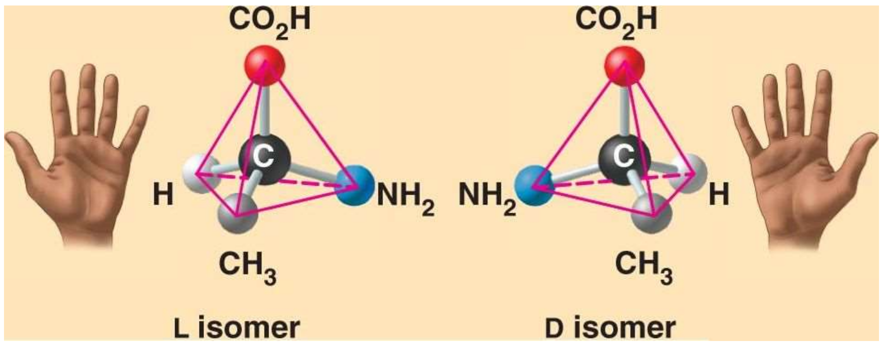
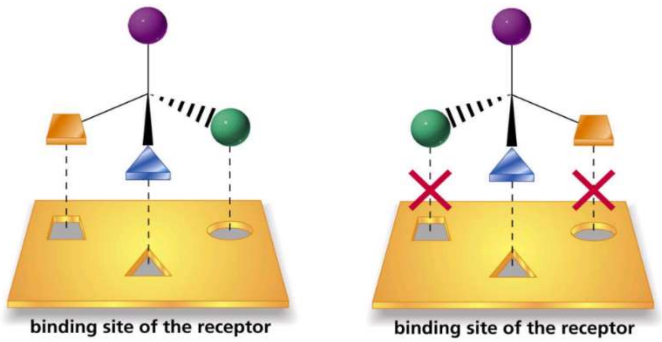
CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture 33 (11-04-2018)

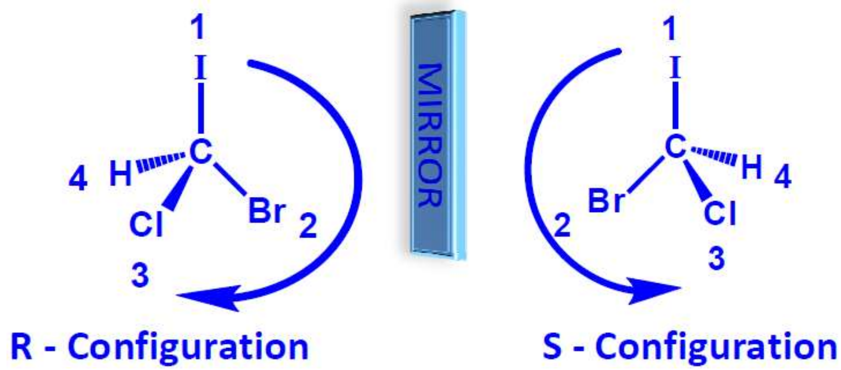
Summary of Lecture 33

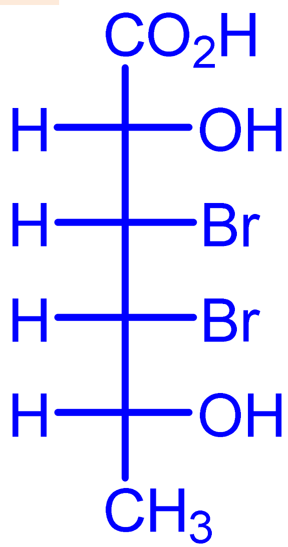




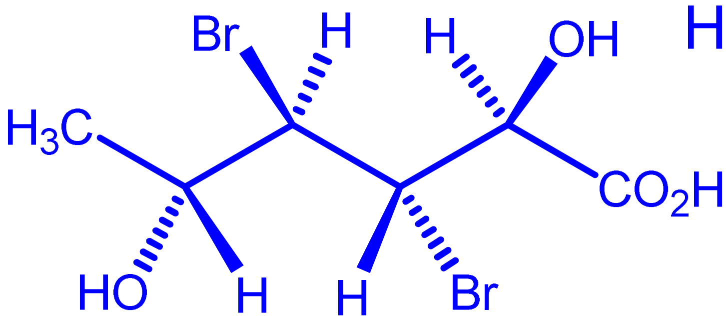
Enantiomers behaves differently in chiral medium

How do we "name" an enantiomers?? Cahn-Ingold-Prelog rules: THE *R/S* SYSTEM





The sign of optical rotation is not related to the *R,S* designation. Either of them can be dextrorotatory or levorotatory.



