
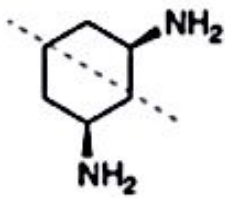
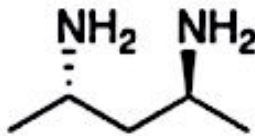

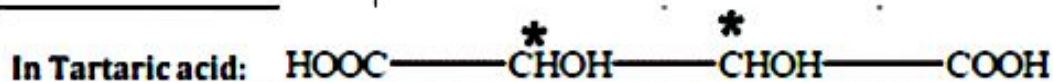


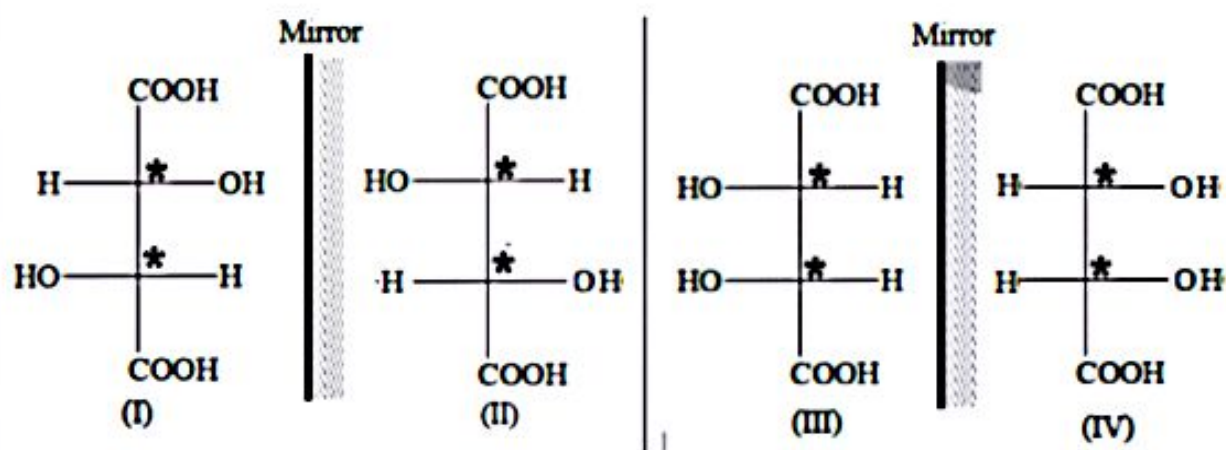
## ❖ Meso Compound

- An optically inactive compound whose molecule is superimposable on its mirror image inspite of the presence of chiral carbon atoms is called a meso compound.
- If a molecule has two or more chiral centers, it is usually chiral. The exceptions are meso-molecules, which are not chiral. These are molecules that due to symmetry have chiral centers that 'cancel' each other out.
- Has two or more chiral centers
- Has a plane of symmetry.

	<p>A person is meso (NOT CHIRAL) even though they have chiral elements (hands and feet). There is a plane of symmetry down the middle of a person, which makes a person the same as their mirror image.</p>
	<p>This molecule is meso (NOT CHIRAL). It has two chiral centers and a plane of symmetry.</p>
	<p>This molecule is not meso (CHIRAL). It has two chiral centers but no plane of symmetry.</p>
	<p>This molecule is not meso (NOT CHIRAL). It has a plane of symmetry but no chiral centers. The carbons attached to the NH<sub>2</sub> groups may look like chiral centers but they are not.</p>



The molecule contains two chiral carbons and the number of optical isomers should be  $2^n = 2^2 = 4$  but number of optical isomer is reduced to 3 because one molecule has a plane of symmetry. The stereoisomers of tartaric acid are,



I and II are enantiomers (non-superimposable); III and IV are meso form (superimposable).

• Calculation of number of optical isomers in compounds (containing 'n' chiral atoms)

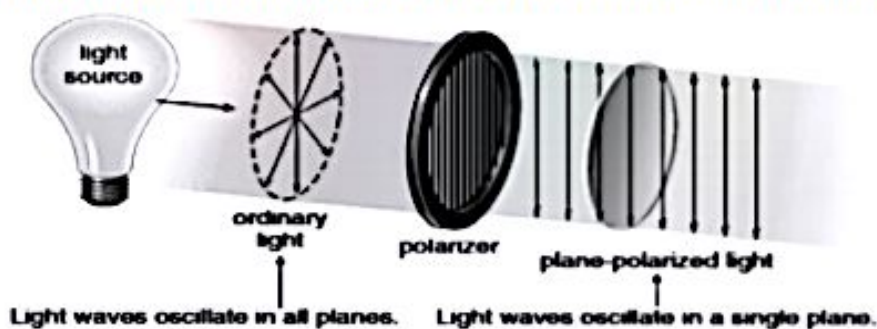
S. No.	Compounds	Number of optical active forms (a)	Number of meso forms (m)	Number of Racemic mixture (a/2)	Total number of optical isomers
1	The molecule has no symmetry	$2^n$	0	$2^{n-1}$	$a+m$
2a	The molecule has symmetry:- <b>Case1:</b> When compound has even number of chiral carbon atom	$2^{n-1}$	$2^{n/2-1}$	$2^{n-1/2}$	$a+m$
2b	The molecule has symmetry:- <b>Case1:</b> When compound has odd number of chiral carbon atom	$2^{n-1} - 2^{(n-1)/2}$	$2^{n-1/2}$	$a/2$	$2^{n-1}$

