Chapter 4

Isomers: The Arrangement of Atoms in Space

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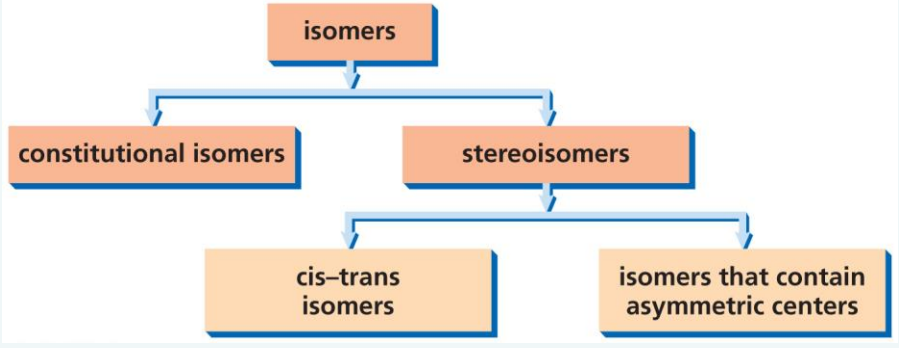
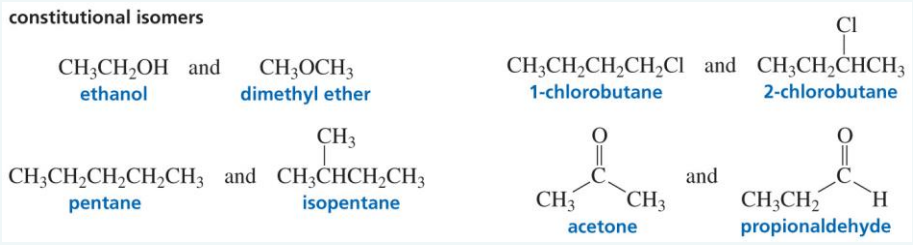
Isomers

Compounds that have the same molecular formula but different structures.



Constitutional Isomers

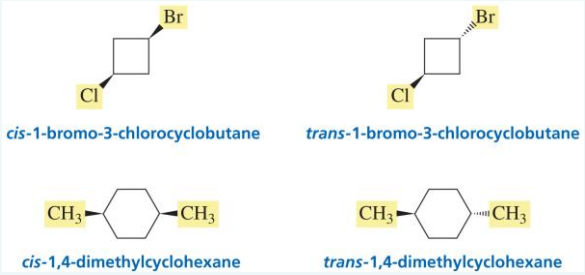


Constitutional isomers differ in the way the atoms are connected.

Stereoisomers: Cis–Trans Isomers

Cis–trans isomers result from restricted rotation.

Cyclic structures have restricted rotation.

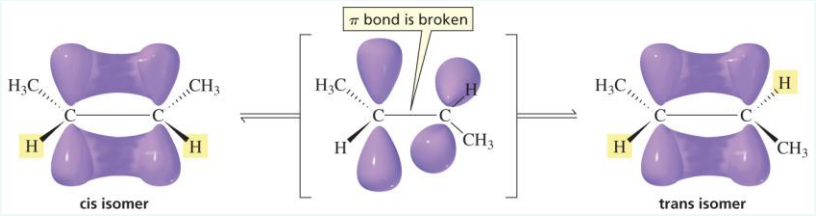


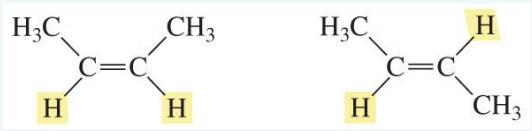
Cis: The substituents are on the same side of the ring.

Trans: The substituents are on opposite sides of the ring.

Cis–Trans Isomers

Double bonds restrict rotation.

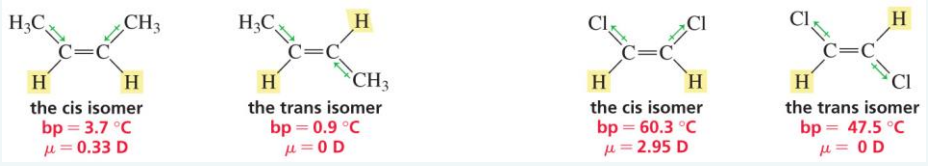




Cis: The hydrogens are on the same side of the double bond.