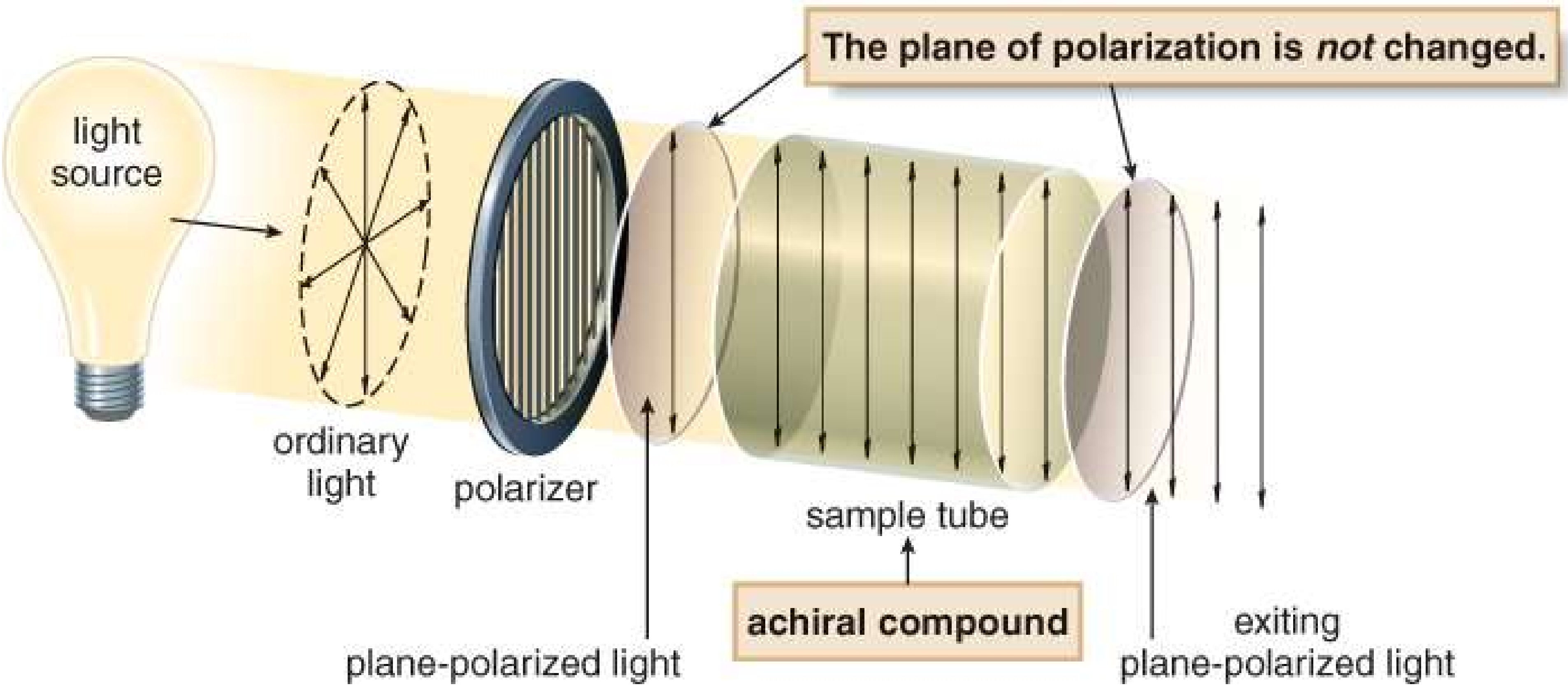
Physical Properties of Stereoisomers—Optical Activity

- The chemical and physical properties of two enantiomers are identical except in their interaction with chiral substances. They have identical physical properties, except for how they interact with plane-polarized light.

- Plane-polarized (polarized) light is light that has an electric vector that oscillates in a single plane. Plane-polarized light arises from passing ordinary light through a polarizer -Polaroid filter. The resulting light is said to be polarized - all its vibrations are parallel to a single plane.
- A polarimeter is an instrument that allows polarized light to travel through a sample tube containing an organic compound. It permits the measurement of the degree to which an organic compound rotates plane-polarized light.

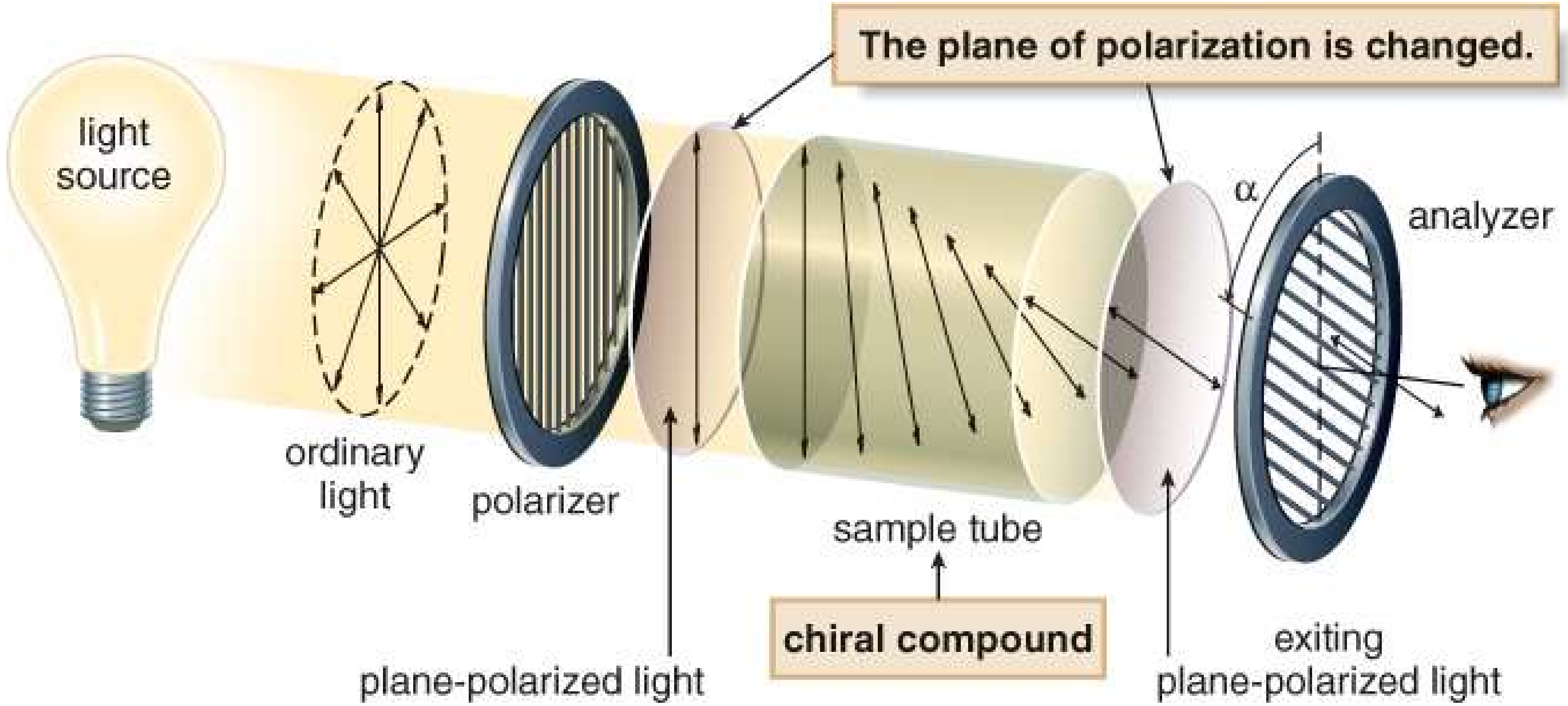
Plane-Polarized Light and Polarimeter

- With achiral compounds, the light that exits the sample tube remains unchanged. A compound that does not change the plane of polarized light is said to be optically inactive.



