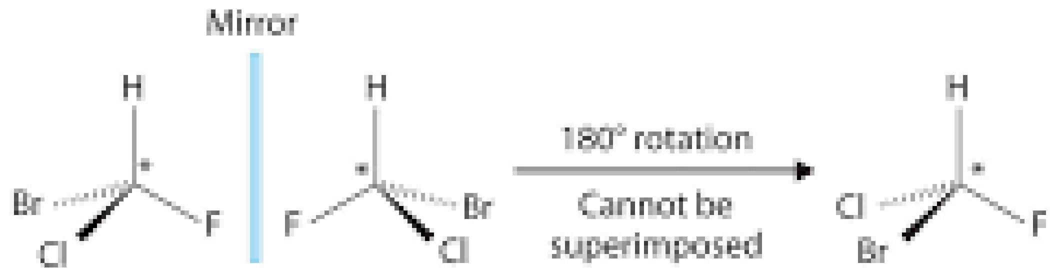
Achiral/Asymmetric carbon atom



CHIRAL

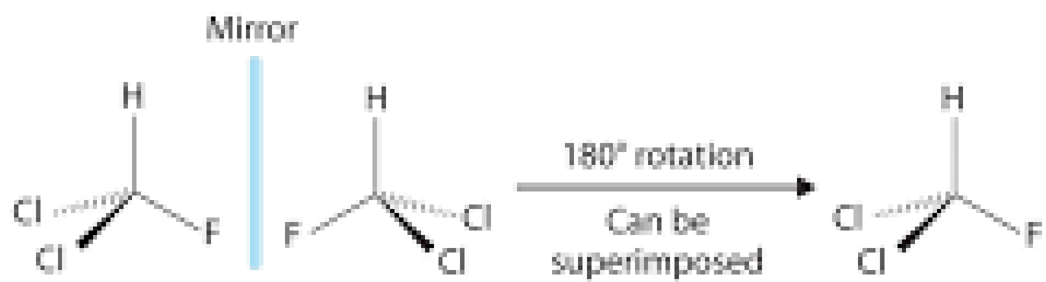


ACHIRAL



(a) Bromochlorofluoromethane

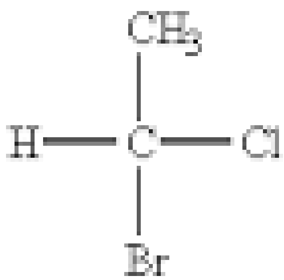
CHIRAL



ACHIRAL

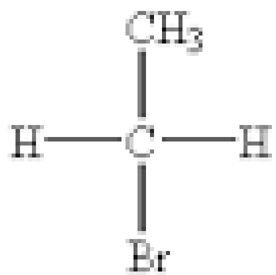
(b) Dichlorofluoromethane

Achiral/Asymmetric carbon atom



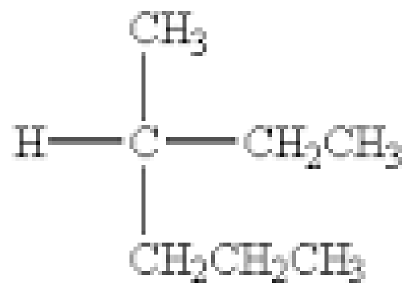
chiral

Has 4 different atoms bonded to the carbon



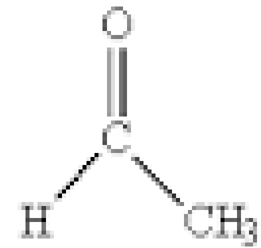
achiral

Does not have 4 different atoms or groups bonded to the carbon (2 hydrogens)