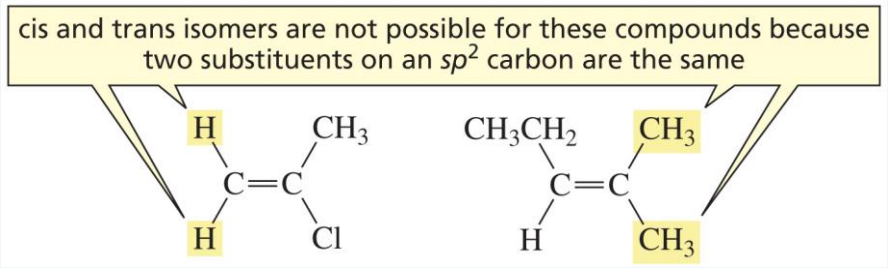
Trans: The hydrogens are on opposite sides of the double bond.

Cis–Trans Isomers

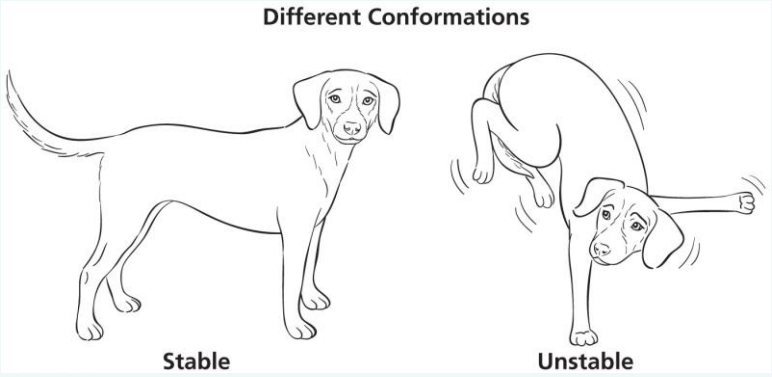


Cis–trans isomers have different physical properties.

Some Alkenes do not have Cis–Trans Isomers

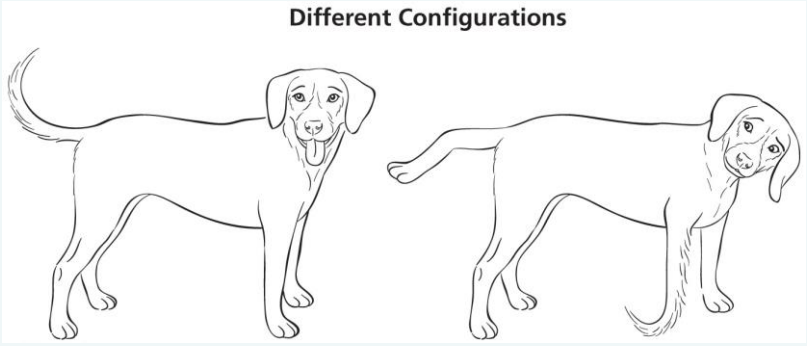


Different Conformations



Compounds with different conformations (conformers) cannot be separated.

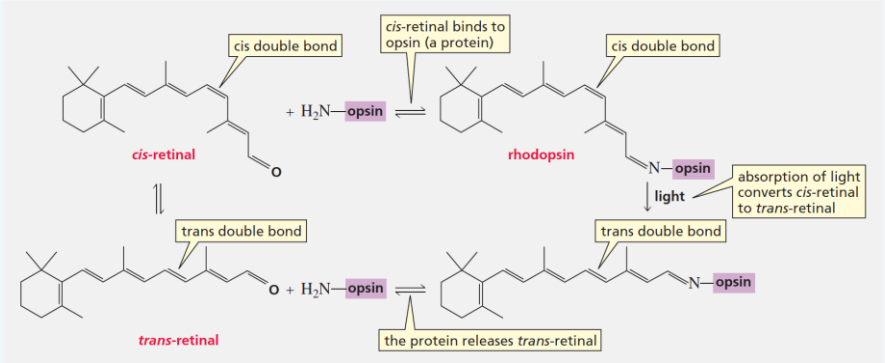
Different Configurations



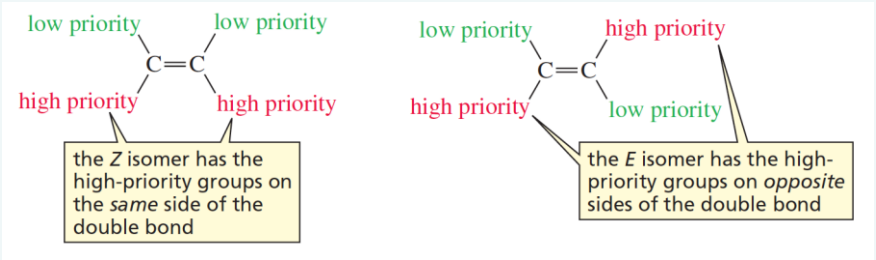
Compounds with different configurations can be separated.