Plane-Polarized Light and Polarimeter

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



The angle of rotation of plane polarized light by an optically active substance is proportional to the number of atoms in the path of the light.

Specific Rotation

Specific rotation is a standardized physical constant for the amount that a chiral compound rotates plane-polarized light. Specific rotation is denoted by the symbol $[\alpha]$ and defined using a specific sample tube length (*l*, in dm), concentration (*c* in g/mL), temperature (25 °C) and wavelength (589 nm).

$$[\alpha]_D = \frac{\text{(observed rotation in degrees)}}{\text{(pathlength in dm)(concentration in g/ml)}} = \frac{\alpha}{l \times C}$$

Where $[\alpha]_D$ = Specific rotation, α = observed rotation, C = concentration in g/mL, l = length of tube in dm.

Q: A compound was isolated in the lab and the observed roation was +15 when measured in a 1 dm. tube containing 2.0 g of sample in 10 mL of water. What is the specific rotation of this compound?

$[\alpha]_D = \alpha/(\text{length x (g/ml)}) = 15/(1\text{ dm. X }(2.0\text{ g}/10\text{ ml})) = +75^o$

Dextrorotary designated as *d* or (+), clockwise rotation

Levorotary designated as *l* or (-), counter-clockwise rotation

Optical Purity and enantiomeric excess (ee)

A quick word on enantiomeric excess (ee)

Enantiomeric excess (ee) is the most common way to report the level of enantioselectivity Observed for a reaction.

The **ee is the amount (in %) of one enantiomer present subtracted from the amount of the other, thus…..**

50:50	**0% ee**
75:25	**50% ee**
80:20	**60% ee**
90:10	**80% ee**
95:5	**90% ee**
99:1	**98% ee**
99.5:0.5	**99% ee**

Q: What is the ee of the racemic mixture with 95% A and 5% B?

ee = % of A - % of B = 95 – 5 = 90%

If the mixture contain one of the enantiomer in excess to other, the mixture will show optical activity. If a substance contain exclusively one enantiomers, the substance is called optically pure substance

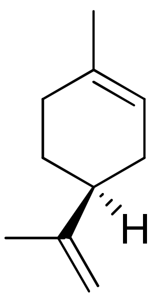
Optical Purity and enantiomeric excess (ee)

Enantiomeric excess (optical purity) is a measurement of how much one enantiomer is present in excess of the racemic mixture. It is denoted by the symbol *ee*.

$$\text{\% Enantiomeric excess (\% ee)} = \frac{\text{Observed rotation}}{\text{Rotation of pure enantimer}} \times 100$$

(Optical purity)

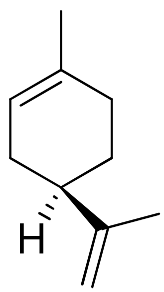
Q: The observed rotation for an enantiomeric mixture of limonene is +109^{o}. Calculate the (%) of each enantiomer present in the solution. (Rotation of pure enantiomer +123^{o}).



(-)-Lemonene

$[\alpha] = -123^{o}$

from Lemons



(+)-Lemonene

$[\alpha] = +123^{o}$

from oranges

Observed rotation is 109.0^{o}

$$\%ee = \frac{109.0}{123.0} \times 100$$

$$= 88.6$$

This means the sample contains 88.6% pure (+)-lemonene and 11.4% is racemic [out of half is (+) isomer]. Total (+) isomer is 94.3% and (-) isomer is 5.7%

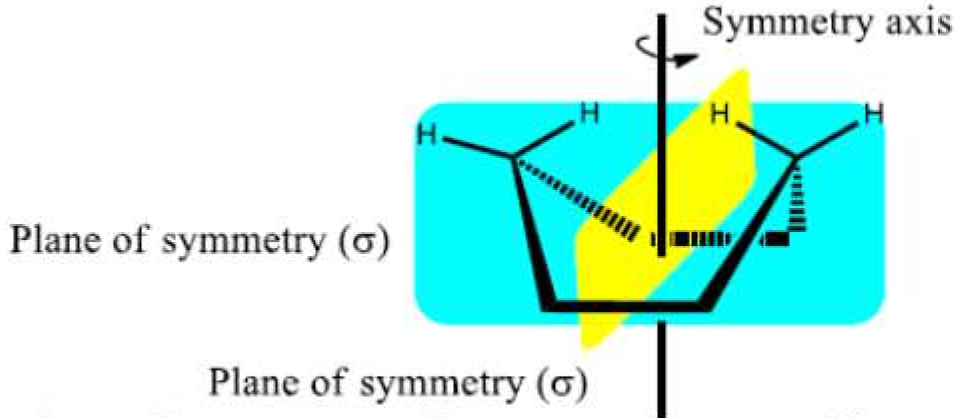
Molecular Symmetry

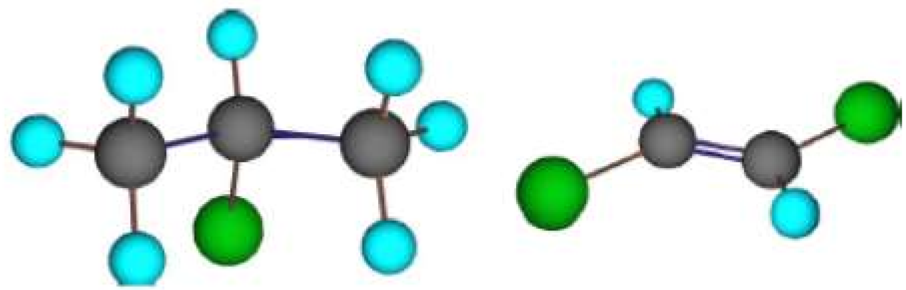
1. Plane of symmetry (σ)