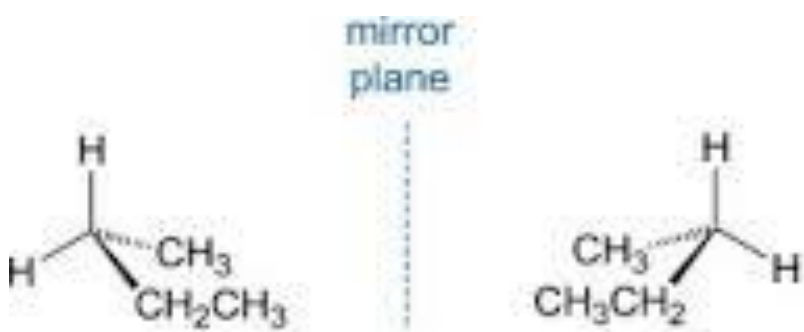
chiral

Has 4 different groups bonded to the carbon

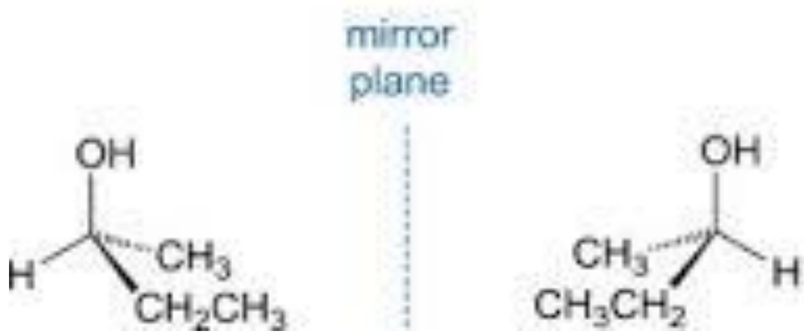


achiral

Only has 3 atoms bonded to the carbon



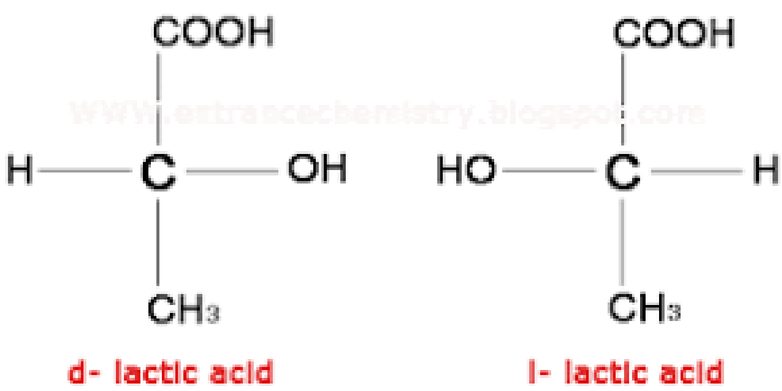
Achiral molecule
Mirror images are superimposable



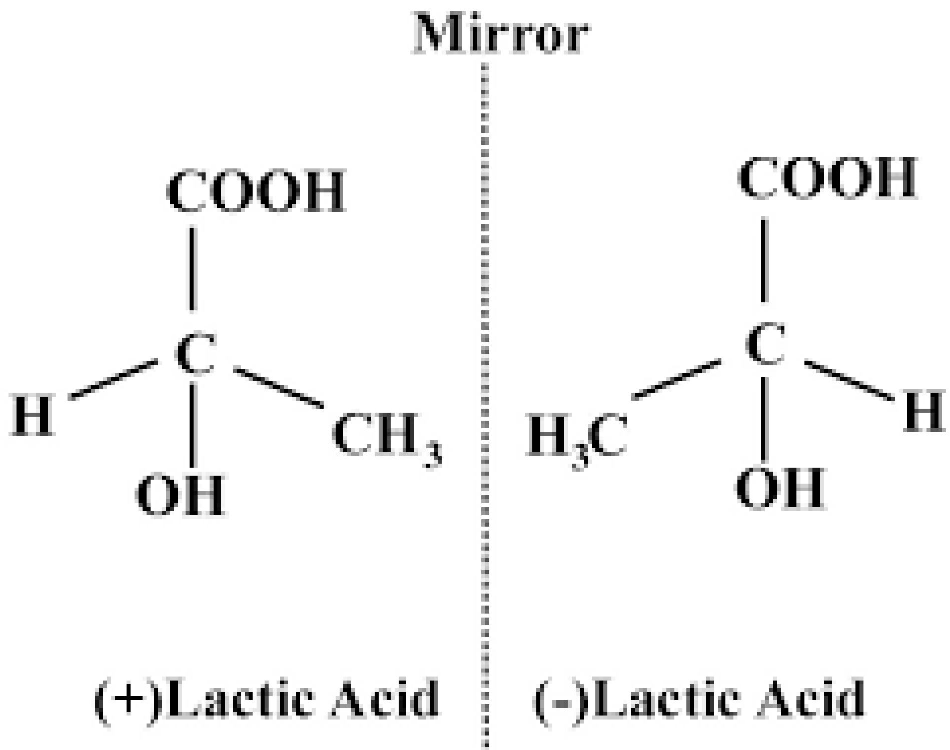
Chiral molecule
Mirror images are non-superimposable

