Essential Organic Chemistry

Paula Yurkanis Bruice

Chapter 6

Isomers and Stereochemistry

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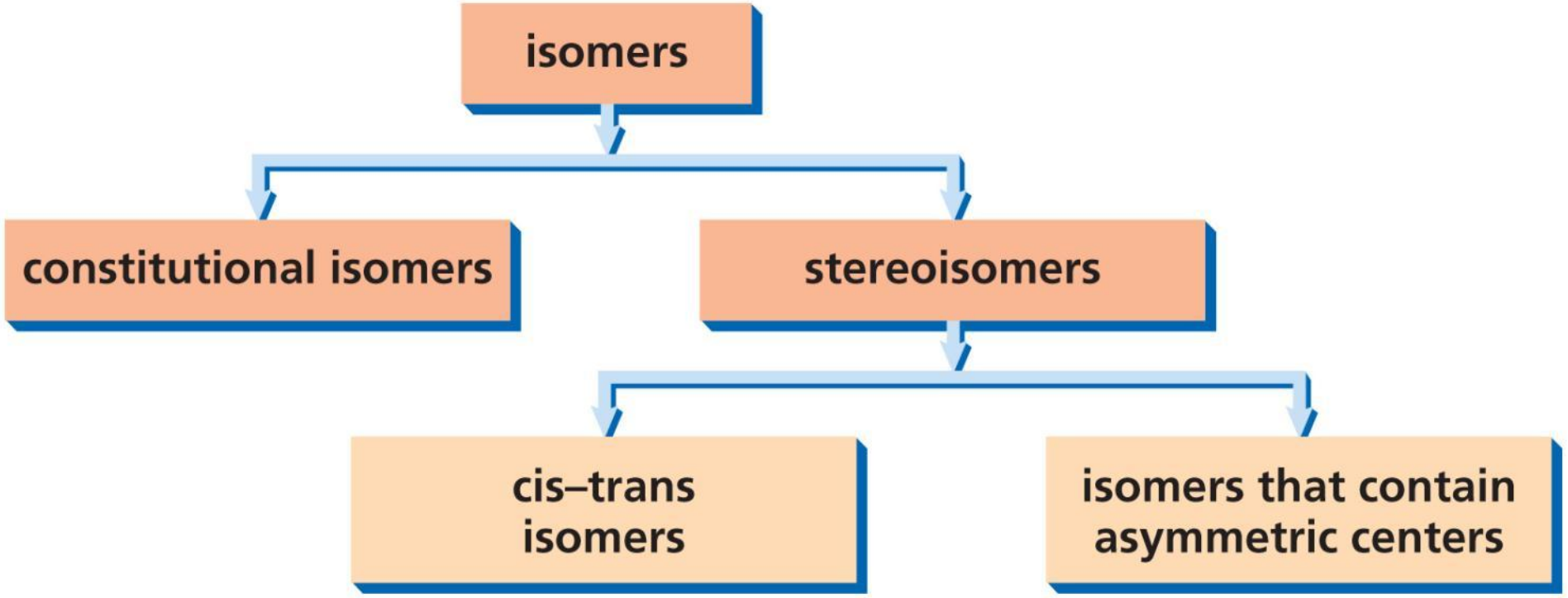
2013



Review of Isomerism

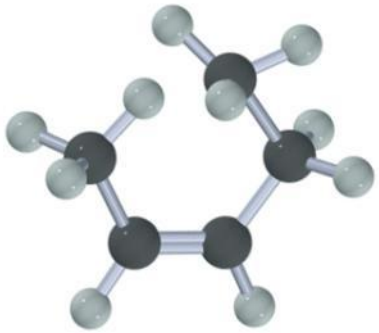
- ***Isomers*** – Compounds that have the same molecular formula but do not have identical structures.
- ***Constitutional Isomers*** – differ in the way their atoms are connected.
- ***Stereoisomers*** – differ in the way their atoms are arrange in space.

Constitutional Isomers

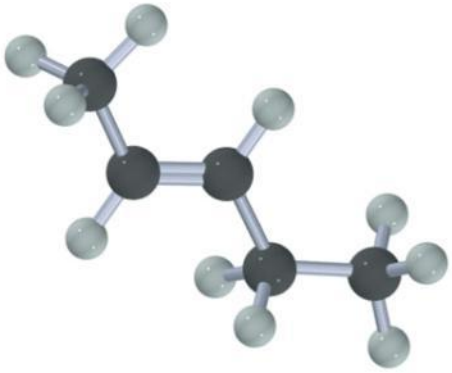
constitutional isomers

6.1 Cis-trans isomers

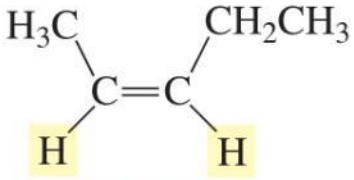
- Differ in the arrangement of their atoms in space (cannot interconvert)- ***Alkenes***.



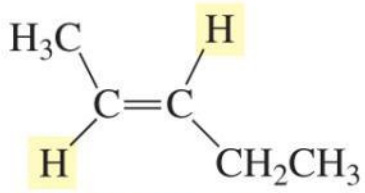
cis-2-pentene



trans-2-pentene



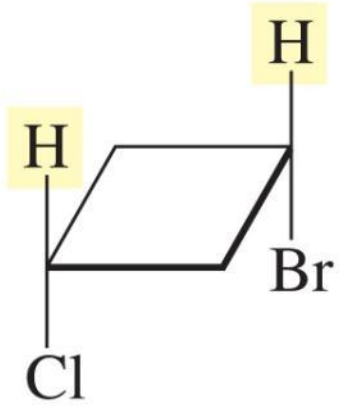
cis-2-pentene



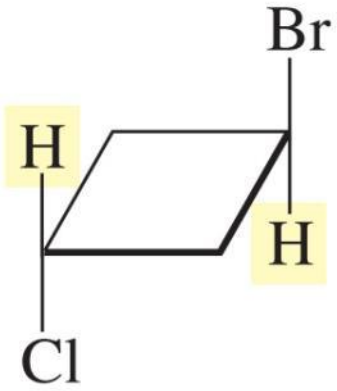
trans-2-pentene

6.1 Cis-trans isomers

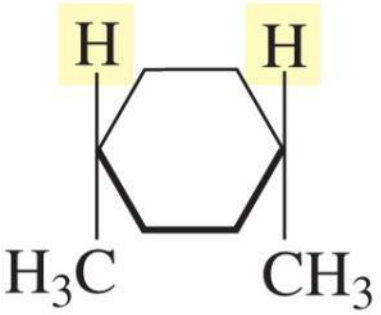
- ***Cyclic structure***.