- a plane bisects a molecule so that one half of molecule is the mirror image

or

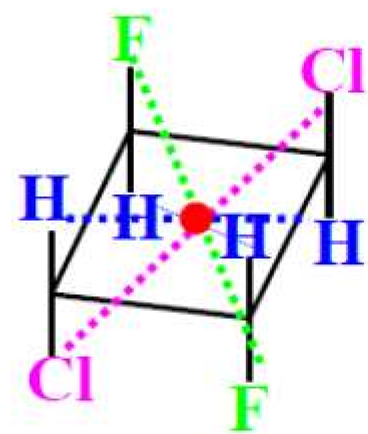
- all atoms in a molecule are on a plane





2. Center of symmetry (i):

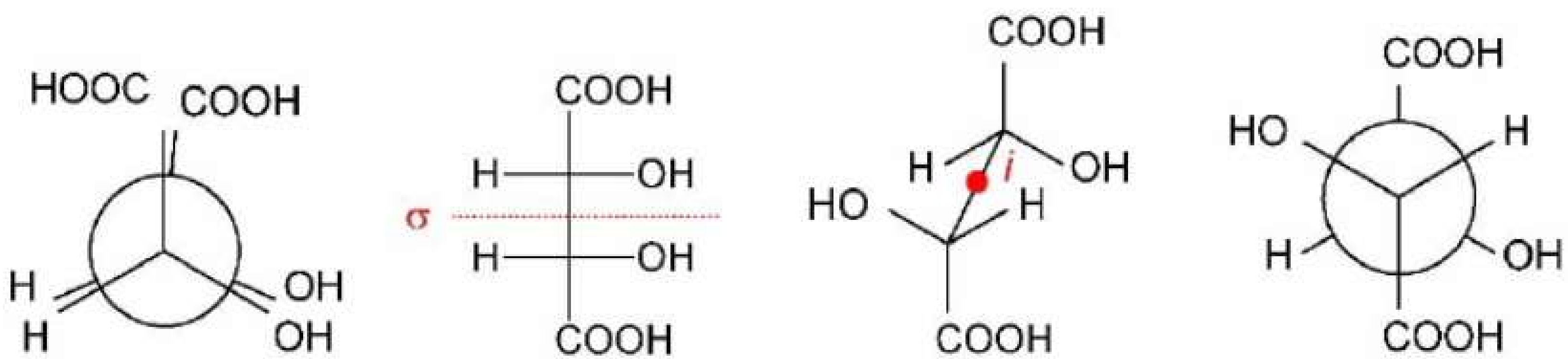
If any straight line passes a atom and molecular center, the same atom or group is encountered on the site at equal distance but in the opposite direction.



Molecular Symmetry and Chirality

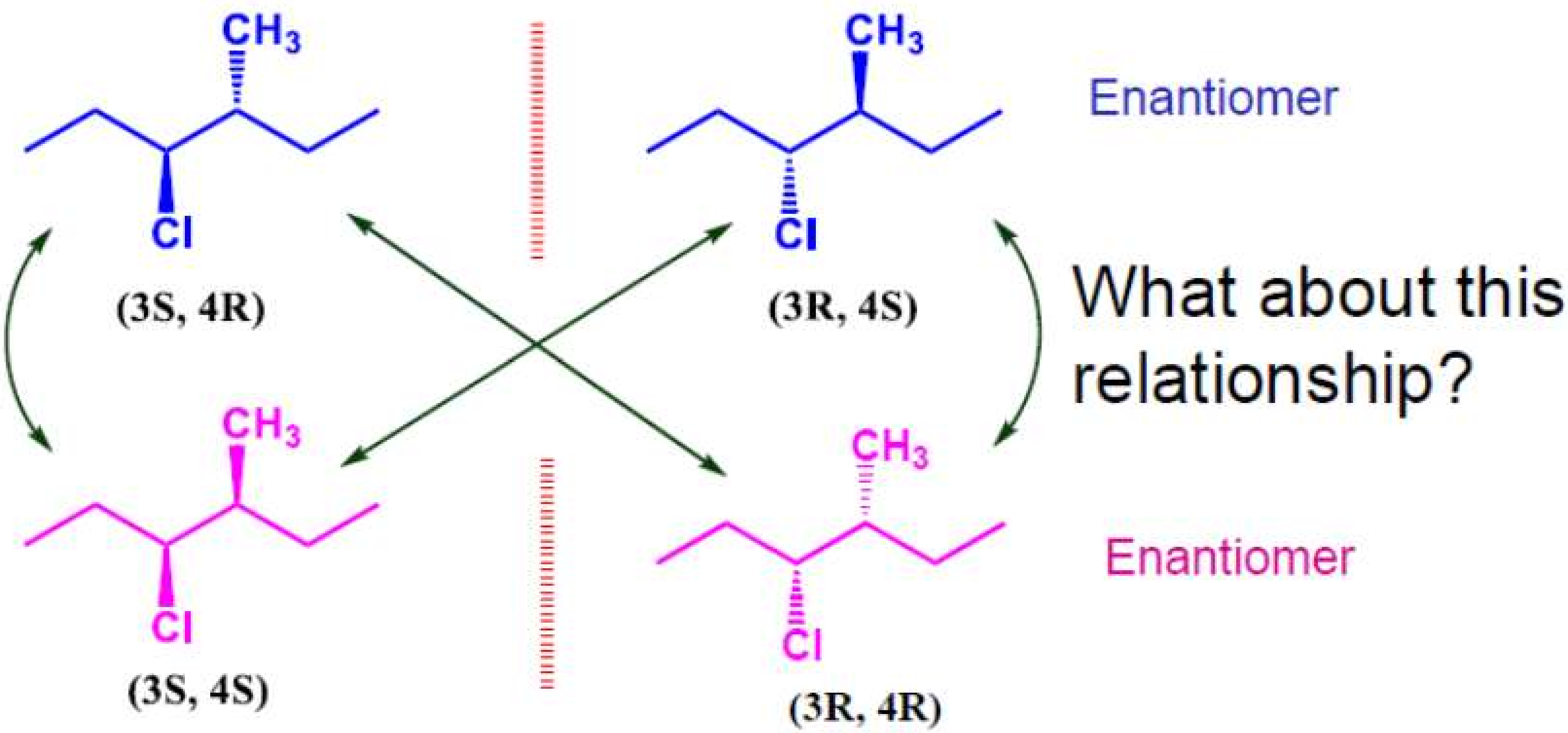
Mirror Planes and Centers of Inversion: They are another test to assess whether the chirality is present in an object.