Cis–trans isomers have different configurations.

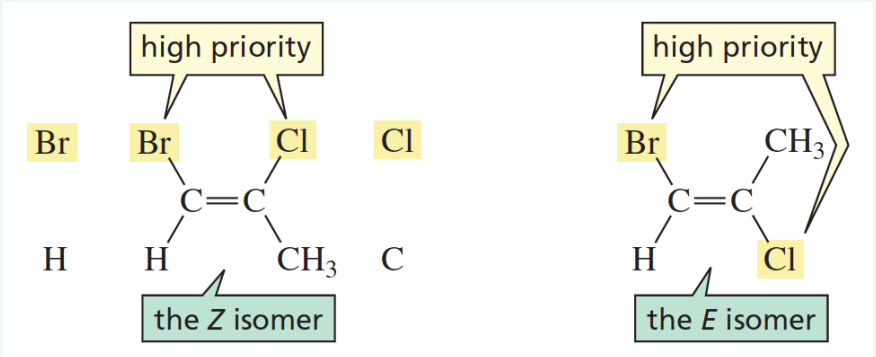
Cis-Trans Isomerization in Vision



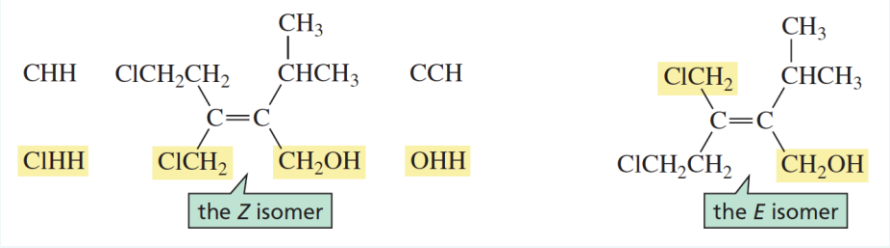
The *E,Z* System for Designating Geometric Isomers



The *E,Z* System for Designating Geometric Isomers

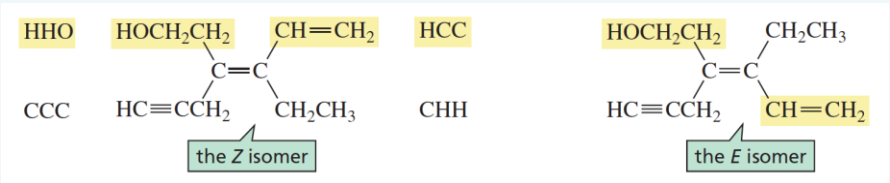


The *E,Z* System for Designating Geometric Isomers



If the atoms attached to the sp^2 carbon are the same, the atoms attached to the tied atoms are compared; the one with the greater atomic number belongs to the group with the higher priority.

The *E,Z* System for Designating Geometric Isomers



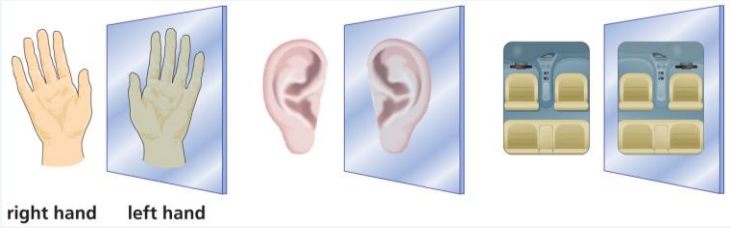
If an atom is doubly bonded to another atom, treat it as if it were singly bonded to two of those atoms.

If an atom is triply bonded to another atom, treat it as if it were singly bonded to three of those atoms.

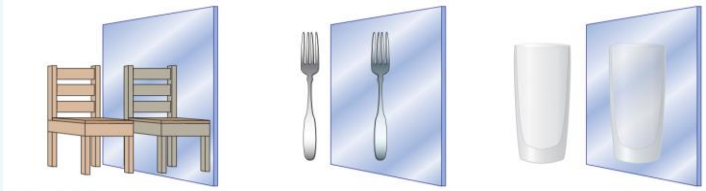
Cancel atoms that are identical in the two groups; use the remaining atoms to determine the group with the higher priority.