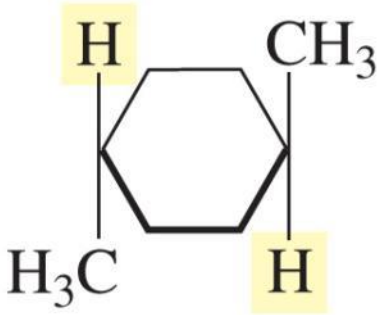
cis-1-bromo-3-chlorocyclobutane



trans-1-bromo-3-chlorocyclobutane



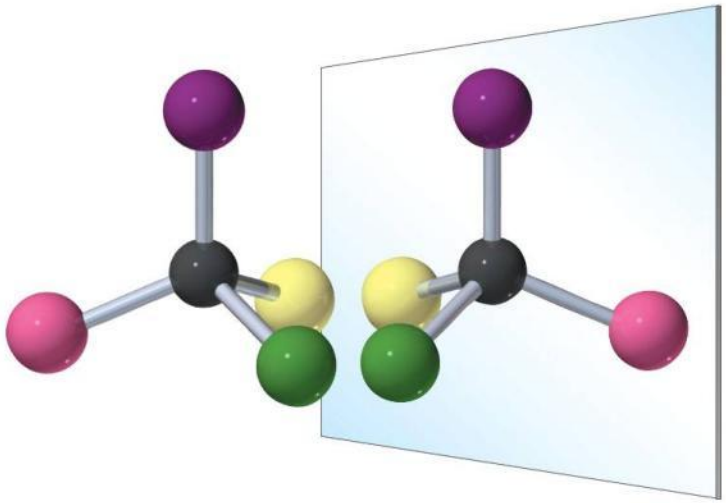
cis-1,4-dimethylcyclohexane



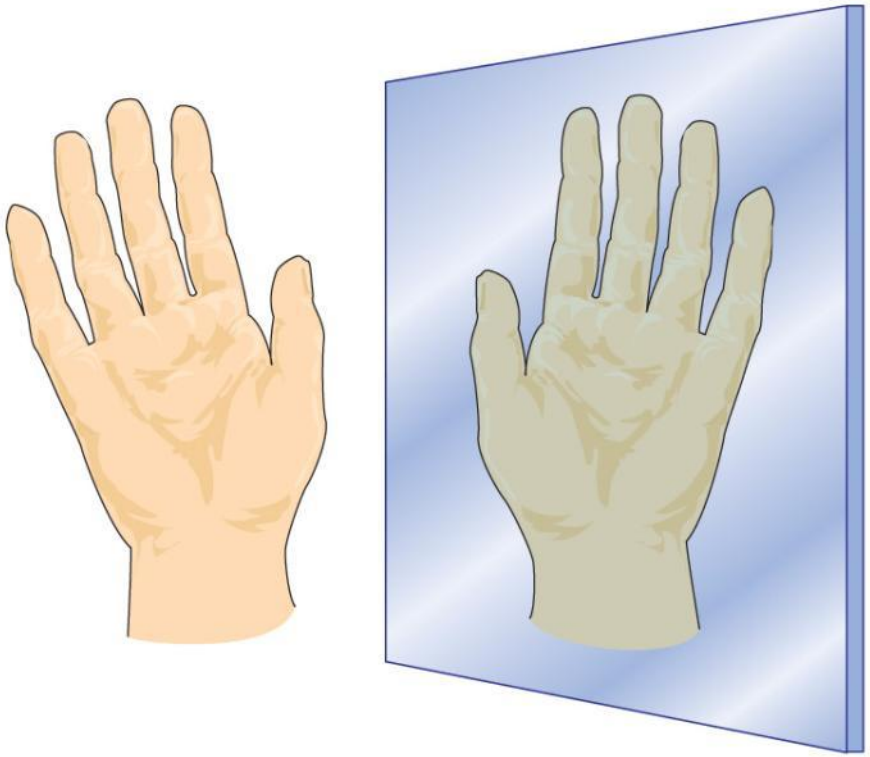
trans-1,4-dimethylcyclohexane

6.2 Chirality

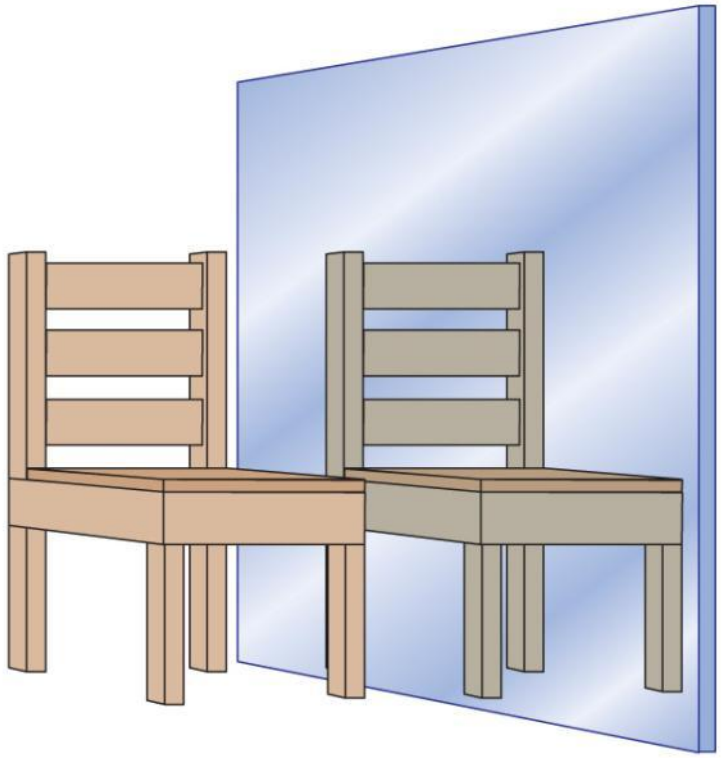
- ***Chiral*** – Nonsuperimposable on its mirror image.
- ***Achiral*** – Superimposable on its mirror image.
- If a molecule (or object) has a mirror plane or an inversion center, it cannot be chiral.



nonsuperimposable mirror images



right hand left hand



Chiral or Achiral?

- Brandy snifter

achiral

Chiral or Achiral?

- Shears

chiral

Chiral or Achiral?

- Beer mug

achiral

Chiral or Achiral?

- Hiking boot

chiral

Chiral or Achiral?

- Baseball glove

chiral

Chiral or Achiral?

- Boat propeller

chiral

Chiral or Achiral?

- Desk chair

achiral

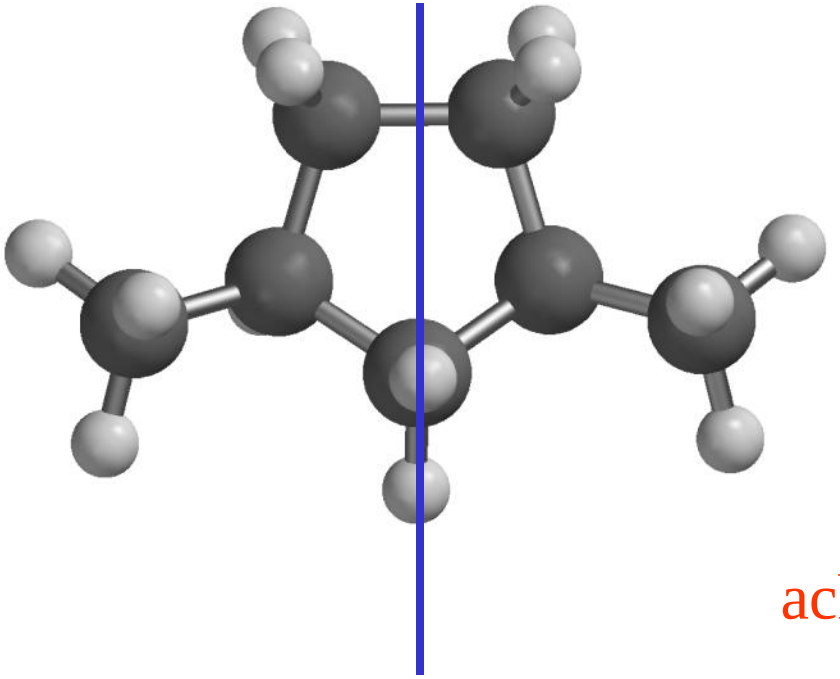
Chiral or Achiral?

- School desk

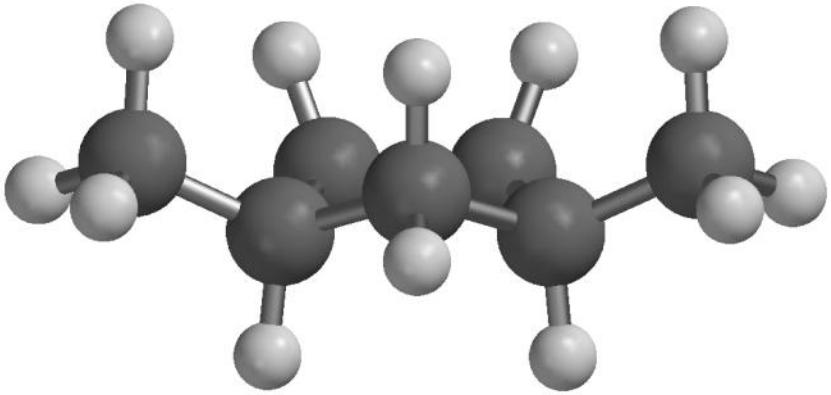
chiral

Chiral or Achiral?

- *cis*-1,3-dimethylcyclopentane



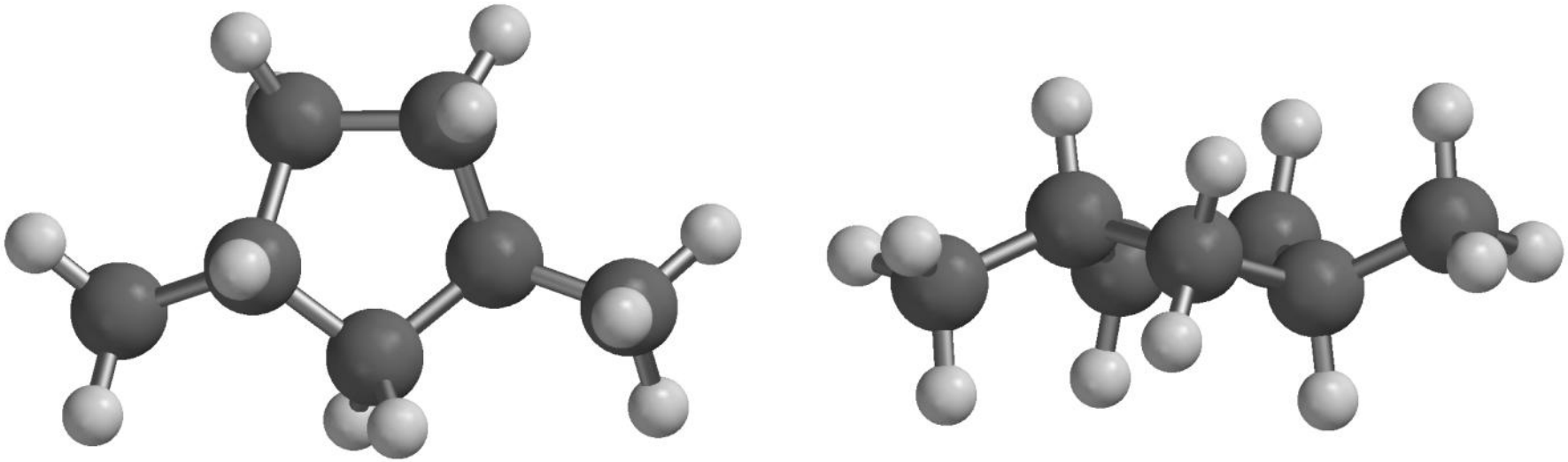
mirror plane



achiral

Chiral or Achiral?