- Objects (molecules) with mirror planes or center of inversion (point of inversion) are achiral (NOT chiral). They have superimposable mirror image.
- Objects (molecules) without a mirror plane or point of inversion are chiral. They are non-superposable on their mirror images.



Multiple Stereocenters

3-Chloro-4-methylhexane **There are two chiral centers**



They have diastereomeric relationship. Stereoisomers that are not enantiomers (non-superimosable mirror images) are called diastereoisomers.

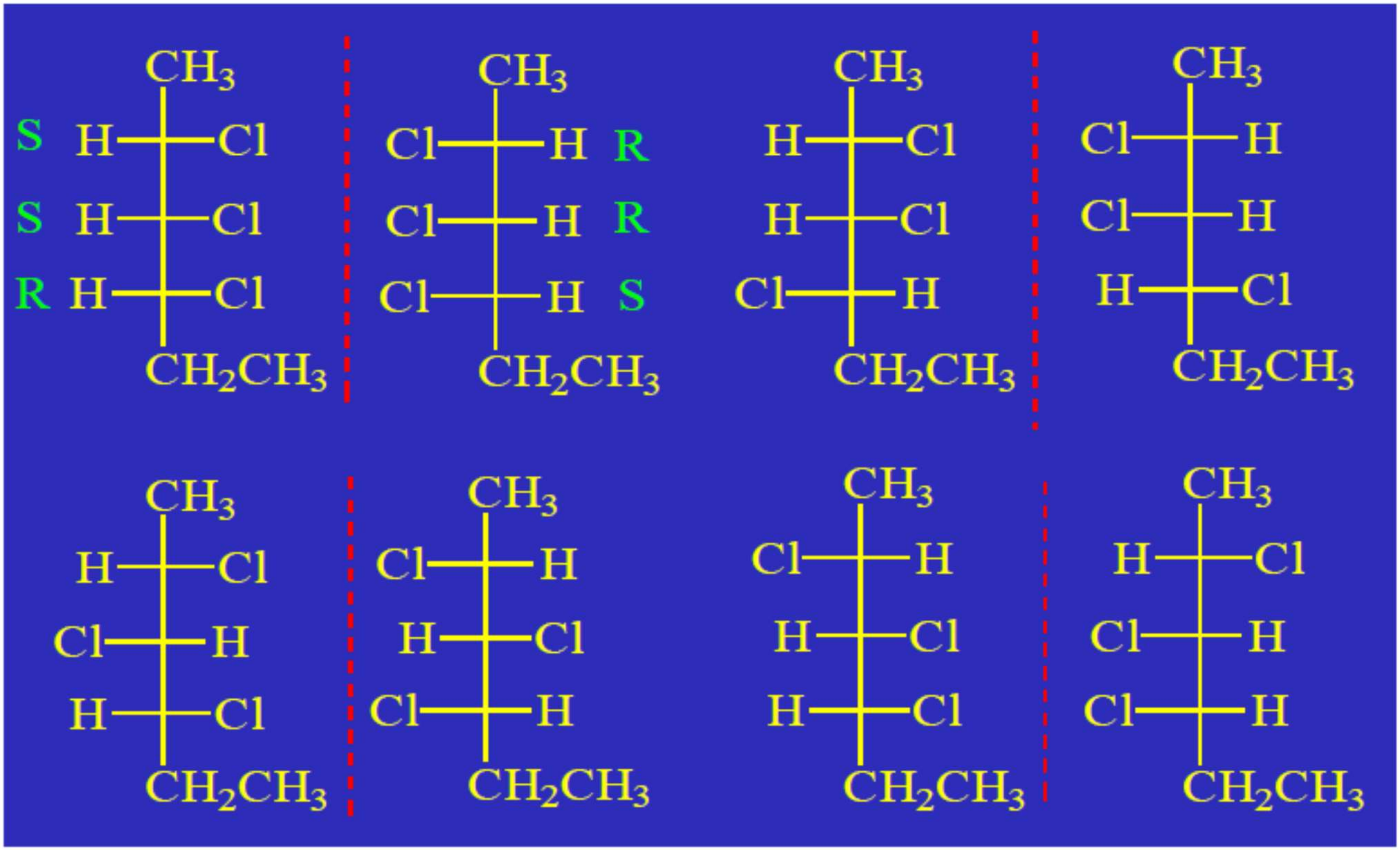
Diastereoisomers have different physical and chemical property.

For ***n*** chiral centers = $\mathbf{2}^{n}$ maximum stereoisomers

Multiple Stereocenters

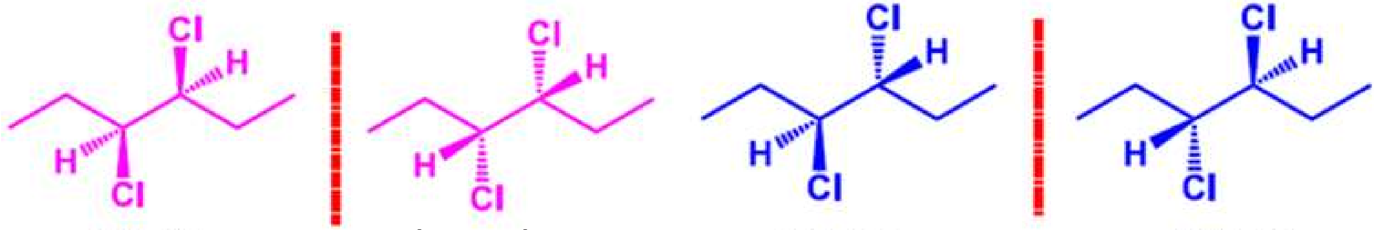
How many stereoisomers for 2,3,4-trichlorohexane?