Example:

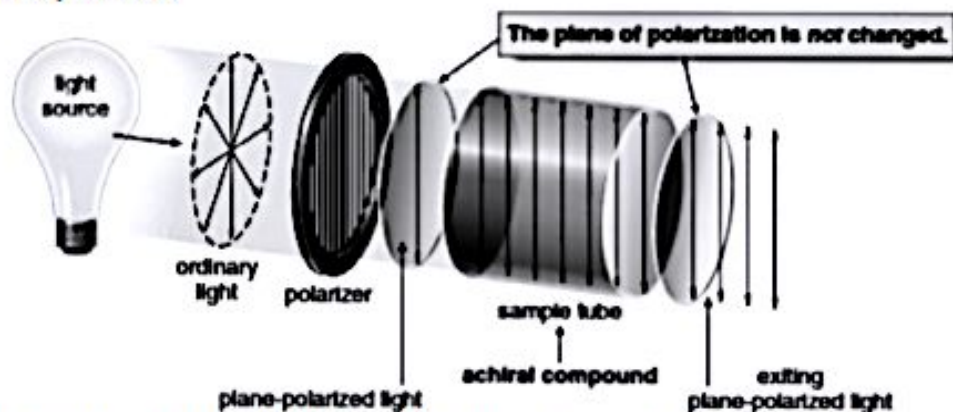
1.	$\text{H}_5\text{C}_6 - \text{CHOH}^* - \text{CHOH}^* - \text{CHOH}^* - \text{CH}_3$ <p>Number of optically active forms: <math>a = 2^n = 2^3 = 8</math>            Number of Racemic mixture: <math>(a/2) = 2^{n-1} = 2^{3-1} = 4</math>            Total number of optical isomers: <math>a+m = 8+0 = 8</math></p>
2.	$\text{HOOC} - \text{CHOH}^* - \text{CHOH}^* - \text{COOH}$ <p>Number of optical isomer: <math>a = 2^{n-1} = [2^{2-1}] = 2</math>            Number of meso form: <math>m = 2^{n/2-1} = [2^{2/2-1}] = [2^0] = 1</math>            Total number of configuration isomer: <math>a+m = [2+1] = 3</math></p>
3.	$\text{HOH}_2\text{C} - \text{CHOH}^* - \text{CHOH}^* - \text{CHOH}^* - \text{CH}_2\text{OH}$ <p>Number of optical isomer: <math>a = 2^{n-1} - 2^{(n-1)/2} = [2^{3-1} - 2^{(3-1)/2}] = [2^2 - 2^1] = [4-2] = 2</math>            Number of meso form: <math>2^{n-1/2} = [2^{3-1/2}] = 2</math>            Number of Racemic mixture: <math>(a/2) = 2/2 = 1</math>            Total no. of configurational isomers: <math>2^{n-1} = [2^{3-1}] = [2^2] = 4</math></p>

## ❖ Optical Activity

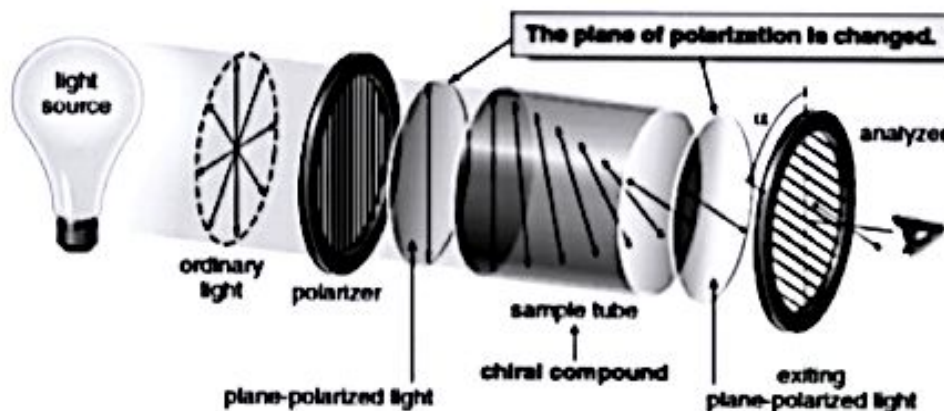
- **Sir Christiaan Huygens** (1629-1695). Dutch astronomer, mathematician, and physicist. He discovers plane polarized light.
- **What is plane-polarized light?**
  - Ordinary light consists of electromagnetic waves that oscillate in all planes perpendicular to the direction in which the light travels. Passing light through a polarizer allows light in only one plane to come through. This is plane-polarized light (or simply polarized light), and it has an electric vector that oscillates in a single plane.