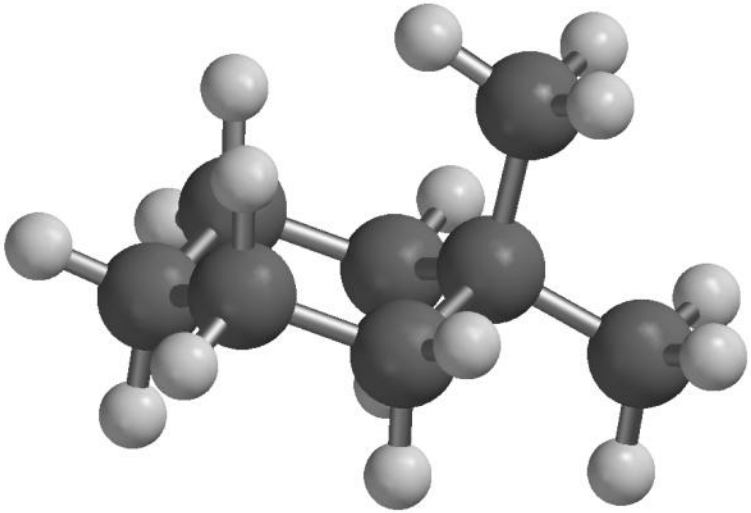
- *trans*-1,3-dimethylcyclopentane

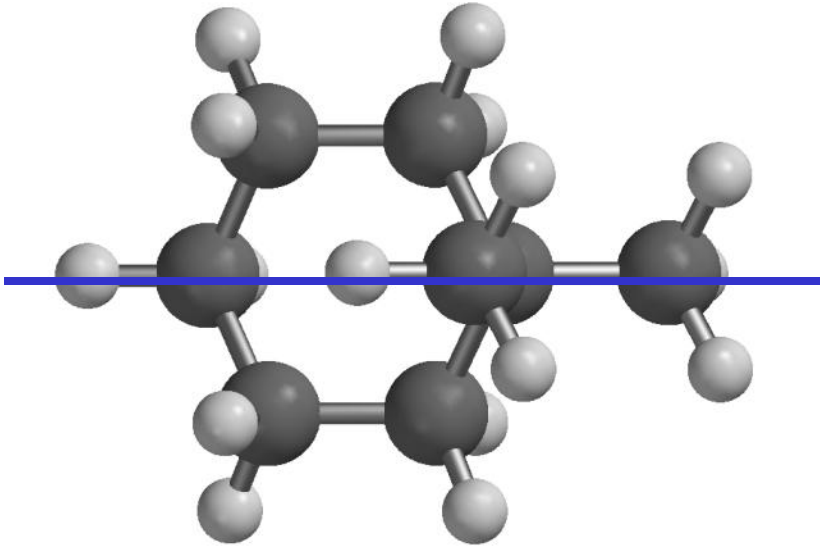


chiral

Chiral or Achiral?

- 1,1-dimethylcyclohexane

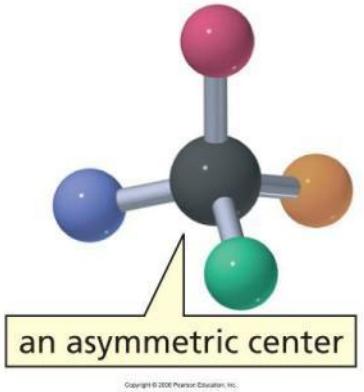


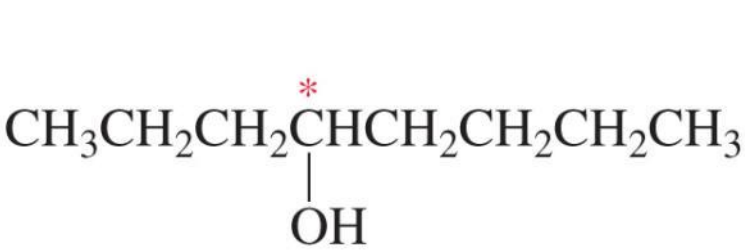


achiral

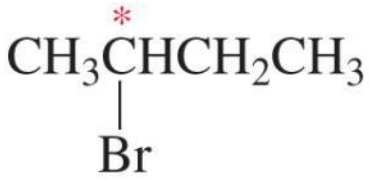
6.3 Asymmetric centers

- An **asymmetric center** is an atom that is bonded to four different groups.

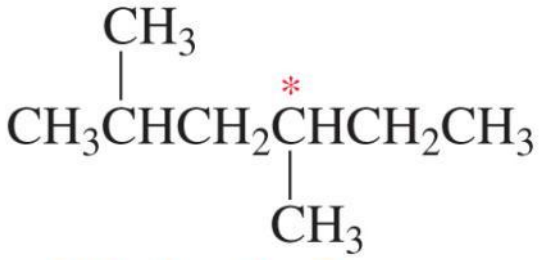




4-octanol



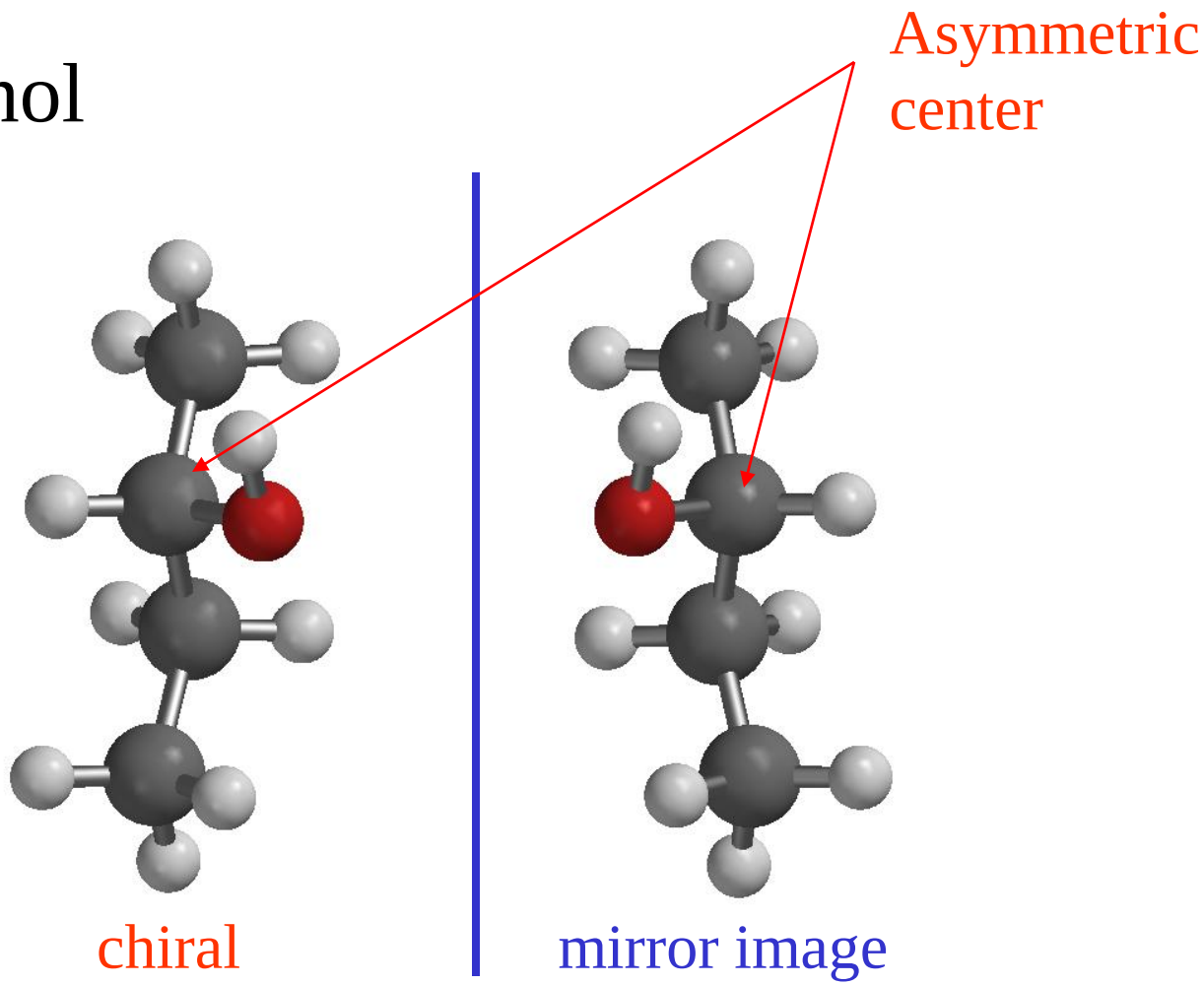
2-bromobutane



2,4-dimethylhexane

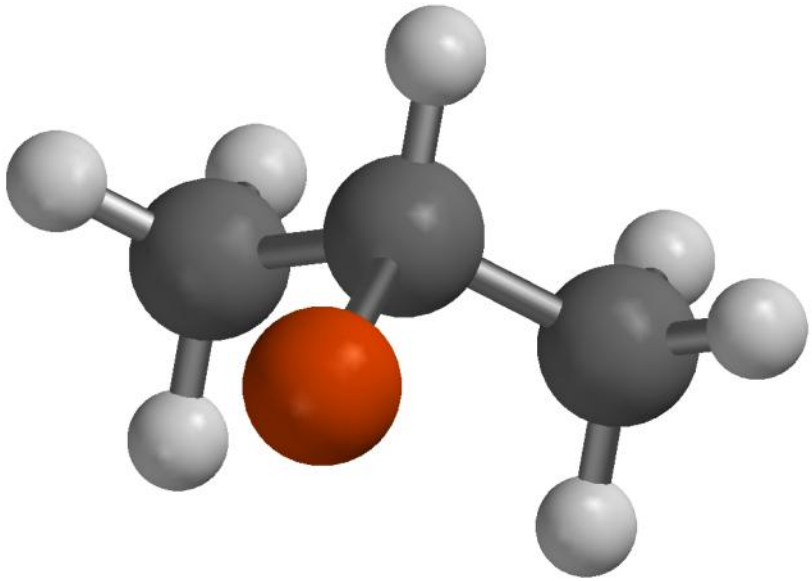
Chiral or Achiral?