Chiral and Achiral Objects

Chiral objects



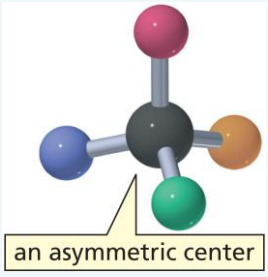
Achiral objects

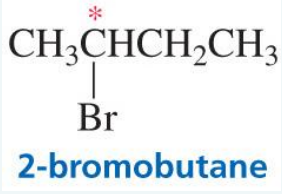


Chiral Molecules

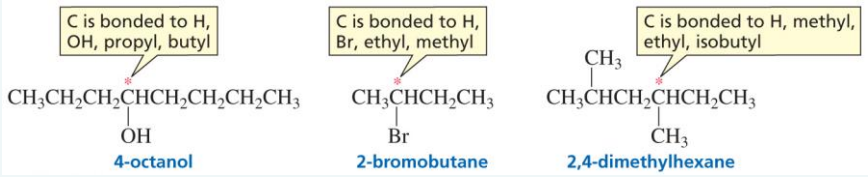
Chiral molecules have an asymmetric center.

An asymmetric center is an atom that is attached to four different groups.

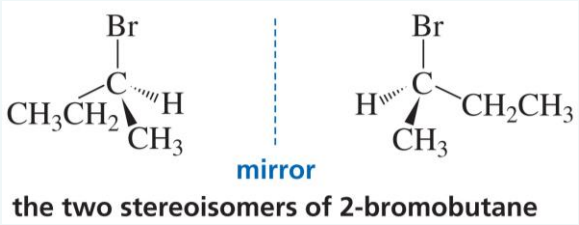




Compounds with an Asymmetric Center



Enantiomers

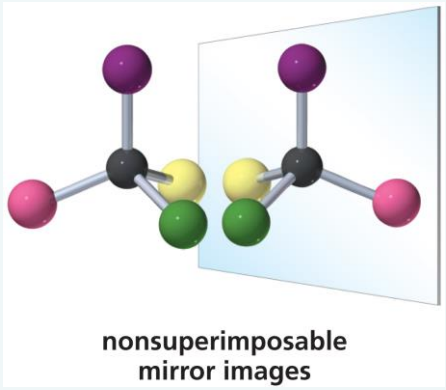


The two isomers are called enantiomers.

Enantiomers are different compounds: they can be separated.

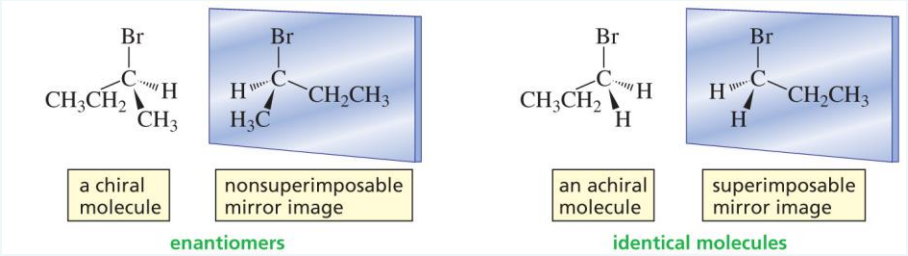
Enantiomers have the same physical and chemical properties.

Enantiomers



Enantiomers are nonsuperimposable mirror images.

Chiral and Achiral Molecules

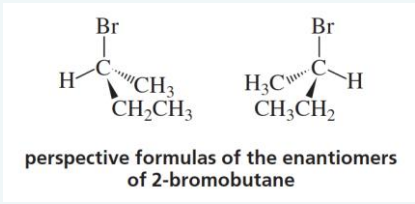


Chiral compounds have nonsuperimposable mirror images.

Achiral compounds have superimposable mirror images (they are identical molecules).

How to draw Enantiomers

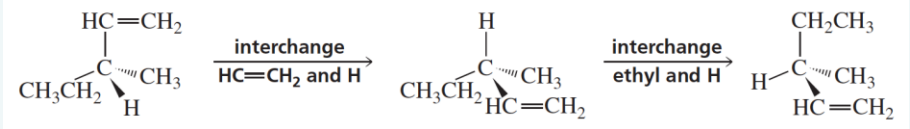
Perspective formulas



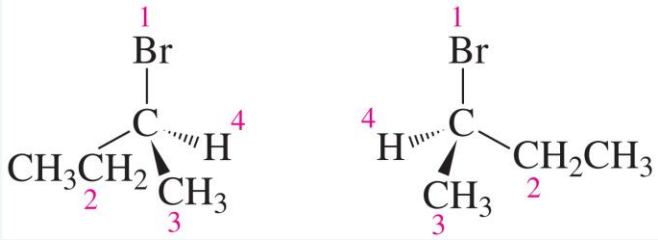
perspective formulas of the enantiomers of 2-bromobutane

Interchanging two atoms or groups attached to an asymmetric center produces an enantiomer.