- A **POLARIMETER** is an instrument that allows plane-polarized light to travel through a sample tube containing an organic compound. After the light exits the sample tube, an analyzer slit is rotated to determine the direction of the plane of the polarized light exiting the sample tube. There are two possible results. With achiral compounds, the light exits the sample tube unchanged, and the plane of the polarized light is in the same position it was before entering the sample tube. A compound that does not change the plane of polarized light is said to be optically inactive.



- With chiral compounds, the plane of the polarized light is rotated through an angle  $\alpha$ . The angle  $\alpha$ , measured in degrees ( $^\circ$ ), is called the observed rotation. A compound that rotates the plane of polarized light is said to be optically active.



- The rotation of polarized light can be in the clockwise or counterclockwise direction.
  - ✓ If the rotation is clockwise (to the right from the noon position), the compound is called **dextrorotatory**. The rotation is labeled *d* or (+).
  - ✓ If the rotation is counterclockwise (to the left from noon), the compound is called **levorotatory**. The rotation is labeled *l* or (-).

## • SPECIFIC ROTATION

- The observed rotation depends on the number of chiral molecules that interact with polarized light. This in turn depends on the concentration of the sample and the length of the sample tube. To standardize optical rotation data, the quantity specific rotation ( $[\alpha]$ ) is defined using a specific sample tube length (usually 1 dm), concentration, temperature (25 °C), and wavelength (589 nm, the D line emitted by a sodium lamp).
- Specific rotations are physical constants just like melting points or boiling points, and are reported in chemical reference books for a wide variety of compounds.

$$\text{Specific Rotation} \Rightarrow [\alpha] = \frac{\alpha}{l \times c}$$

$\alpha$  : observed rotation (°)  
 $l$  : length of sample tube (dm)  
 $c$  : concentration (g/mL)  
 dm : Decimeter  
 1 dm : 10 cm

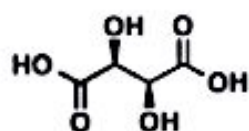
## • OPTICAL INACTIVITY DUE TO COMPENSATION

- The optical inactivity is also possible due to compensation. There are two types of compensation. They are,
  - (a) Internal compensation
  - (b) External compensation.
- a) **Internal compensation:** If the rotation of polarized light caused by one half of the molecule is exactly cancelled by equal and opposite rotation caused by the other half of the molecule and the molecule becomes optically inactive, then the optical inactivity of molecule is due to internal compensation (within the molecule).  
Example: Mesotartaric acid
- b) **External compensation:** If two enantiomers are mixed together in equimolar amount, then the mixture becomes optically inactive. The rotation caused by one enantiomer is exactly cancelled by other enantiomers and is due to external compensation. The resulting optically inactive mixture is called racemic mixture.  
Example: Equimolar amount of d (Dextrorotatory) and l (Levorotatory) form of tartaric acid.

## • OPTICAL PURITY

- The "**optical purity**" is a comparison of the optical rotation of a pure sample of unknown stereochemistry versus the optical rotation of a sample of pure enantiomer.
- An "**optically pure**" (or "enantiomerically pure") solution of 100% (S,S) tartaric acid and 0% (R,R) tartaric acid will have an optical rotation of (-)12°.
- An "**optically pure**" solution of 100% (R,R) tartaric acid and 0% (S,S) tartaric acid will have an optical rotation of (+)12°.

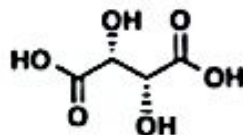
Individually, when the pure crystals of the (-) and (+) forms were re-dissolved in water, they each rotated plane-polarized light, with equal and opposite specific rotations:



(S,S) tartaric acid  
(-)-tartaric acid

Specific rotation:

$$[\alpha]_D^{20} - 12^\circ, (c = 20, \text{H}_2\text{O})$$

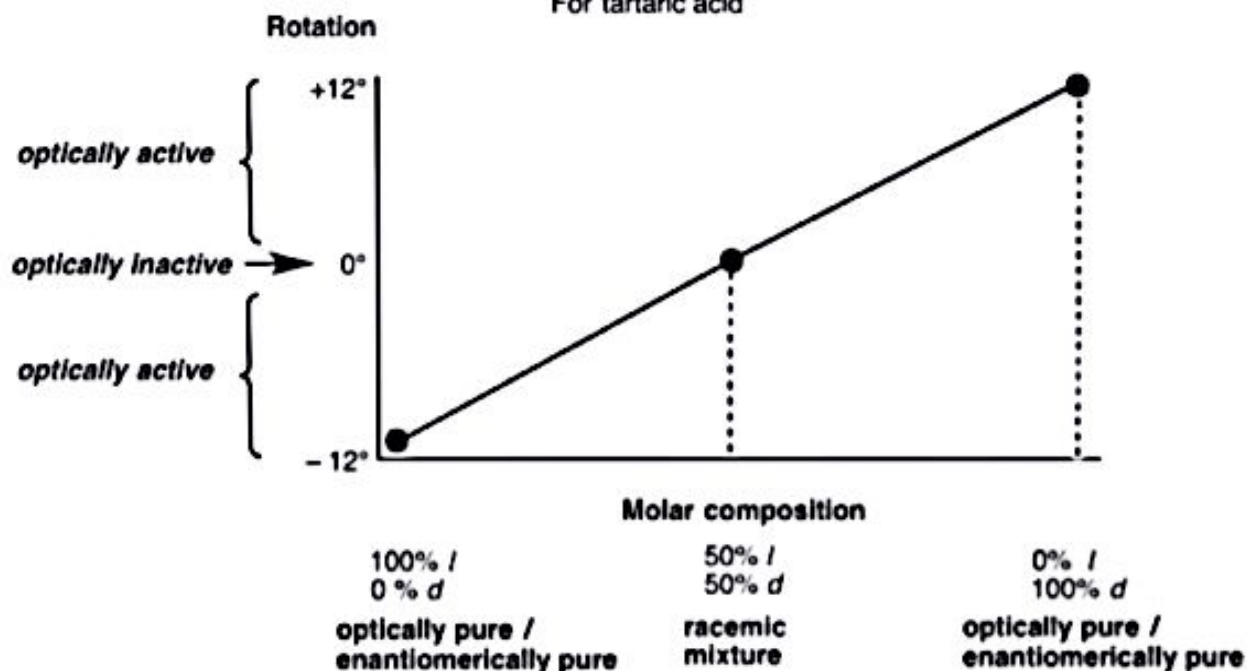


(R,R) tartaric acid  
(+)-tartaric acid

Specific rotation:

$$[\alpha]_D^{20} + 12^\circ, (c = 20, \text{H}_2\text{O})$$

**Optical Rotation Versus Molar Composition: Tartaric Acid**  
For tartaric acid



100% optically pure *l*-tartaric acid has a specific rotation of  $-12^\circ$ , which gradually rises to  $0^\circ$  as the proportion of the *d* enantiomer is raised to 50%. As the molar composition of the *d* form increases, so does the optical rotation, going up to  $+12^\circ$  again for the optically pure *d*-enantiomer.

- The optical purity as the observed rotation of a mixture divided by the specific rotation of the pure enantiomer (obtained under identical conditions).

$$\text{Optical Purity} = \frac{\text{Observed Rotation of Mixture}}{\text{Specific Rotation of Pure Enantiomer}}$$

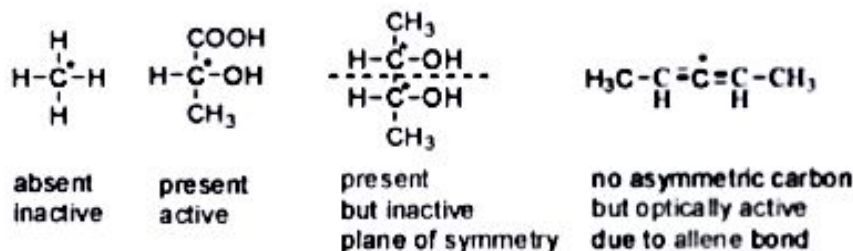
## • CONDITIONS FOR OPTICAL ACTIVITY

- 1) To exhibit optical activity molecule must possess asymmetric carbon: Asymmetric carbon compounds are optically active. But, presence of asymmetric is not only the requirement.

Asymmetry:

if asymmetric centre present = optically active (may / may not check for other criteria)

if asymmetric centre absent = optically inactive (may / may not check for other criteria)



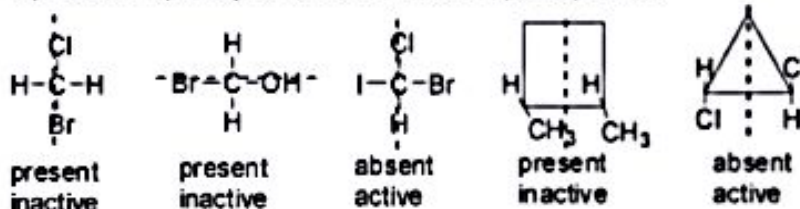
- 2) To exhibit optical activity molecule must not have the symmetry elements, (a) plane of symmetry (b) centre of symmetry (c) n-fold alternating access of symmetry. If these three are absent then only the compounds exhibits optical activity.

(a) **Plane of symmetry:** A plane which bisects the molecules into two mirror images are called plane of symmetry.

If the plane of symmetry is present then the molecule is optically inactive, if absent then optically active.