- 2-butanol



Chiral or Achiral?

- 2-bromopropane



achiral

PROBLEM 4◆

Which of the following compounds have an asymmetric center?

a. $CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$

b. $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

c. $CH_3CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}CH_2CH_2CH_3$

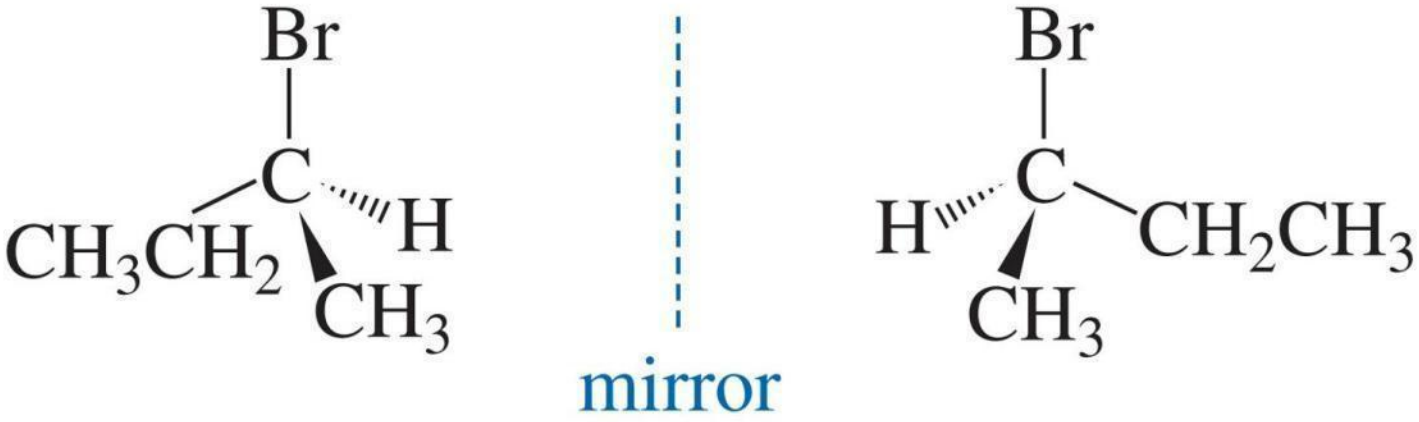
d. CH_3CH_2OH

e. $CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_3$

f. $CH_2{=}CH\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$

6.4 Isomers with one asymmetric center

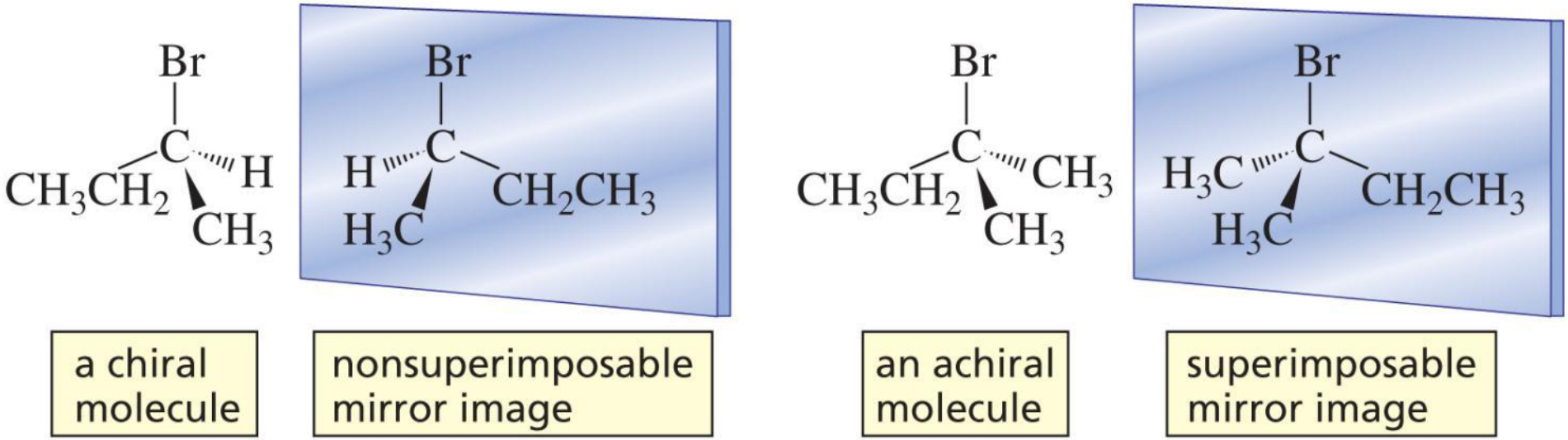
2-bromobutane



the two isomers of 2-bromobutane

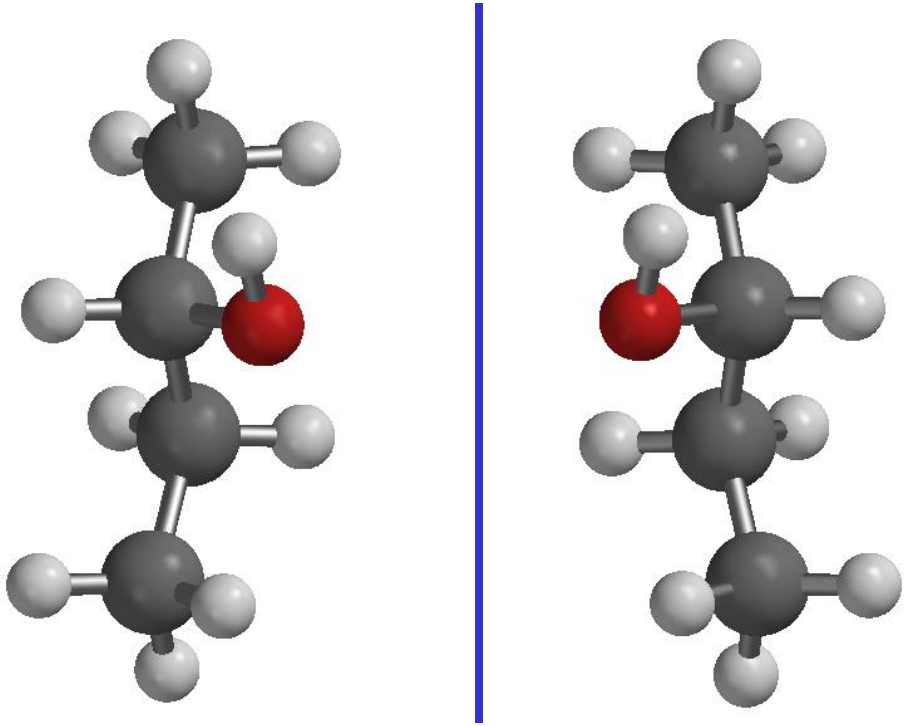
enantiomers

6.4 Isomers with one asymmetric center



Enantiomers

- A chiral compound and its mirror image are called ***enantiomers***.
- 2-butanol:

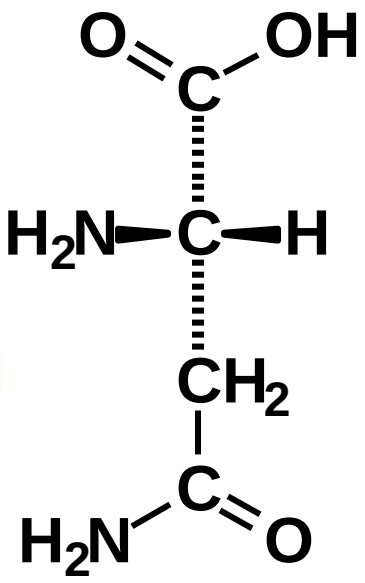


enantiomers

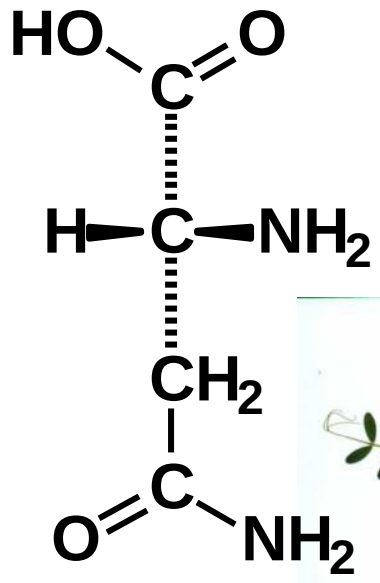
Enantiomers

- Asparagine:

mirror plane



L-asparagine
(from asparagus)
bitter taste



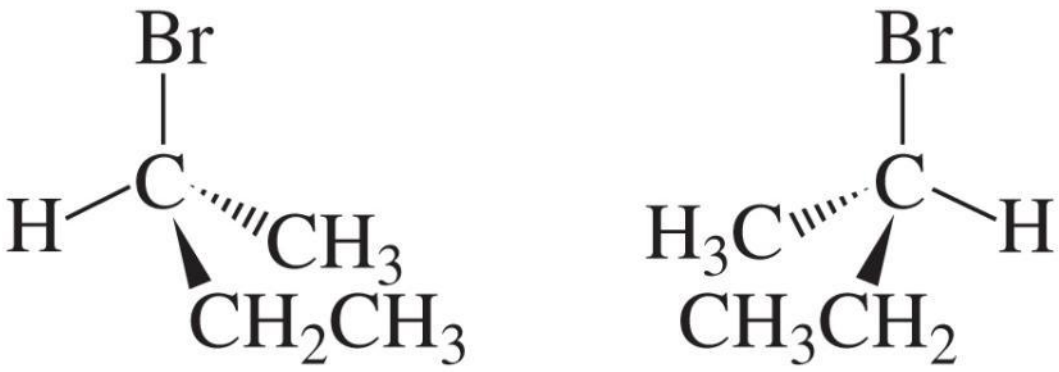
D-asparagine
(from vetch)
sweet taste

enantiomers

PROBLEM 6◆

Which of the compounds in Problem 4 can exist as enantiomers?

6.5 How to draw enantiomers

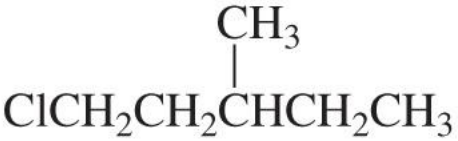


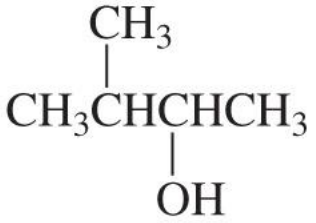
perspective formulas of the enantiomers of 2-bromobutane

PROBLEM 7◆

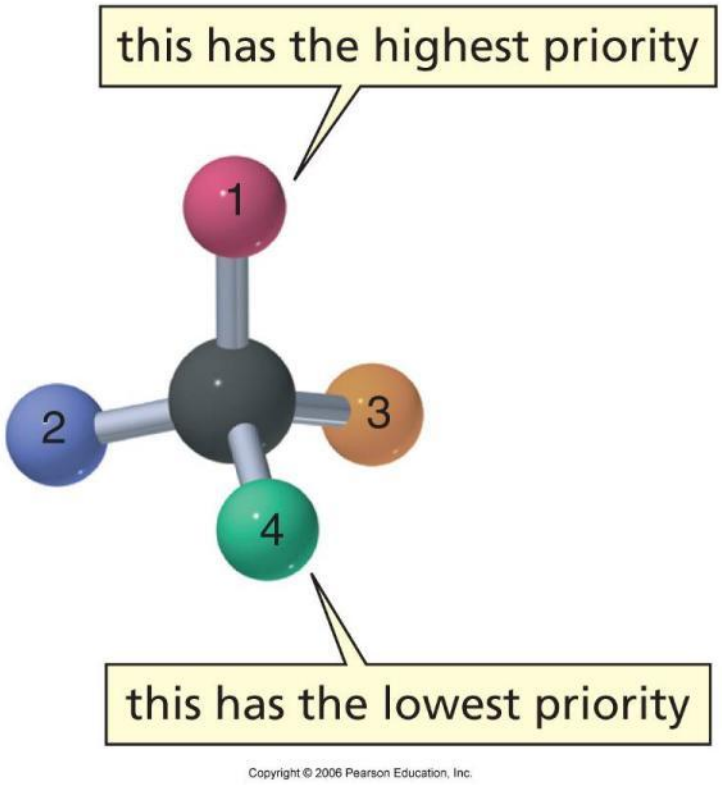
Draw the enantiomers of each of the following compounds using perspective formulas:

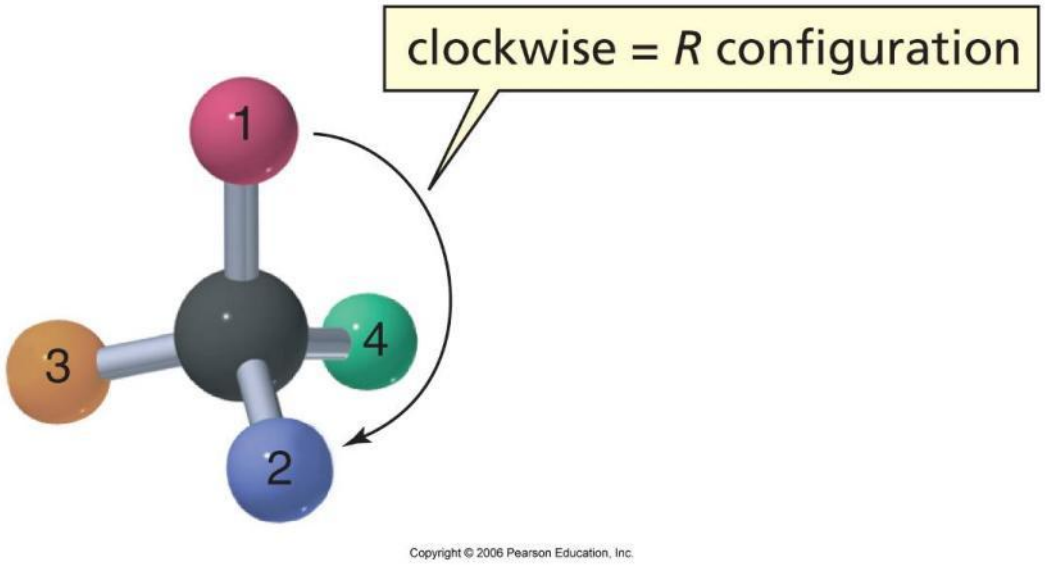
a. 

b. 

c. 

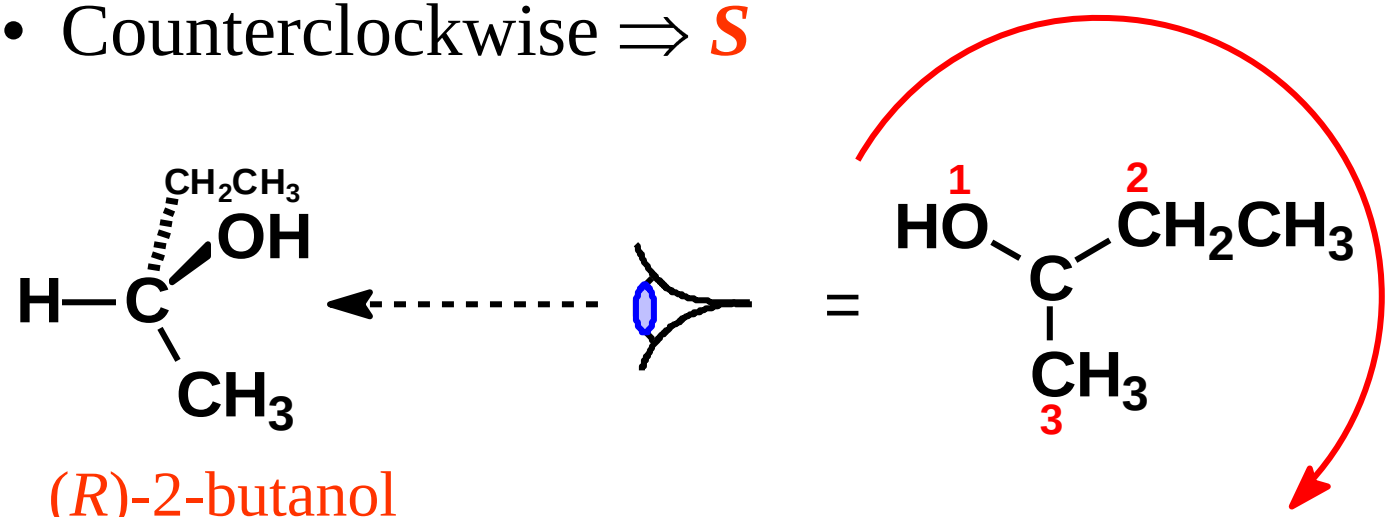
6.6 Naming enantiomers: the *R*,*S* system