Asymmetric centers n = 3; 2^n = 8



Multiple Stereocenters

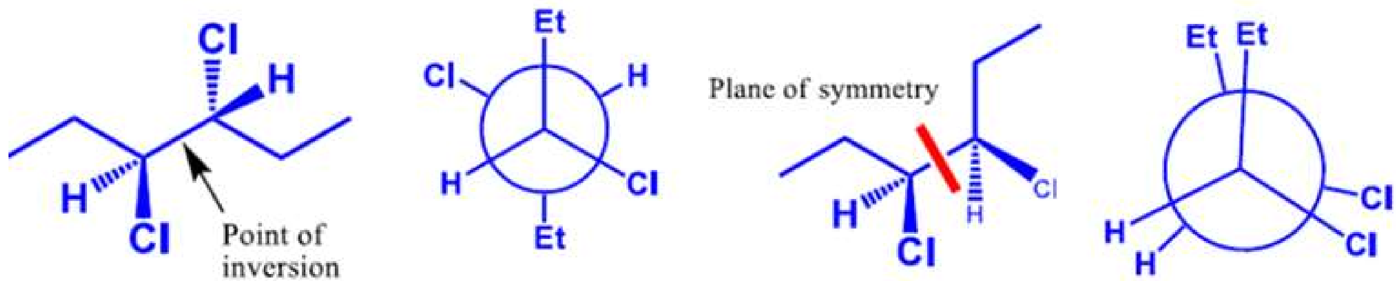
3,4-Dichlorohexane



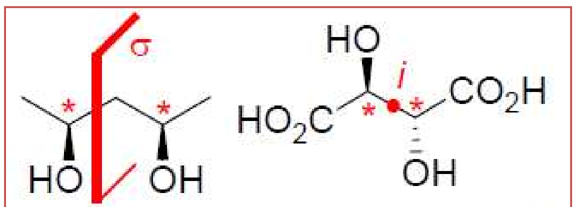
(3S, 4S) (3R, 4R) (3S, 4R) (3R, 4S)

Enantiomer

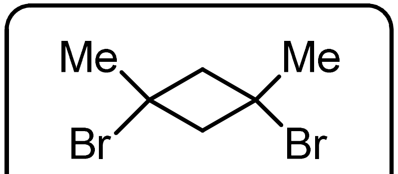
Meso compound ??



A meso-compound is one which is superimposable on its mirror image even though it contains stereogenic centers. The molecule is achiral.

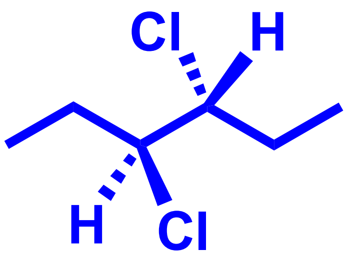


meso *meso*-tartaric acid

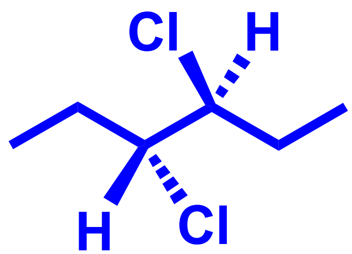


meso-compound
achiral

Multiple Stereocenters: Meso compounds

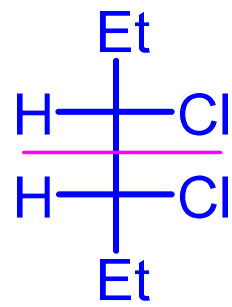


(3S, 4R)

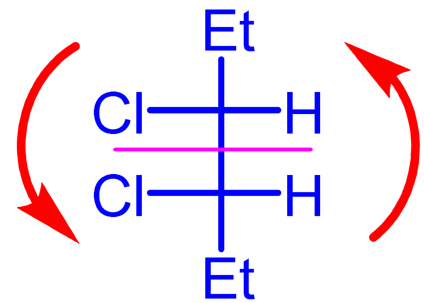


(3R, 4S)

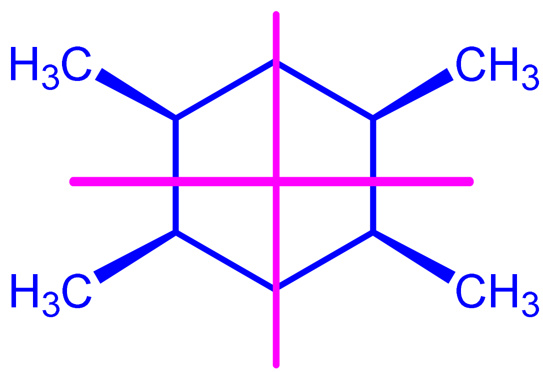
Meso compound



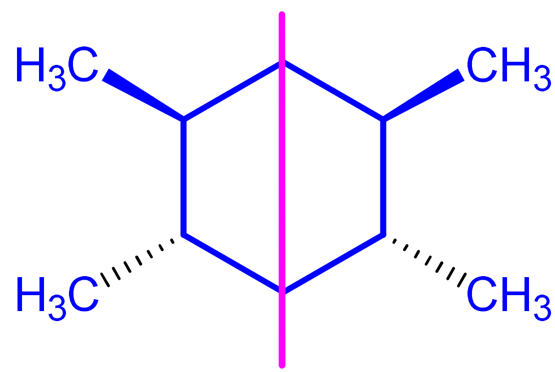
Plane of symmetry



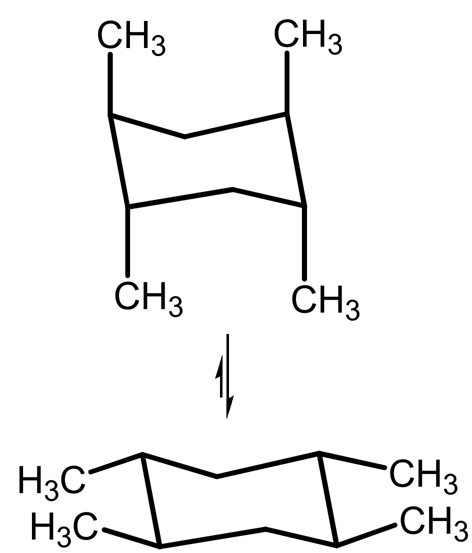
Superimposable
Optically inactive



Internal plane of symmetry
Optically inactive

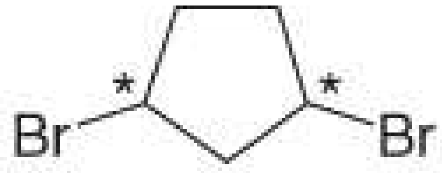


Internal plane of symmetry
Point of inversion or
center of symmetry
Optically inactive



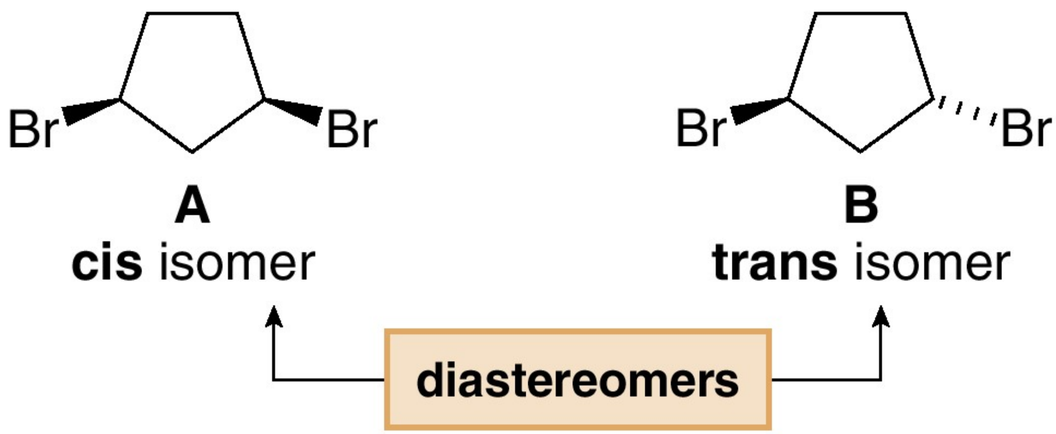
Disubstituted cyclic molecules

- Consider 1,3-dibromocyclopentane. Since it has two stereogenic centers, it has a maximum of four stereoisomers.

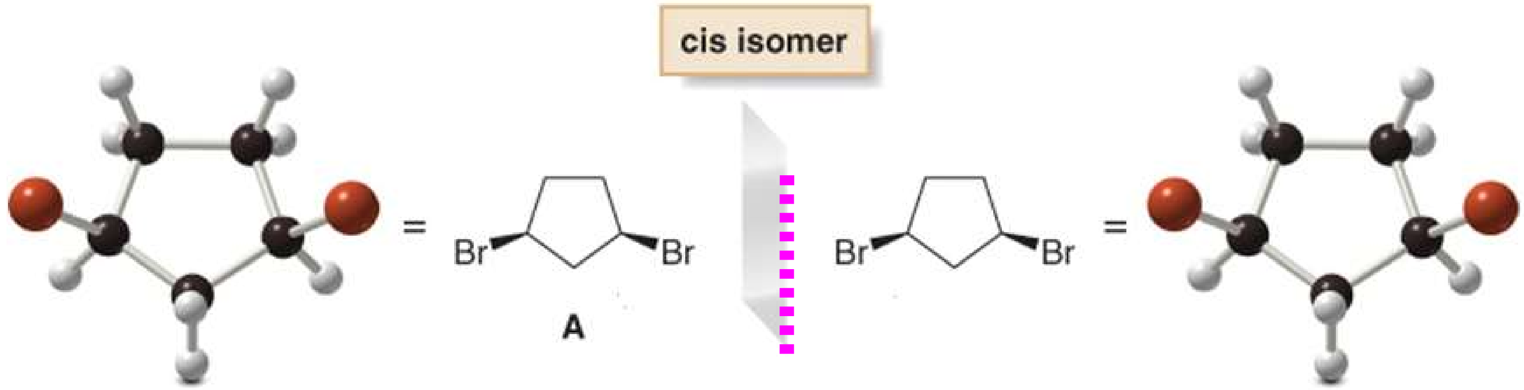


1,3-dibromocyclopentane
[* = stereogenic center]

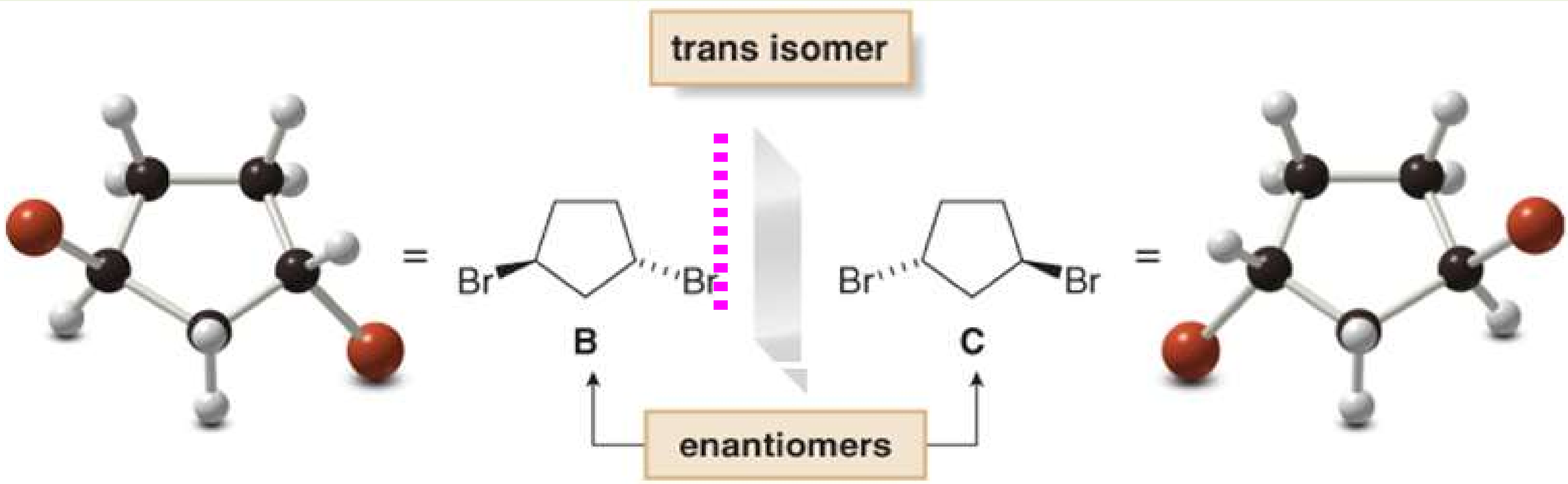
- A disubstituted cycloalkane can have two substituents on the same side of the ring (*cis* isomer, A) or on opposite sides of the ring (*trans* isomer, B). These compounds are stereoisomers but not mirror images.



Disubstituted cyclic molecules

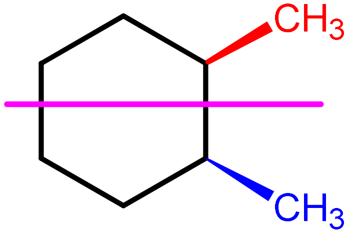


The *cis* isomer is superimposable on its mirror image, making the images identical. Thus, A is an achiral meso compound.

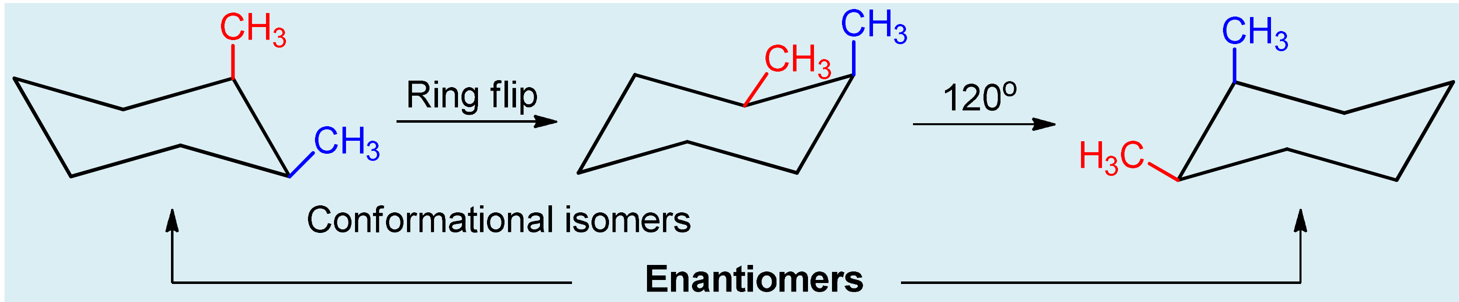


The trans isomer is not superimposable on its mirror image, labeled C, making B and C different compounds. Thus, B and C are enantiomers.

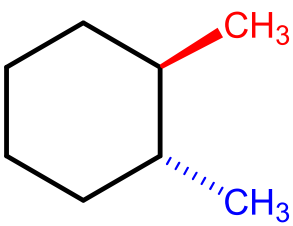
Disubstituted cyclic molecules



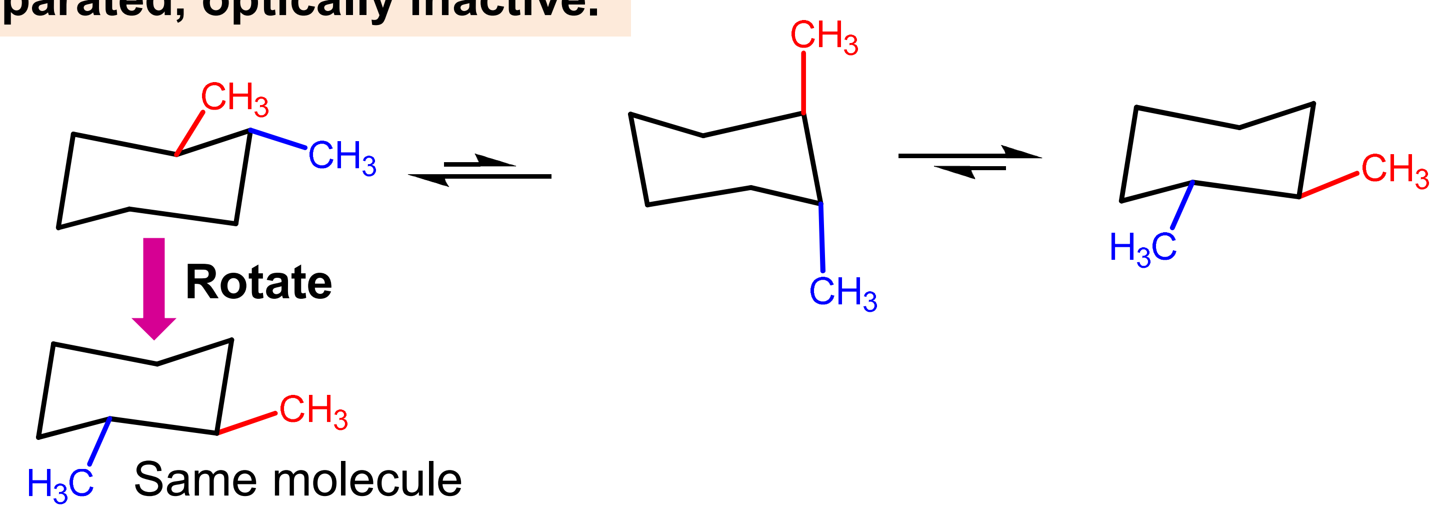
Non-superimposable mirror image



Two can not be separated, optically inactive.



Optically active



- If the contributing conformations average out to an achiral conformation, then the molecule is considered achiral and If a chiral conformation prevails over the others, then the molecule is considered chiral and it will show optical activity.