Interchanging two atoms or groups a second time brings you back to the original compound:



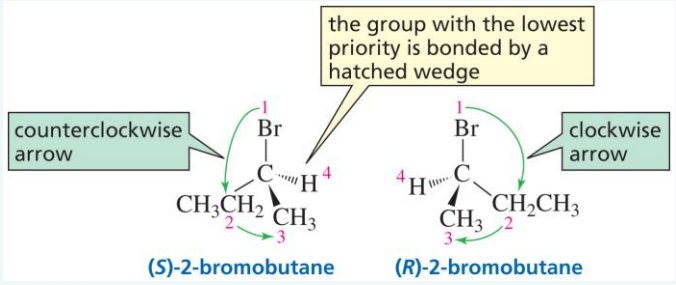
Naming Enantiomers



Assign relative priorities to the four groups.

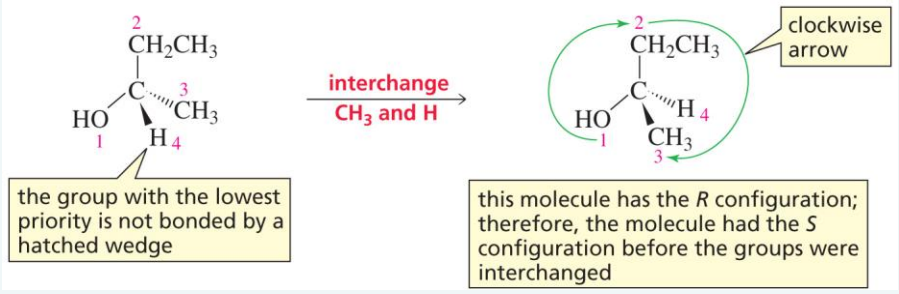
Naming Enantiomers

draw an arrow from 1 to 2 to 3



If the lowest priority group is on a hatched wedge, then
clockwise = *R*
and
counterclockwise = *S*

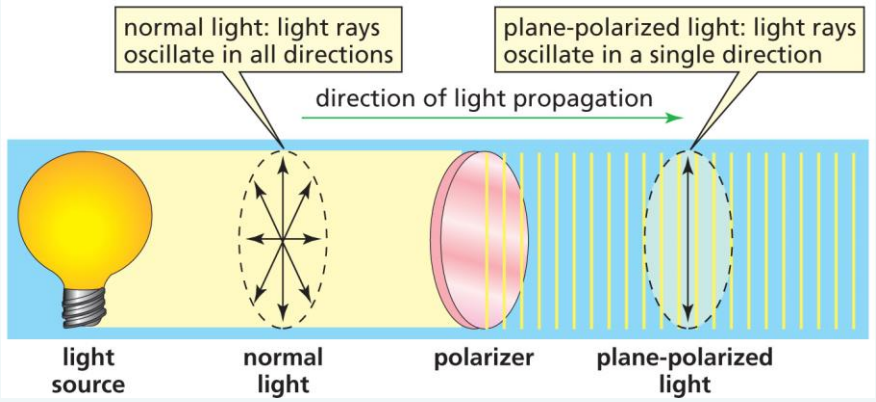
Naming Enantiomers



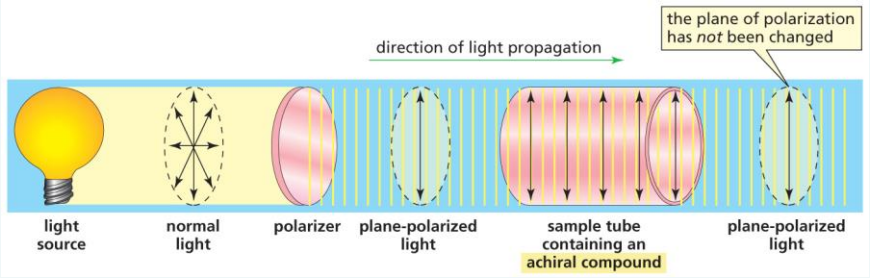
If the lowest priority group is not on a hatched wedge, switch a pair so it is on a hatched wedge.

Then, name the new compound.

Plane-Polarized Light

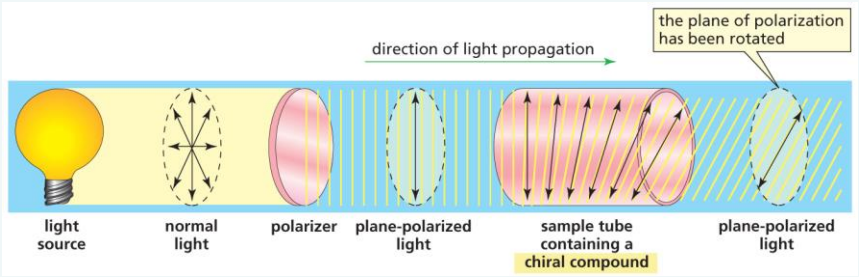


An Achiral Compound is optically Inactive



An achiral compound does not rotate the plane of polarization of plane-polarized light.

A Chiral Compound is optically Active



A chiral compound rotates the plane of polarization of plane-polarized light.

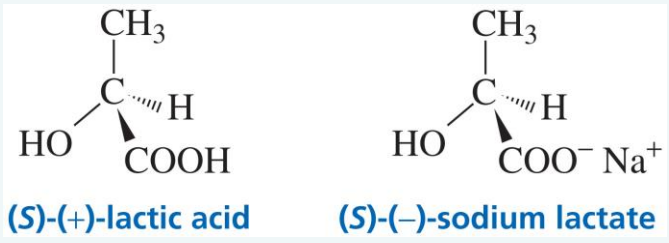
If it rotates the plane clockwise = (+)

If it rotates the place counterclockwise = (–)

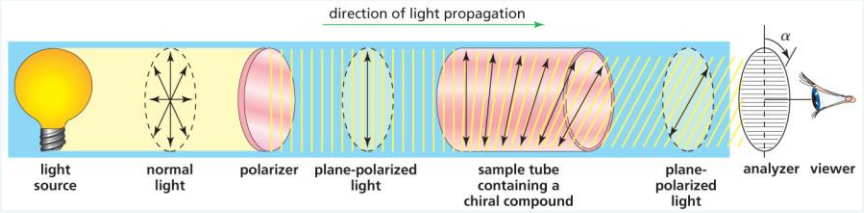
R and *S* Versus (+) and (–)

Some *R* enantiomers are (+) and some are (–).

Some *S* enantiomers are (+) and some are (–).

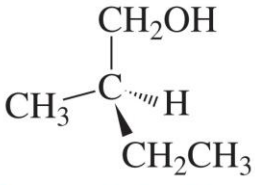


Polarimeter



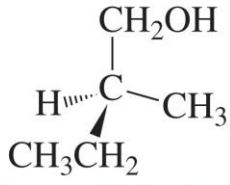
$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l \times c}$$

If one Enantiomer is (+), the other is (–)



(*R*)-2-methyl-1-butanol

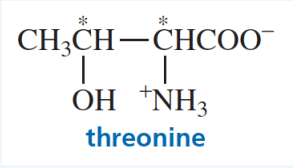
$[\alpha]_{D}^{20\,°C} = +5.75$



(*S*)-2-methyl-1-butanol

$[\alpha]_{D}^{20\,°C} = -5.75$

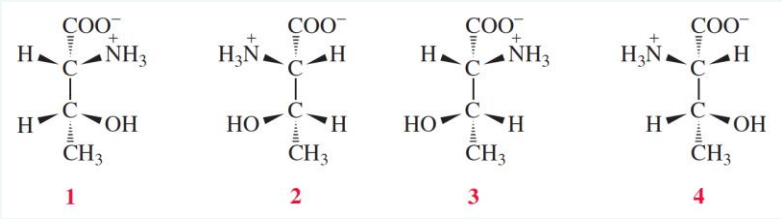
Compounds with two Asymmetric Centers



threonine

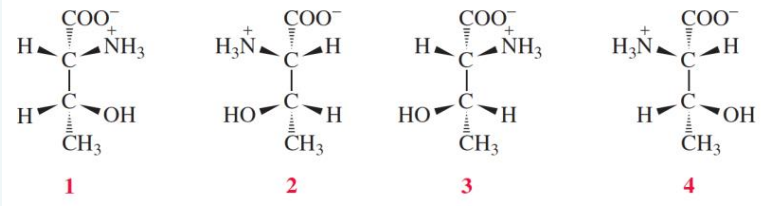
maximum # of stereoisomers = 2^n

(n = # of asymmetric centers)



1 and 2 are enantiomers. 3 and 4 are enantiomers.

Diastereomers



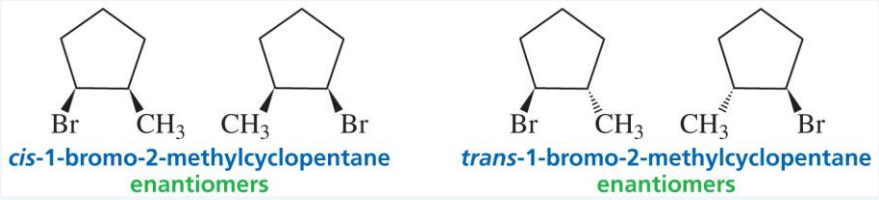
1 and 2 are enantiomers. 3 and 4 are enantiomers.

Diastereomers are stereoisomers that are not enantiomers.

1 and 3 are diastereomers. 2 and 3 are diastereomers.
1 and 4 are diastereomers. 2 and 4 are diastereomers.

Diastereomers have different physical and chemical properties.

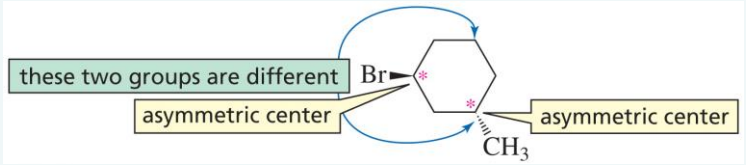
Two Asymmetric Centers, Four Stereoisomers



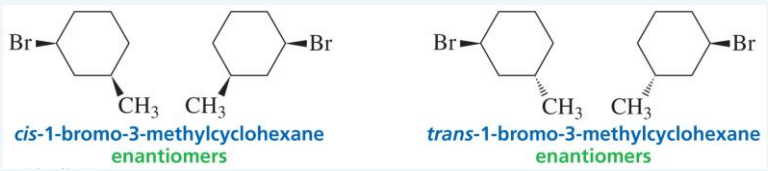
The cis stereoisomers are a pair of enantiomers.

The trans stereoisomers are a pair of enantiomers.

Identifying an Asymmetric Center

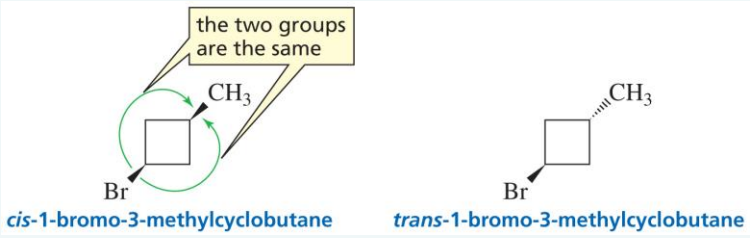


An asymmetric center is attached to four different groups.



two asymmetric centers, four stereoisomers

No Asymmetric Centers



cis-1-bromo-3-methylcyclobutane *trans*-1-bromo-3-methylcyclobutane

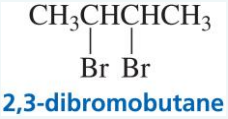
There are only two stereoisomers: cis and trans.

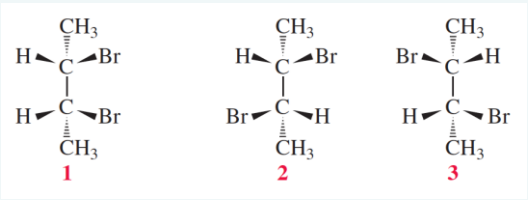
No Asymmetric Centers

cis-1-bromo-4-methylcyclohexane *trans*-1-bromo-4-methylcyclohexane

There are only two stereoisomers: cis and trans.

Two Asymmetric Centers: Three Stereoisomers (a meso compound and a pair of enantiomers)

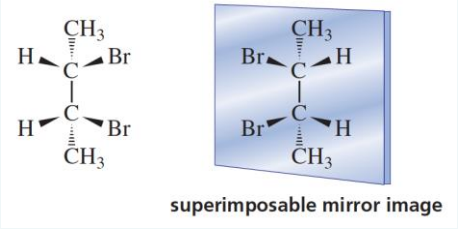


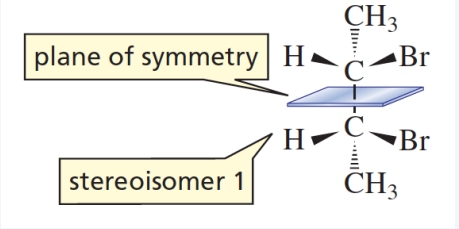


A compound with two asymmetric centers that has the same four groups bonded to each asymmetric center will have three stereoisomers:

a meso compound (1) and a
pair of enantiomers (2 and 3)

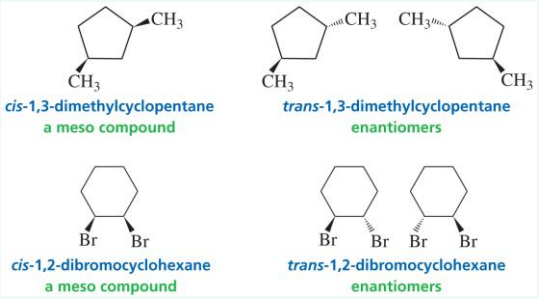
A Meso Compound has a Superimposable Mirror Image





Meso compounds are optically inactive even though they have asymmetric centers.

Cyclic Meso Compounds



For cyclic compounds with the same substituent bonded to two asymmetric centers,

cis = a meso compound
and
trans = a pair of enantiomers.

Physical Properties of Stereoisomers

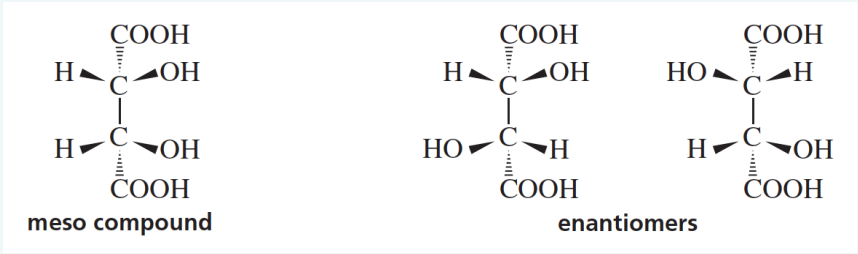
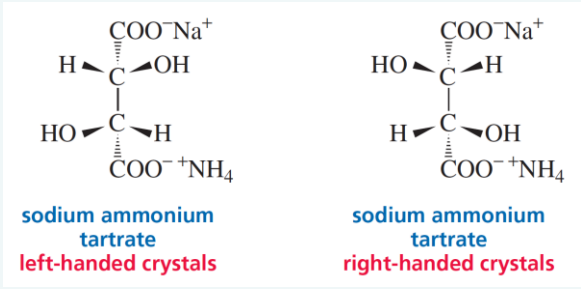


Table 4.2 Physical Properties of the Stereoisomers of Tartaric Acid

	Melting point, °C	Specific rotation	Solubility, g/100 g H_2O at 15 °C
(2*R*,3*R*)-(+)-Tartaric acid	171	+11.98	139
(2*S*,3*S*)-(−)-Tartaric acid	171	−11.98	139
(2*R*,3*S*)-Tartaric acid (meso)	146	0	125
(±)-Tartaric acid	206	0	139

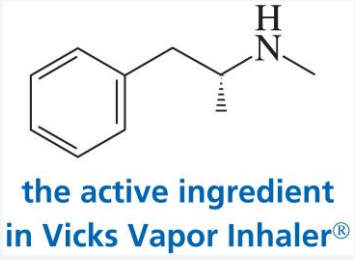
Separating Enantiomers

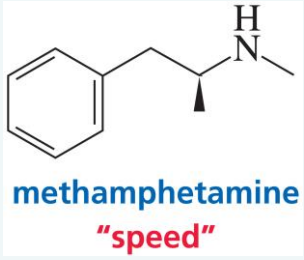


separating by hand

separating by chromatography

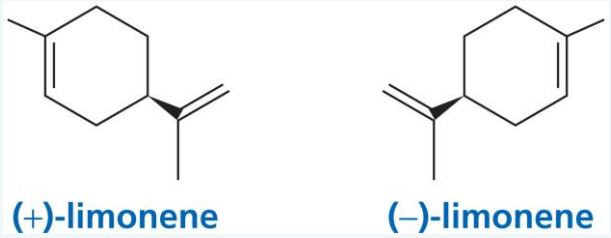
Physiological Properties of Enantiomers





Enantiomers can have very different physiological properties.

Oranges and Lemons



found in oranges

found in spruce trees