Absolute Configuration

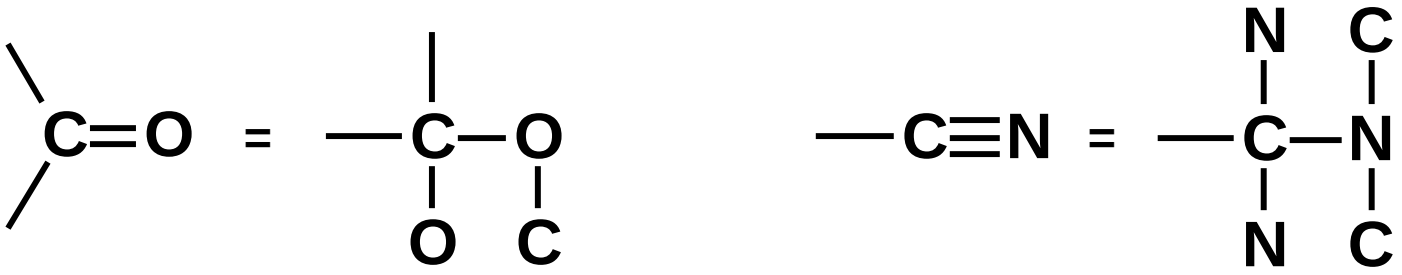
- ***R*** and ***S***
  - Assign priorities to the remaining groups based on atomic numbers.
  - Clockwise (highest to lowest priority) ⇒ ***R***
  - Counterclockwise ⇒ ***S***



(*R*)-2-butanol

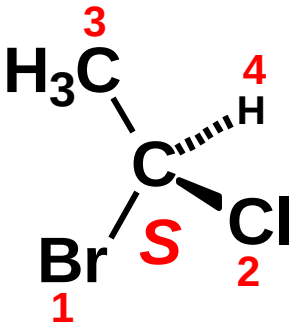
Absolute Configuration

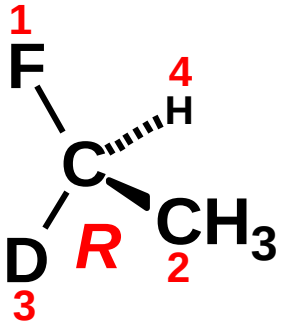
- Assign priority:
  - Atomic number of atom directly bonded.
  - If the same atom is bonded, go to the next atom, etc.
  - Groups containing multiple bonds are treated as though multiple atoms were attached:

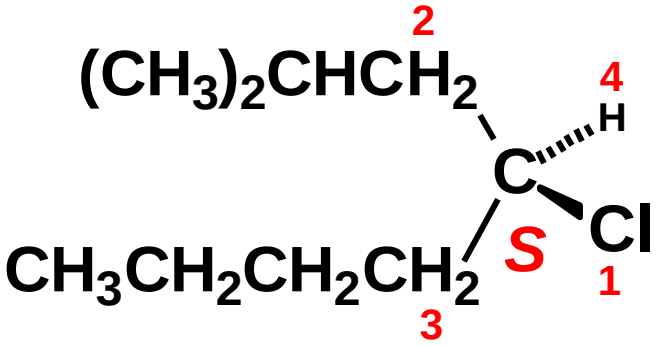


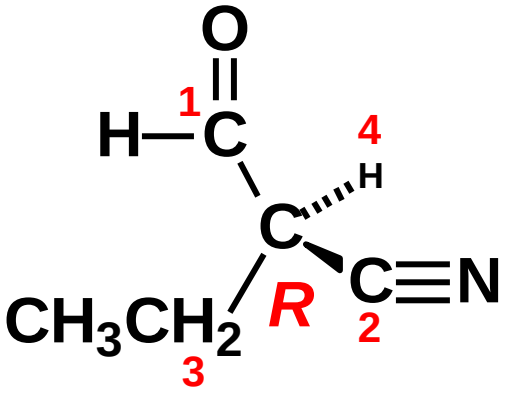
Absolute Configuration

- Determine the absolute configuration of the following compounds:



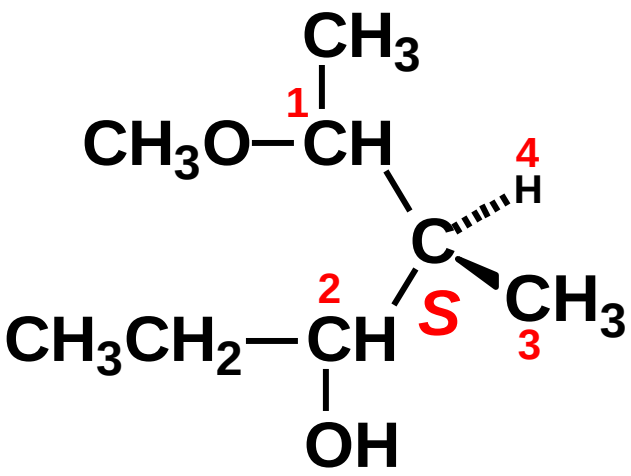


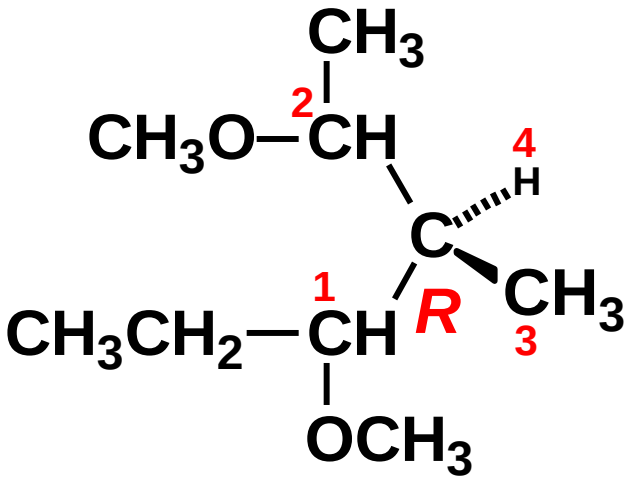


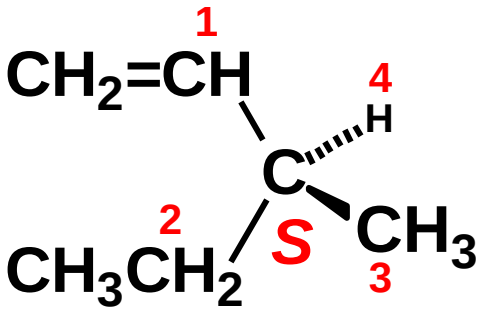


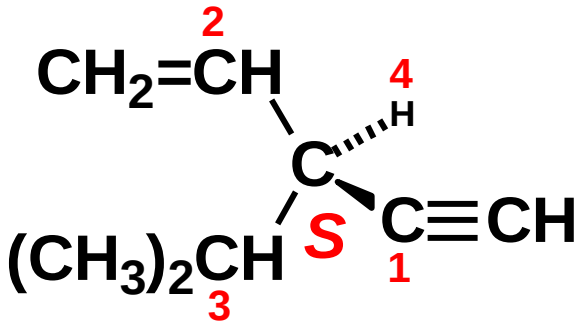
Absolute Configuration

- Determine the absolute configuration of the following compounds:



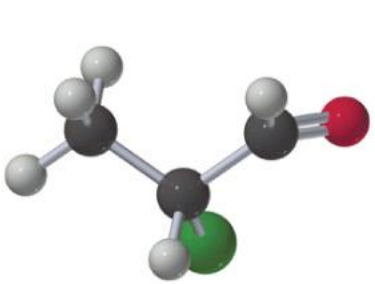




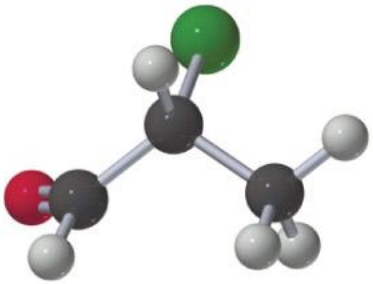


PROBLEM 8◆

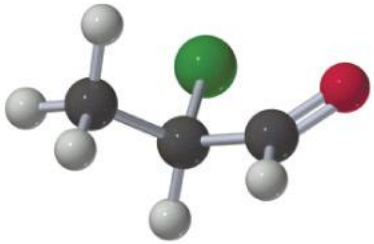
Which of the following molecular models are identical?