EXAMPLES OF OPTICAL ISOMERISM

ONE CHIRAL CARBON ATOM OR ONE ASYMMETRIC CENTRE



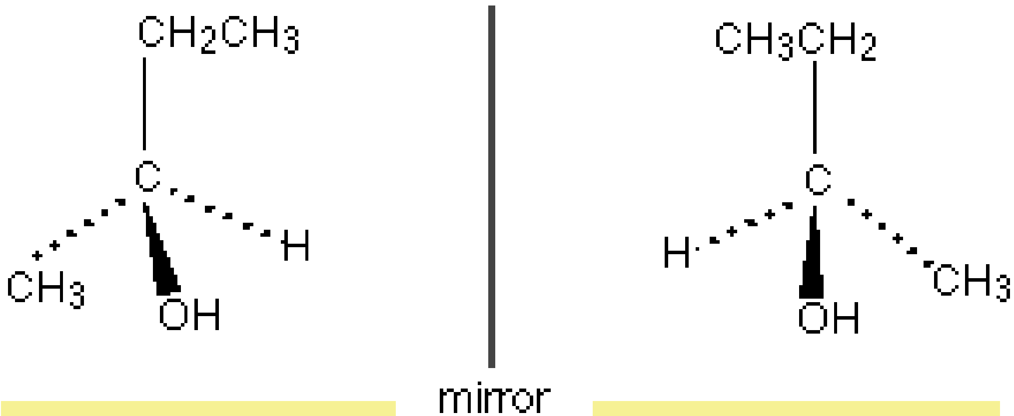
LACTIC ACID



MIRROR IMAGES
ENANTIOMORPHS
NON SUPERIMPOSABLE

1. Dextro (+) OA
2. Leavo (-) OA
3. Racemic mixture (+/-) OI

ONE CHIRAL CARBON ATOM OR ONE ASYMMETRIC CENTRE

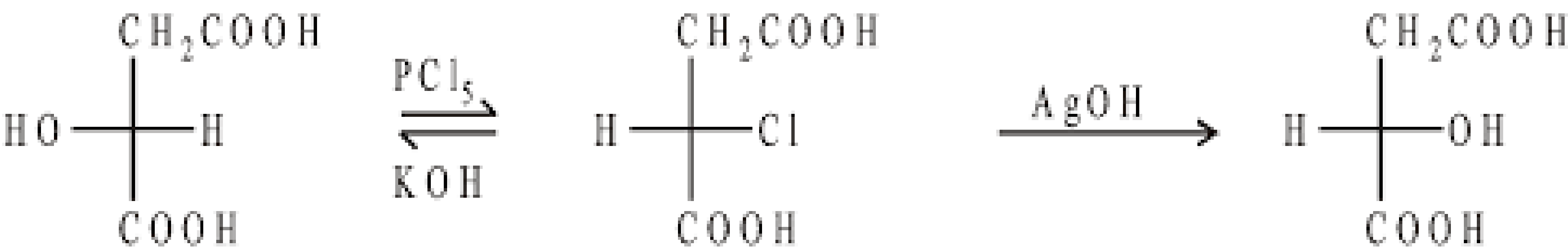


2 BUTANOL (l)

2 BUTANOL (d)

MIRROR IMAGES
ENANTIOMORPHS
NON SUPERIMPOSABLE

1. Dextro (+) OA
2. Leavo (-) OA
3. Racemic mixture (+/-) OI



d-Malic acid

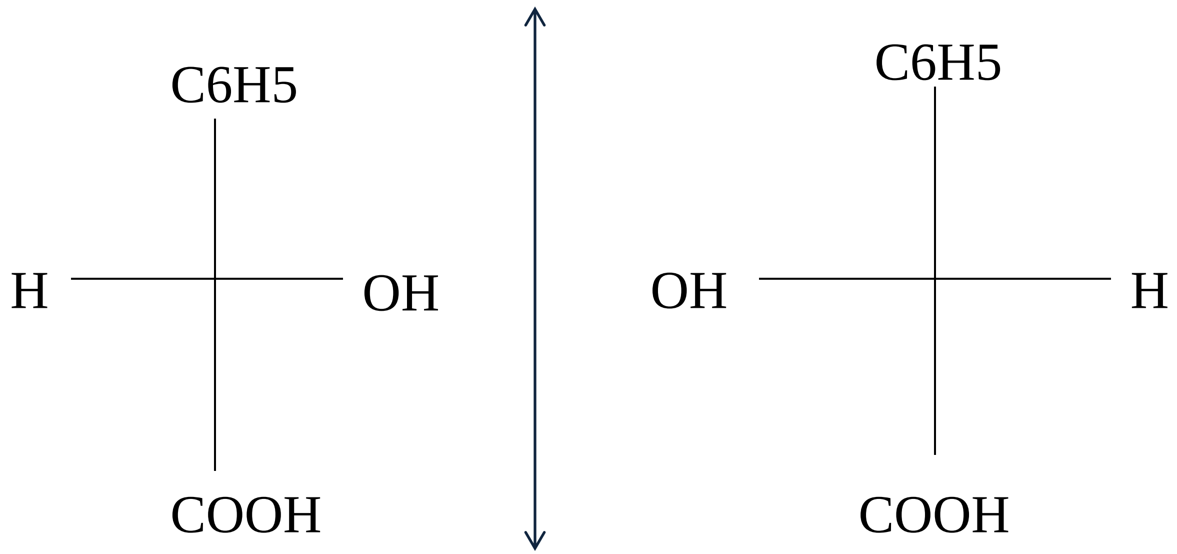
l-Chlorosuccinic acid

l-Malic acid

d- MALIC ACID

l- MALIC ACID

ONE CHIRAL CARBON ATOM OR ONE ASYMMETRIC CENTRE



d (+) Mandelic Acid

MIRROR

l (-) Mandelic Acid

MIRROR IMAGES
ENANTIOMORPHS
NON SUPERIMPOSABLE

1. Dextro (+) OA
2. Leavo (-) OA
3. Racemic mixture (+/-) OI

ONE CHIRAL CARBON ATOM OR ONE ASYMMETRIC CENTRE

OPTICAL ACTIVE compounds with one Chiral carbon atom /one chiral centre exists in THREE isomeric forms.

Two forms are Optically Active – **Dextro and Leavo**
One form is Optically Inactive - **Racemic mixture**

Dextro an Leavo are related to each other as OBJECT to IMAGE in a mirror. These are called **ENANTIOMORPHS or ENANTIOMERS.**