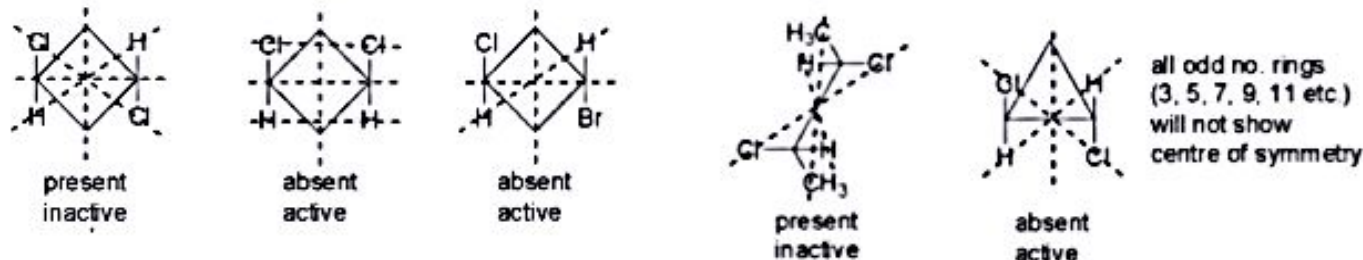
Plane of symmetry:

if present = optically inactive; if absent = optically active



(b) **Centre of symmetry:** If all the lines two identical groups pass through a single point or a central point is called centre of symmetry.

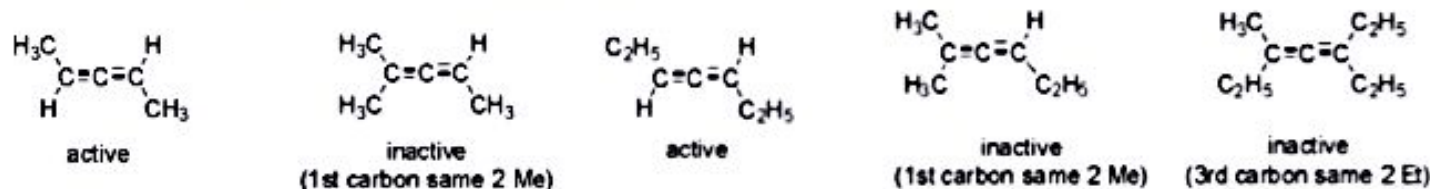
Centre of symmetry: if present = optically inactive; if absent = optically active



(c) **n-Fold alternating access of symmetry:** If a rotation by  $360^\circ/n$  degrees ( $n = 1, 2, 3, \dots$ ) followed by reflection in plane perpendicular to the axis taken results in identical molecule the compound said to be possess n-fold alternating access of symmetry. If plane of symmetry or centre of symmetry is present then n-fold alternative access of symmetry is present. If plane of symmetry or centres of symmetry are absent then n-fold alternating access of symmetry will be absent. If the n-fold alternating access of symmetry present then the molecule is optically inactive, if absent then optically active.

Allenes are optically active because absence of plane of symmetry.

However, if on first or third carbon two same groups present it will be inactive.



## ❖ STEREOISOMERISM IN ORGANIC COMPOUNDS

• The isomerism which arises due to different spatial arrangements of atoms or groups is called stereo isomerism. It is broadly divided into:

- I. Geometrical isomerism
- ii. Optical isomerism
- iii. Conformational isomerism

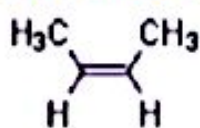
• The stereo isomers have same structural formula i.e., same connectivity order between atoms. However the atoms or groups are arranged differently in space.

### ➤ CIS & TRANS GEOMETRICAL ISOMERISM

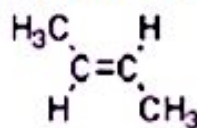
✓ The geometrical isomerism arises when atoms or groups are arranged differently in space due to restricted rotation of a bond or bonds in a molecule.

#### ✓ Example 1:

- Two different spatial arrangements of methyl groups about a double bond in 2-butene give rise to the following geometrical isomers.
- Two forms are not inter convertible due to restricted rotation of double bond. In the cis isomer, the two methyl groups are arranged on the same side of a double bond. Whereas in the Trans isomer, they are on the opposite side.



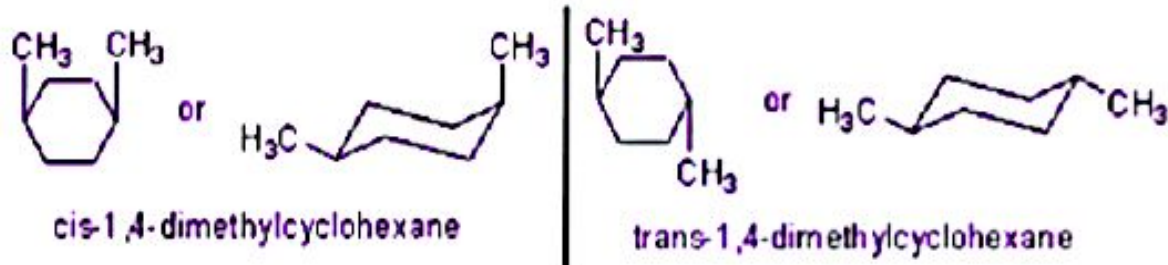
cis-2-butene



trans-2-butene

#### ✓ Example 2:

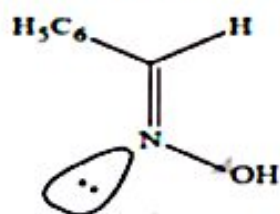
- There are two geometrical isomers (cis & trans) possible in case of 1,4-dimethylcyclohexane.
- Here the methyl groups are arranged differently about the plane of the cyclohexane ring. These isomers are not inter convertible since it is not possible to rotate the bonds in the cyclohexane ring.



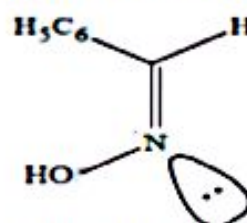
cis-1,4-dimethylcyclohexane

trans-1,4-dimethylcyclohexane

- ✓ The geometrical isomers often show different physical and chemical properties.
- ✓ The difference in their physical properties is more significant when there is more difference in their polarity.
- ✓ Usually the dipole moment of *cis isomers* is greater than that of *trans isomers*. Hence the cis isomers usually have more solubility in polar solvents.
- ✓ In general, the Trans isomers are more stable than cis isomers.
- ✓ **Geometrical isomerism in nitrogen compounds.** Geometrical isomerism due to restricted rotation around  $>C=N$  bond. The important class of compounds exhibiting geometrical isomerism due to  $>C=N$  bond are (i) oximes (ii) hydrazones and (iii) semi carbazones.
- In **aldoxime**, when hydrogen and hydroxyl group are on the same side, the isomer is known as **syn** (analogous to *cis*) and when these groups are on the opposite sides, the isomer is known as **anti** (analogous to *trans*).

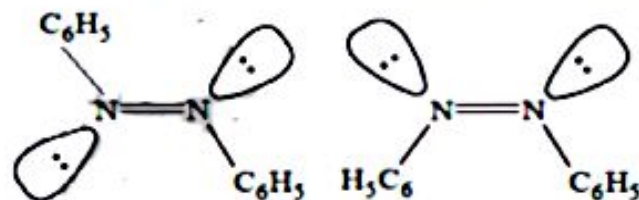


Syn-Benzaldoxime



anti-Benzaldoxime

- Similarly, azo compounds show geometrical isomerism.



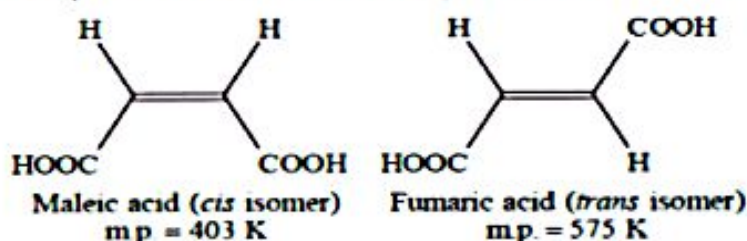
anti-azobenzene

syn-azobenzene

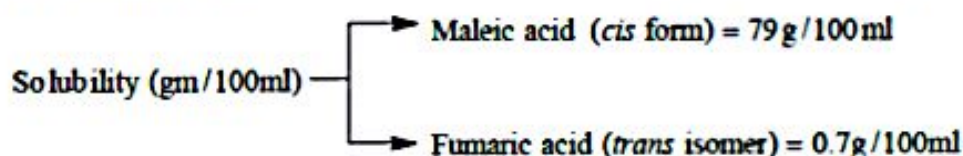
- Distinction between *cis* and *trans* isomers. Distinction between *cis* and *trans* isomers of a compound can be made on the basis of their physical properties such as melting point, boiling point, solubility, dipole moment etc.

### i. Melting point:

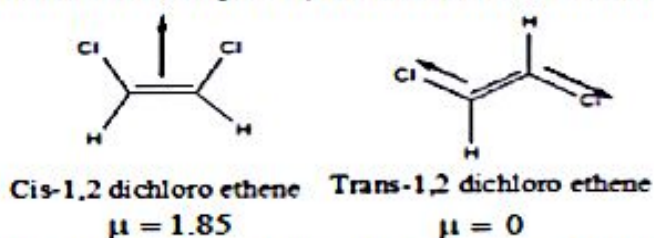
- In general, the melting point of a *trans* isomer is higher than that of the corresponding *cis* isomer. This is due to the reason that the molecules of a *trans* isomer are more symmetrical and hence fit more closely in the crystal lattice as compared to the molecules of a *cis* isomer.
- In order for the intermolecular forces to work well, the molecules must be able to pack together efficiently in the solid. *Trans* isomers pack better than *cis* isomers. The "U" shape of the *cis* isomer doesn't pack as well as the straighter shape of the *trans* isomer. The poorer packing in the *cis* isomers means that the intermolecular forces aren't as effective as they should be and so less energy is needed to melt the molecule a lower melting point.



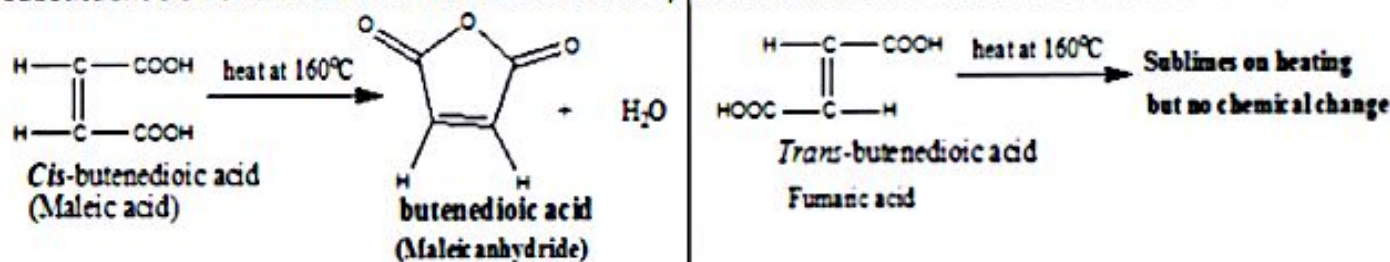
- Solubility:** In general, solubility of a *cis* isomer is higher than that of the corresponding *trans* isomer. This is due to the reason that the molecules of a *cis* isomer are less tightly held in the crystal lattice.



- Dipole moment:** The *cis* isomer has higher dipole moment than the corresponding *trans* isomer.



- Stability:** The *trans* isomer is more stable than *cis* isomer due to steric hindrance. Intermolecular reactions occur easily when reacting groups are close together. Hence, the *cis* isomer will form cyclic derivatives more readily as against *trans* derivatives. But this reaction will take place in only those *cis* isomers in which the substituents on two double bonded carbons are capable of intramolecular reaction with each other.

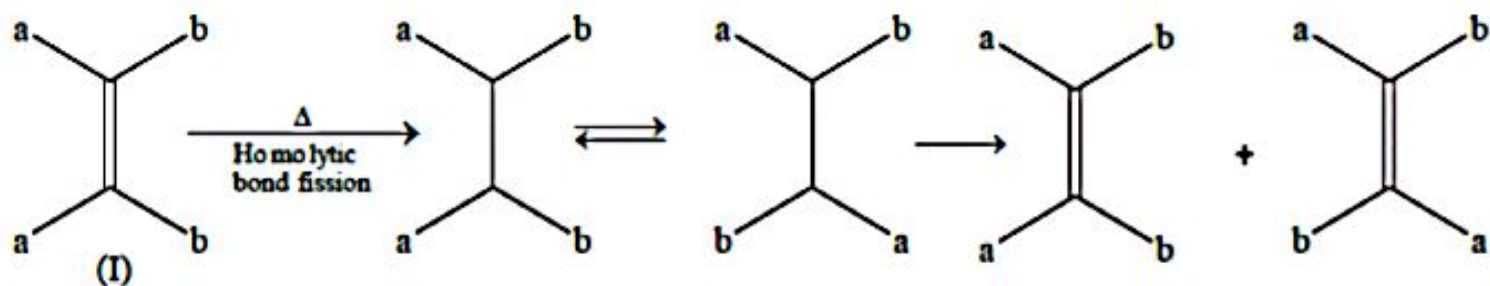


Note By: Fumaric acid forms anhydride via the formation of maleic acid because at high temperature fumaric acid converts into maleic acid

Fumaric acid  $\rightleftharpoons$  Maleic acid  $\longrightarrow$  Maleic anhydride



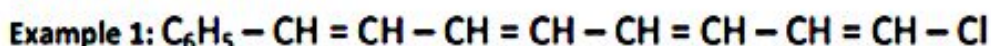
v. Action of heat: On strong heating cis and trans isomers are interconvertible. This interconversion takes place as follows:



Thus, *cis* isomer  $\xrightleftharpoons{\Delta}$  *trans* isomer.

• NUMBER OF GEOMETRICAL ISOMER IN POLYENES

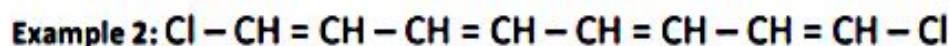
a) When compound has 'n' double bonds and ending groups of a polyene are different, the number of geometrical isomers =  $2^n$ .



Since, the number of double bonds is four and two ends are different, one is  $C_6H_5$  and other is Cl. Therefore, Number of geometrical isomers =  $2^n = 2^4 = 16$

b) When the ending groups of polyene are same

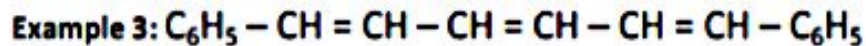
Case - I: When number of double bonds is even then the number of geometrical isomers =  $2^{n-1} + 2^{n/2-1}$



$n = 4$  (even)

Number of geometrical isomers =  $2^{n-1} + 2^{n/2-1} = 2^3 + 2^1 = 10$

Case - II: When number of double bond is odd then no. of geometrical isomer =  $2^{n-1} + 2^{(n+1)/2-1}$

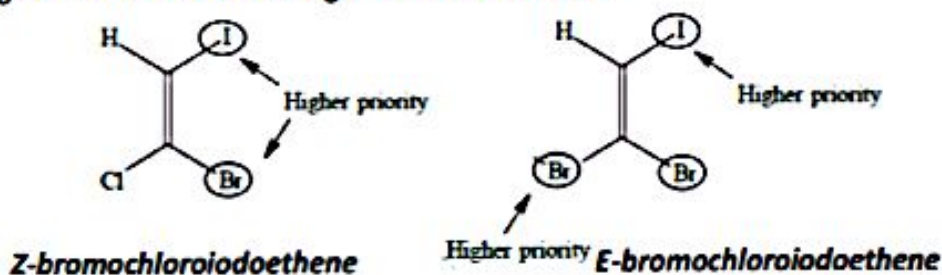


$n = 4$  (odd)

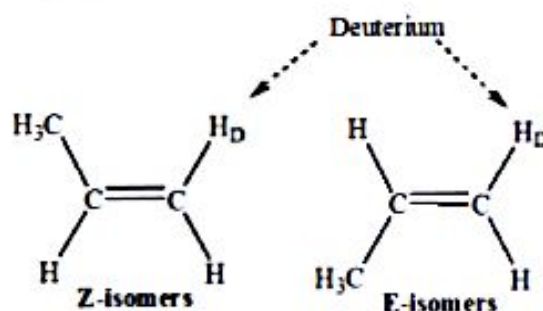
Number of geometrical isomers =  $2^2 + 2^{2-1} = 6$

## ❖ E & Z NOTATION FOR GEOMETRIC ISOMERISM

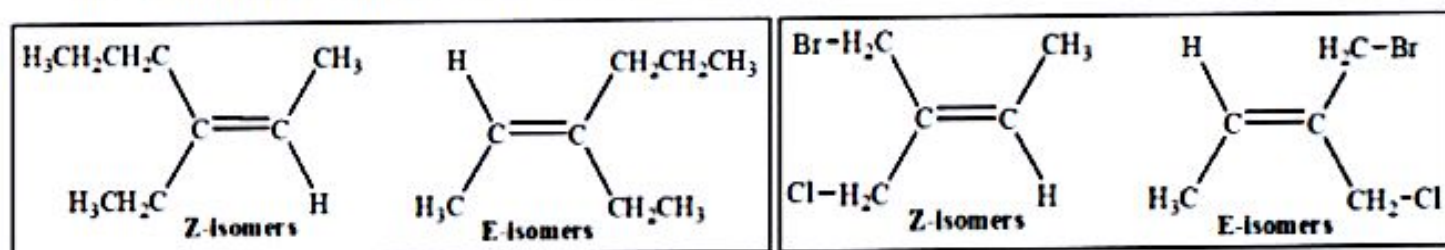
- The simple convention of denoting the geometrical isomers by *cis/trans* descriptors is not sufficient when there are more than two different substituents on a double bond. To differentiate the stereochemistry in them, a new system of nomenclature known as the **E & Z notation** method is to be adopted.
- According to this method, if the groups with higher priorities are present on the opposite sides of the double bond, that isomer is denoted by **E**. Where **E = Entgegen** (the German word for 'opposite') or **E = Enemy**
- However, if the groups with higher priorities are on the same side of the double bond, that isomer is denoted by **Z**. Where **Z = Zusammen** (the German word for 'together')
- The letters **E** and **Z** are represented within parentheses and are separated from the rest of the name with a hyphen.
- Step by step procedure to determine the **E and Z configuration**: *The following procedure is to be adopted to denote the geometrical isomers by E & Z descriptors.*
  - ✓ First determine the higher priority group on each end of the double bond.
  - ✓ If the higher priority groups are on the opposite sides of double bond, the isomer is denoted by the descriptor, **E**.
  - ✓ Otherwise if they are on the same side of double bond, the **Z** descriptor must be used.
- The priorities are assigned by following Cahn-Ingold-Prelog sequence rules:**
  - **Rule 1:** Rank the atoms directly attached to the olefinic carbon according to their atomic number. High priority is given to the atom with higher atomic number.



- **Rule 2:** If isotopes of same element are present, the higher priority is given to the isotope with higher atomic mass. E.g. the Deuterium isotope ( $H^2$  or  $D$ ) has more priority than protium ( $H^1$  or  $H$ ). The  $C^{13}$  isotope has more priority than  $C^{12}$ .



- **Rule 3:** If the relative priority of two groups cannot be decided by Rule 1, it shall be determined by applying to the next atom or sequence of atoms in the group 'X'.  
e.g. for typing groupings in organic molecules where X is more than one atom ....  
 $X = -CH_2CH_2CH_3 > -CH_2CH_3 > -CH_3 > -H$  i.e. the longer the hydrocarbon carbon chain the higher its priority,



- Rule 4:** Treat double and triple bond as if each were a bond to a separate atom. For this methods, imagine that pi ( $\pi$ ) bond is broken and the atoms at both ends duplicate. (or) Atoms participating in double/triple bonds are considered to be bonded to an equivalent number of similar "phantom" atoms by single bonds. Note: "phantom" atoms are bonded to no other atoms.