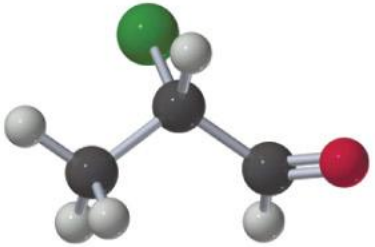
(a)



(b)

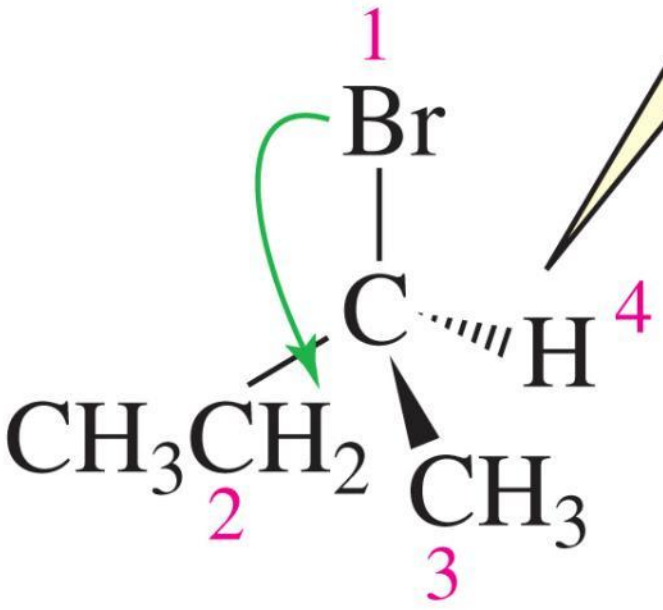


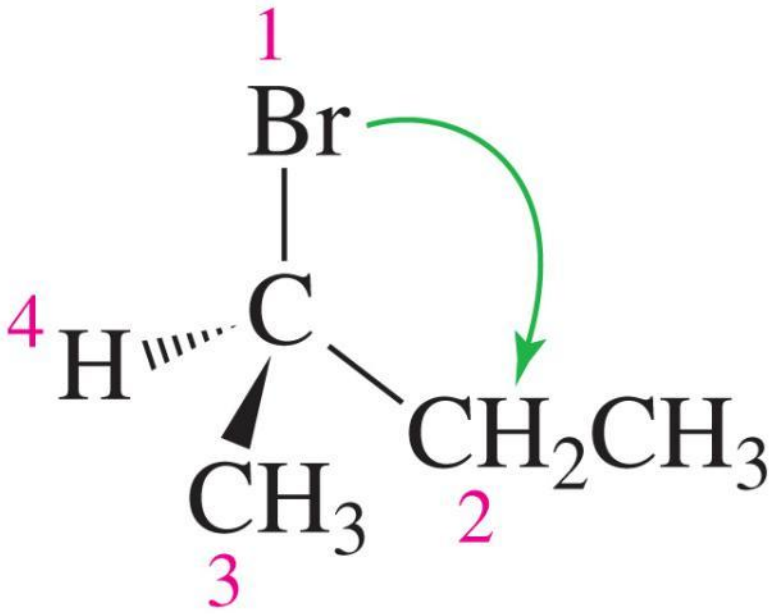
(c)



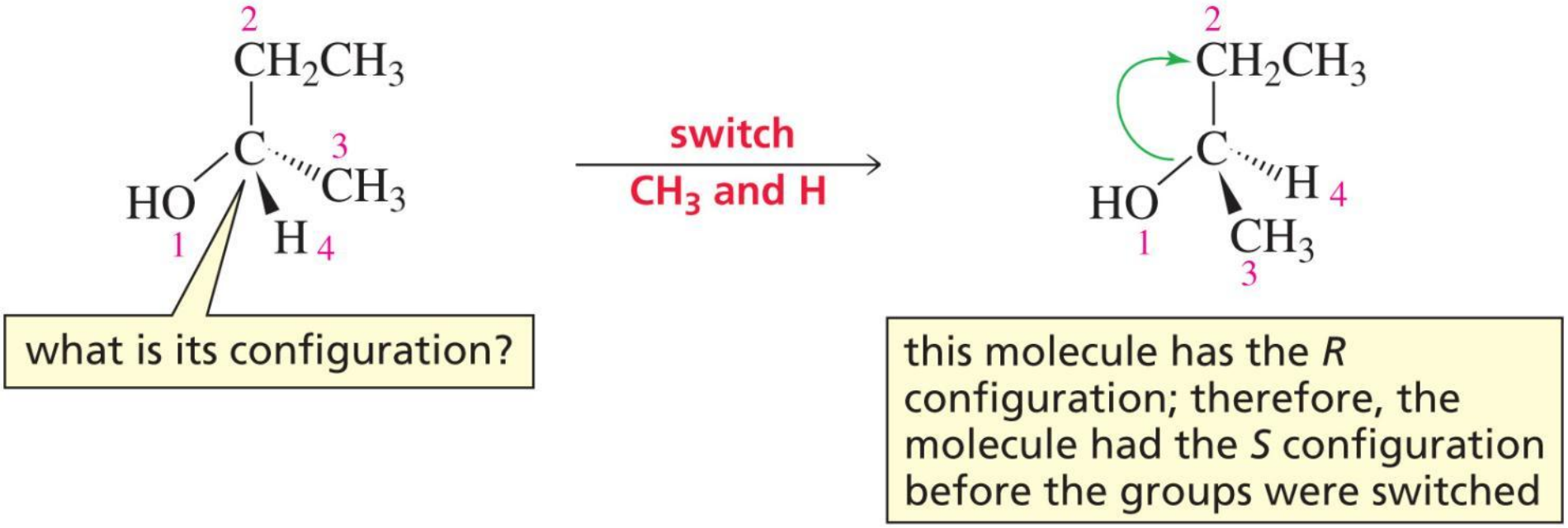
(d)

the group with the lowest priority is bonded by a hatched wedge





(*S*)-2-bromobutane **(*R*)-2-bromobutane**



PROBLEM 9◆

Assign relative priorities to the following groups:

a. $-CH_2OH$ $-CH_3$ $-CH_2CH_2OH$ $-H$

b. $-CH{=}O$ $-OH$ $-CH_3$ $-CH_2OH$

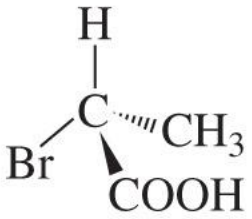
c. $-CH(CH_3)_2$ $-CH_2CH_2Br$ $-Cl$ $-CH_2CH_2CH_2Br$

d. $-CH{=}CH_2$ $-CH_2CH_3$ $-C{\equiv}CH$ $-CH_3$

PROBLEM 10◆

Indicate whether each of the following structures has the *R* or the *S* configuration:

a.

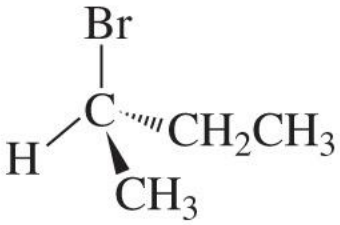


b.

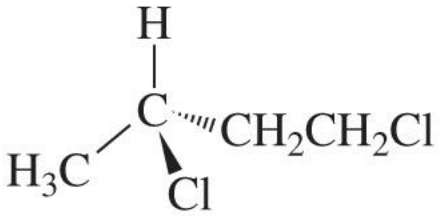
PROBLEM 11◆

Name the following compounds:

a.

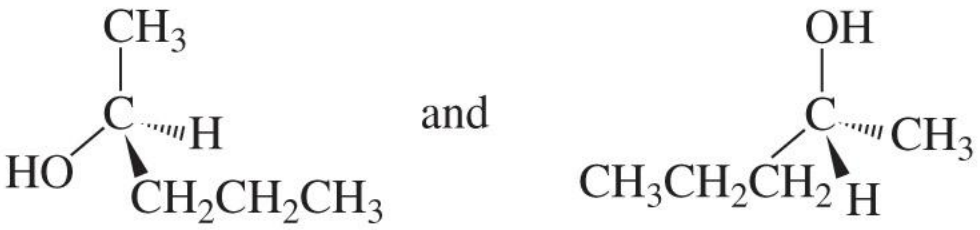


b.



PROBLEM-SOLVING STRATEGY

Do the following structures represent identical molecules or a pair of enantiomers?



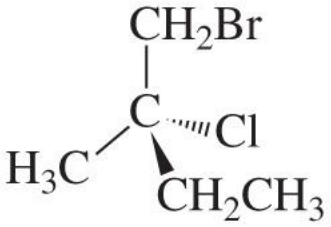
The easiest way to find out whether two molecules are enantiomers or identical molecules is to determine their configurations. If one has the *R* configuration and the other has the *S* configuration, they are enantiomers. If they both have the *R* configuration or both have the *S* configuration, they are identical molecules. Because the structure on the left has the *S* configuration and the structure on the right has the *R* configuration, we know that they represent a pair of enantiomers.

Now continue on to Problem 12.

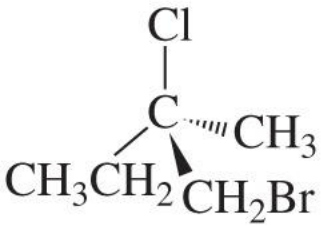
PROBLEM 12◆

Do the following structures represent identical molecules or a pair of enantiomers?

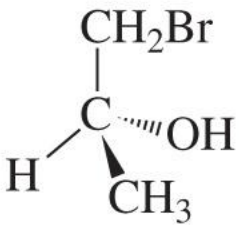
a.



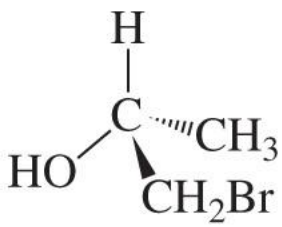
and



b.