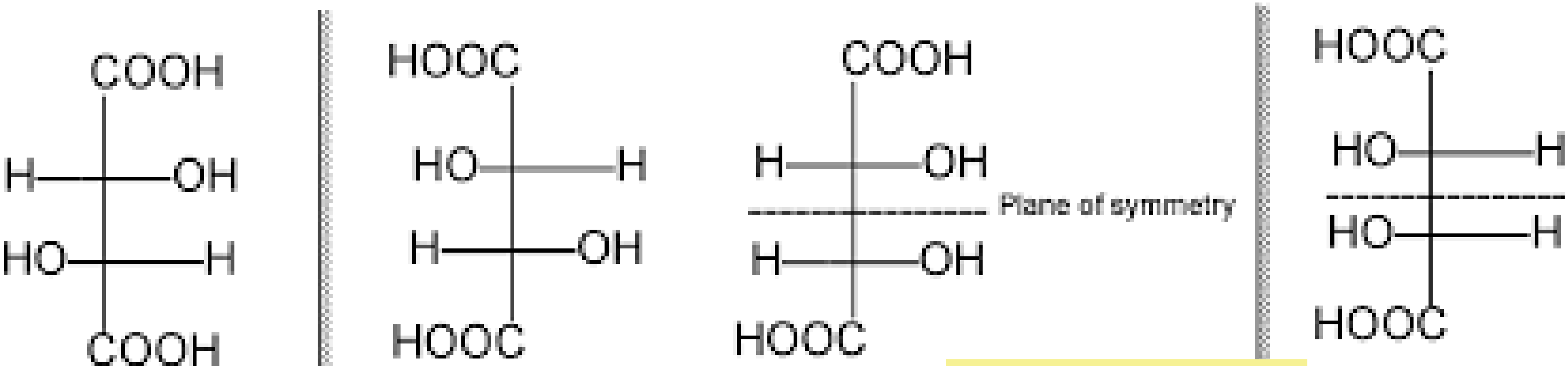
DEXTRO – **Rotation in Clockwise direction**, from H to OH, d(+)
LEAVO - **Rotation in Anti clockwise direction**, from H to OH, l(-)

RACEMIC – Equimolecular mixture of dextro and Leavo variety.
Optical inactivity is due to external compensation. dl (±)
The d and l forms can be separated from this mixture by synthetic methods.

Number of Optical Isomers (a) = 2^n = 2x 1= **2 optical isomers are obtained**
Where, n = 1 = number of Chiral centres/asymmetric centres.

EXAMPLES OF OPTICAL ISOMERISM

TWO SIMILAR CHIRAL CARBON ATOMS OR ASYMMETRIC CENTRES



(i) (ii) (iii) (iv)

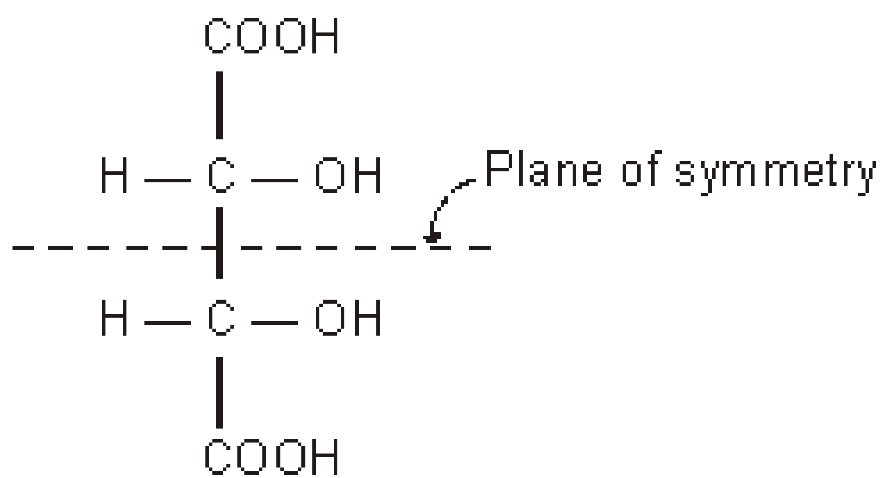
meso Tartaric acid

d Tartaric acid

l Tartaric acid

MIRROR IMAGES
ENANTIOMORPHS
NON SUPERIMPOSABLE

1. Dextro (+) OA (tamarind, grapes)
2. Leavo (-) OA (
3. Meso Variety (+/-) OI



meso-tartaric acid

TWO SIMILAR ASYMMETRIC CENTRES

Number of Optical Isomers (a) = 2^n= 2x 2= 4
Where, n = 2 = number of Chiral centres/asymmetric centres

Four Optical Isomers are obtained.

TARTARIC ACID:

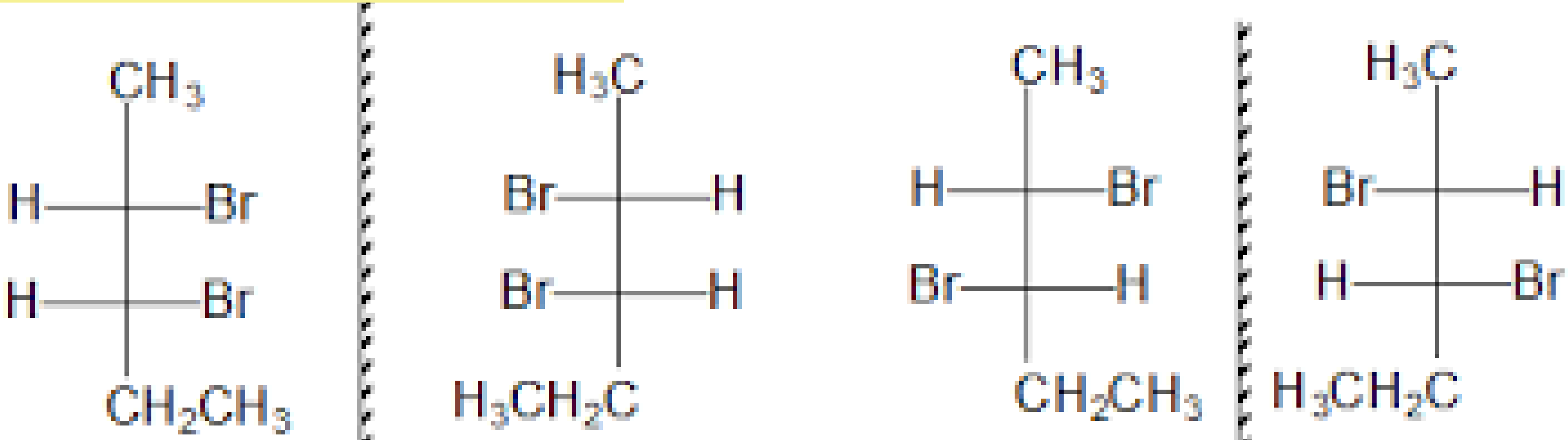
Spatial arrangement can be in two ways (1)OH groups are on different sides
(2) OH groups on same side

When (–OH) groups are on different sides, **Dextro and Leavo** forms are obtained. Both are optically active.
When (-OH) groups are on same side, the molecule loose its asymmetry and becomes symmetrical. This is meso variety. Half molecule rotates PPL to right and half molecule rotates PPL to left. **Meso compound** is optically inactive.
Both the object and mirror image of meso variety is same and super imposable.

Therefore, a = 2n is not applicable for Tartaric acid.

TWO DIFFERENT CHIRAL CARBON ATOMS OR DIASTEREOMERS

2, 3 DI BROMO PENTANE



(i) (ii) (iii) (iv)

MIRROR IMAGES - ENANTIOMORPHS
NON SUPERIMPOSABLE

I and III, I and IV, II and III, II and IV are diastereomers

TWO DIFFERENT ASYMMETRIC CENTRES

Number of Optical Isomers (a) = 2^n= 2x 2= **4**
Where, n = 2 = number of Chiral centres/asymmetric centres

Four Optical Isomers are obtained.

2, 3 DI BROMO PENTANE:
Spatial arrangement can be in two ways (1)(-Br) groups are on different sides
(2) (-Br) groups on same side

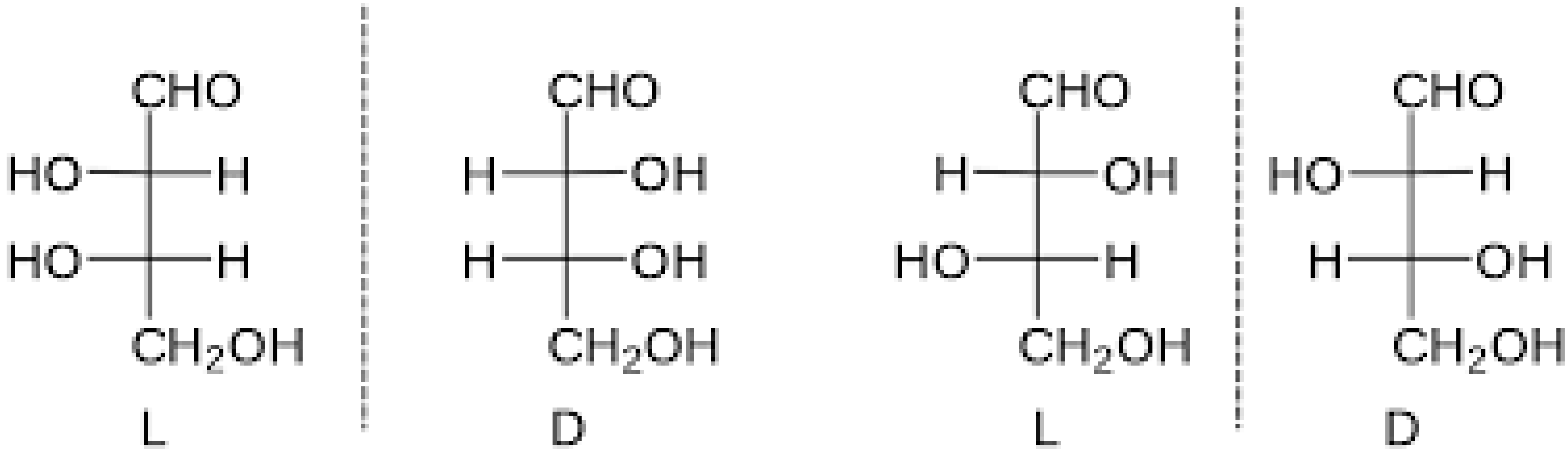
When (–Br) groups are on different sides, **Dextro nd Leavo** forms are obtained. Both are optically active. These are I and II and are Enantiomers (object and mirror, not super imposable)
When (-Br) groups are on same side, **Dextro nd Leavo** forms are obtained. Both are optically active. These are III and IV and are Enantiomers (object and mirror, not super imposable)

Structures I and III, I and IV, II and III, II and IV are isomers but not mirror images. These are called **Diastereomers.**

DIFFERENCE BETWEEN ENANTIOMERS AND DIASTEREOMERS

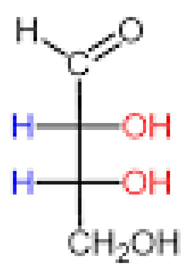
ENANTIOMERS	DIASTEREOMERS
Enantiomers are stereoisomers that are mirror images of each other	Diastereomers are stereoisomers that aren’t a mirror image of each other
Have identical physical properties except for the ability to rotate plane-polarised light	Distinct physical properties
Present in pairs (set of two)	There can be several molecules
Similar molecular shape	Different molecular shape

TWO DIFFERENT CHIRAL CARBON ATOMS: ERYTHRO and THREO



Erythrose

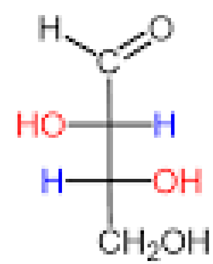
Threose



Erythrose

Two H's on the same side

Two OH's on the same side

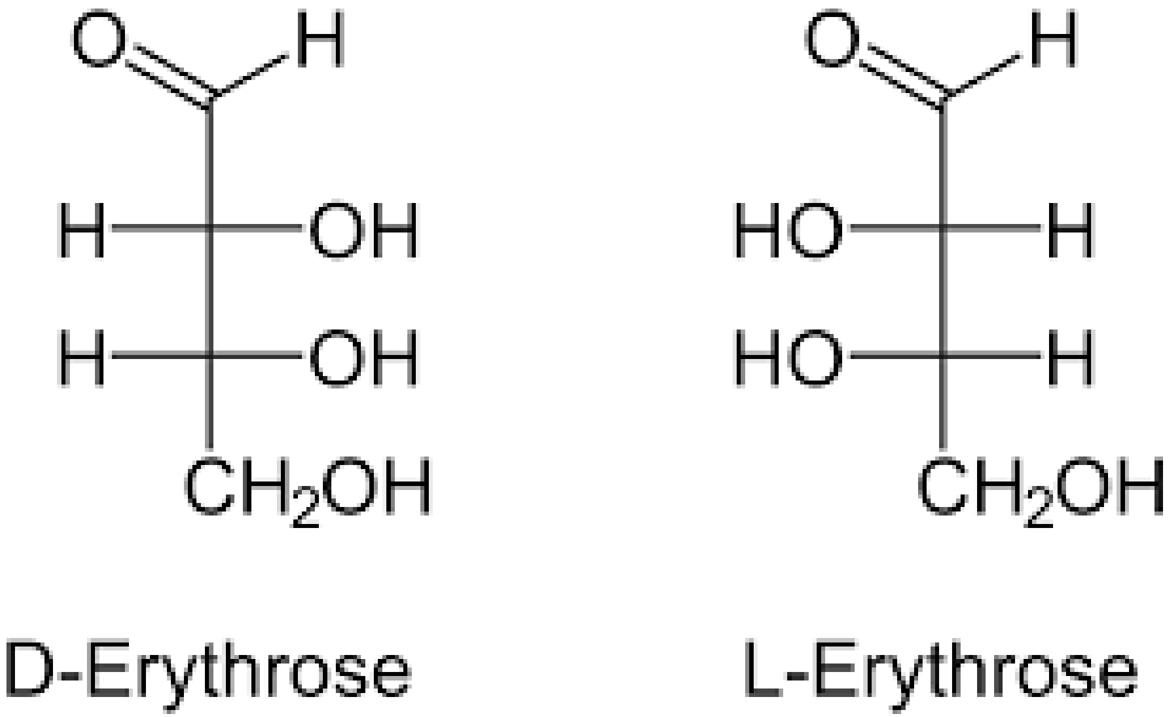


Threose

Two H's on opposite sides

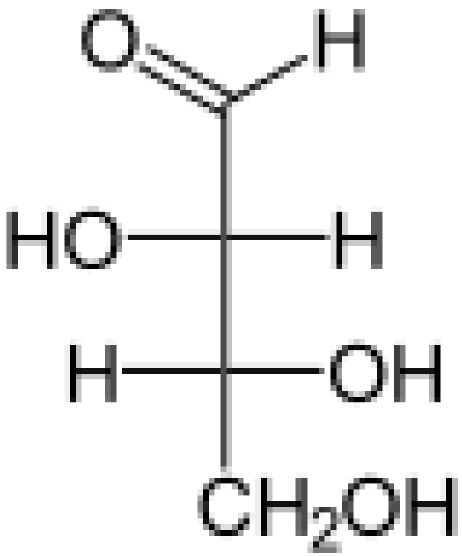
Two OH's on opposite sides

ERYTHROSE



Erythrose is a tetrose saccharide with the chemical formula $C_4H_8O_4$. It has one aldehyde group, and is thus part of the aldose family. The natural isomer is D-Erythrose.

THREOSE



D-Threose L-Threose

Threose is a four-carbon monosaccharide with molecular formula $C_4H_8O_4$. It has a terminal aldehyde group rather than a ketone in its linear chain, and so is considered part of the aldose family of monosaccharides.