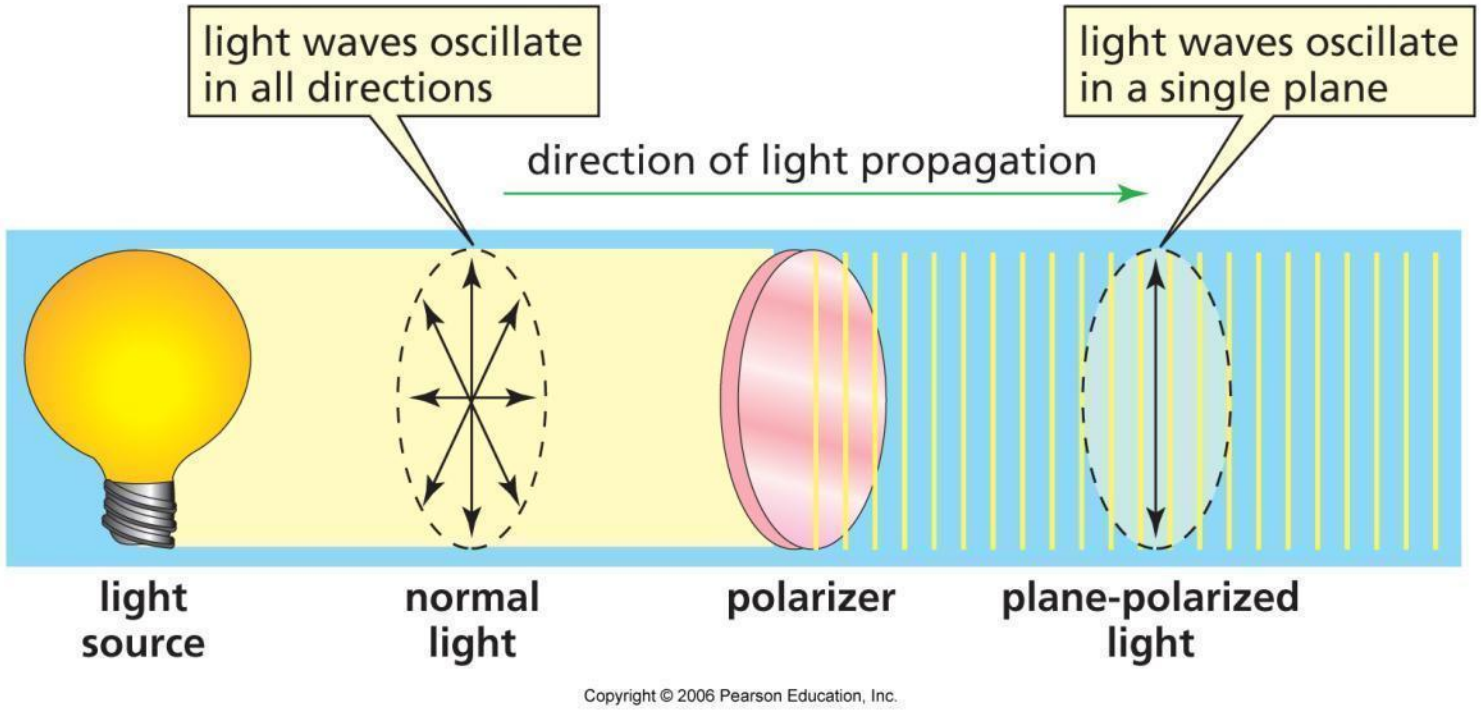


and



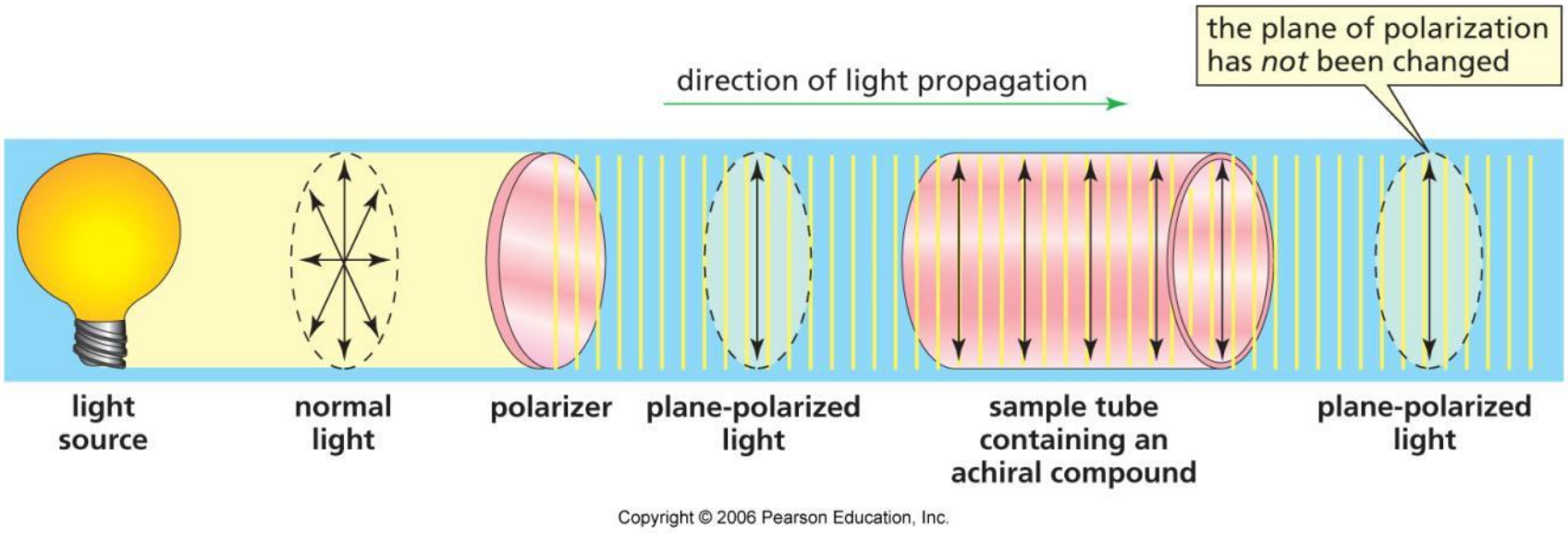
6.7 Chiral compounds are optically active

- **Plane-polarized light** is produced by passing normal light through a polarizer.



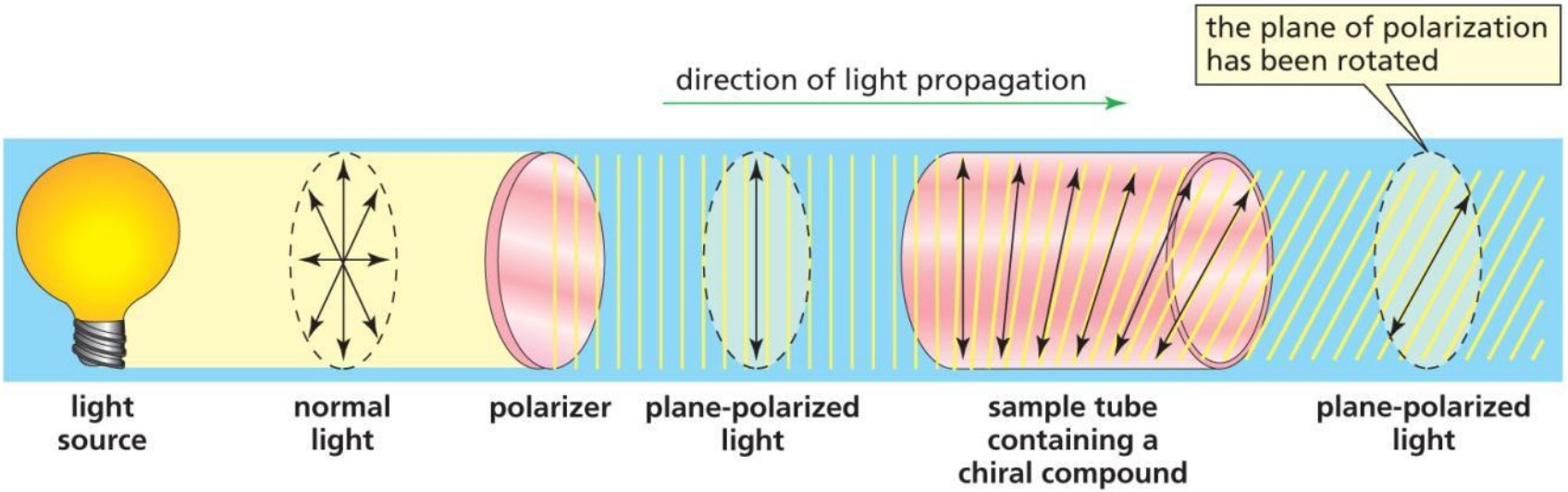
Optical Activity

- When plane-polarized light passes through a solution of achiral molecules, the light emerges from the solution with its plane of polarization unchanged.



Optical Activity

- However, when plane-polarized light passes through a solution of a chiral compound, the light emerges with its plane of polarization changed.



Optical Activity

- ***Optical Activity*** – The ability of a compound to rotate the plane of polarized light.
- A compound that rotates the plane of polarization is said to be ***optically active***.
- **Chiral** compounds are ***optically active*** and **achiral** compounds are ***optically inactive***.
- A ***polarimeter*** is used to make such measurements: