

Chapter 6. Isomers and Stereochemistry

Learning objectives:

1. Differentiate chiral and achiral molecules.
2. Recognize and draw structural isomers (constitutional isomers), stereoisomers including enantiomers and diastereomers, racemic mixture, and meso compounds.
3. Identify the stereocenters in a molecule and assign the configuration as R or S.
4. Know the relationship between enantiomers and their specific rotations.

Sections to be covered (in the order of delivery):

- 6.1 Cis-trans isomers result from restricted rotation
- 6.2 A chiral object has a nonsuperimposable mirror image
- 6.3 An asymmetric center is the cause of chirality in a molecule
- 6.4 Isomers with one asymmetric center
- 6.5 How to draw enantiomers
- 6.6 Naming enantiomers by the R,S system
- 6.7 Chiral compounds are optically active
- 6.8 How specific rotation is measured
- 6.9 Isomers with more than one asymmetric center
- 6.10 Meso compounds have asymmetric centers but are optically inactive
- 6.11 How enantiomers can be separated
- 6.12 Receptors
- 6.13 The stereochemistry of reactions
- 6.14 The stereochemistry of enzyme-catalyzed reactions

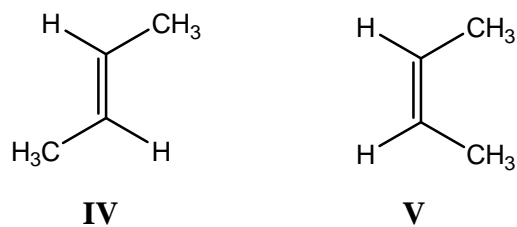
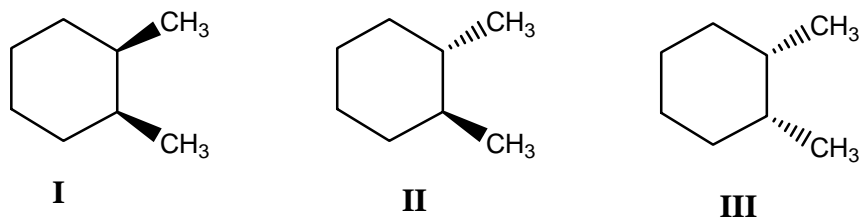
Sections that will be skipped

Recommended additional problems

30, 32, 34, 35, 36, 42, 49, 55

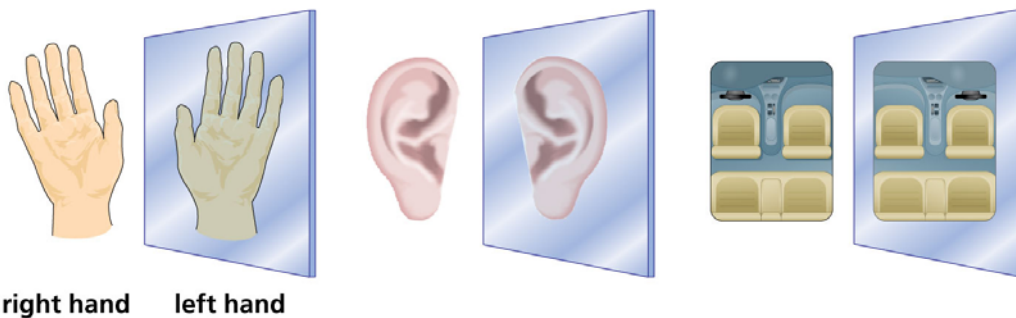
6.1 Cis-trans isomers result from restricted rotation

Alkenes and cycloalkanes

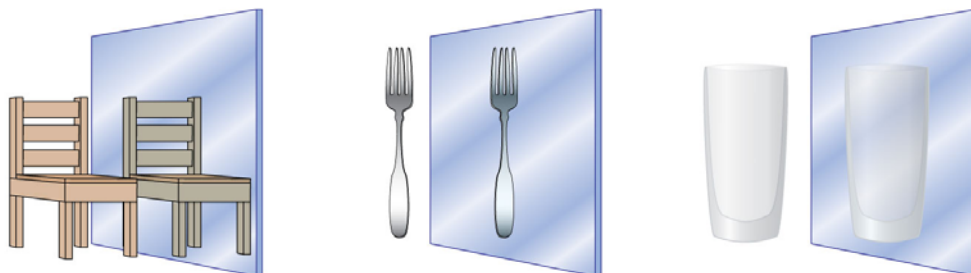


6.2 A chiral object has a nonsuperimposable mirror image

chiral objects



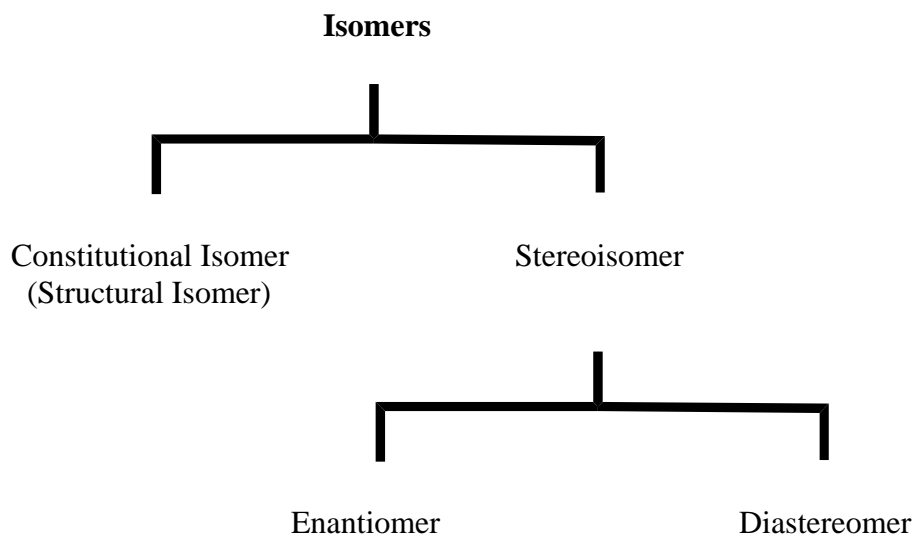
achiral objects



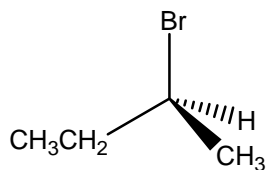
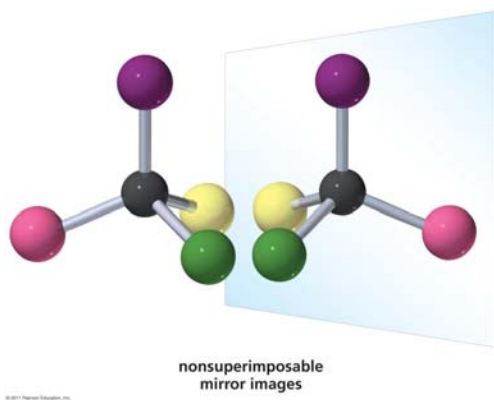
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- 6.3 An asymmetric center is the cause of chirality in a molecule
- 6.4 Isomers with one asymmetric center
- 6.5 How to draw enantiomers

A. What Are Enantiomers?



Enantiomers (a pair of enantiomers): mirror image but not superimposable

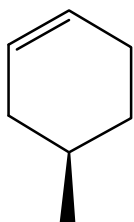
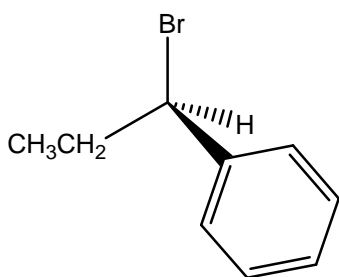
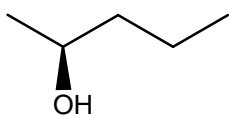


Important Terminologies: achiral, chiral, plane of symmetry, mirror image and stereocenter

B. Drawing Enantiomers:

Criteria of being chiral: four different substituents (sp^3 hybridization) **and** no plane of symmetry.

Examples:



6.6 Naming enantiomers by the R,S system

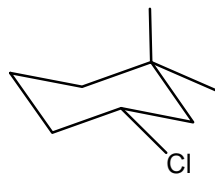
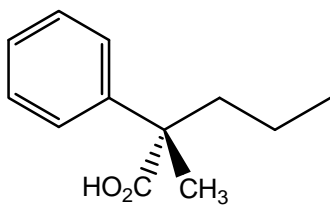
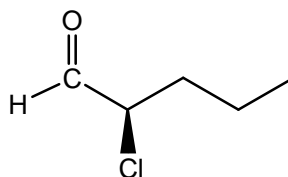
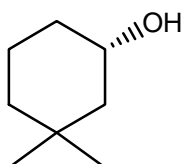
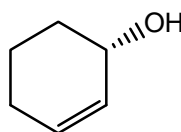
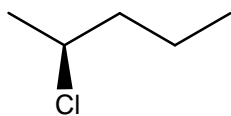
(i) Locate the stereocenter and prioritize its four substituents from 1 (highest) to 4 (lowest).

(ii) Rotate in the order from 1 to 2 to 3.

(iii) If the 4 (lowest) substituent is pointing *away* from you, clockwise rotation will be **R** and counterclockwise rotation will be **S**.

(iv) If the 4 (lowest) substituent is pointing *toward* you, clockwise rotation will be **S** and counterclockwise rotation will be **R**.

(v) Examples



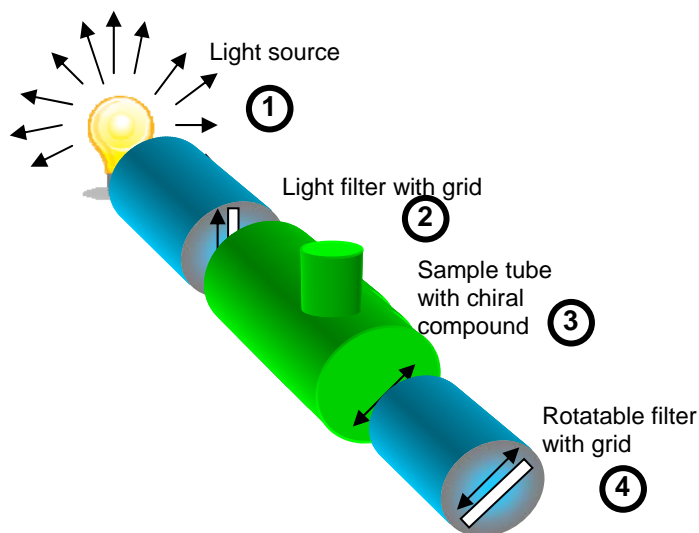
6.7 Chiral compounds are optically active

6.8 How specific rotation is measured

Important Terminologies: plane-polarized light, optically active, optical activity.

A. Plane-Polarized Light

B. A polarimeter



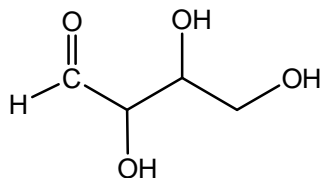
Specific rotation: the observed rotation of an optically active substance at a concentration of 1 g/100 mL in a sample tube 10 cm long; for a pure liquid, concentration is in g/mL (density)

C. Chiral compounds with clockwise rotation is designated as (+). Chiral compounds with counterclockwise rotation is designated as (-).

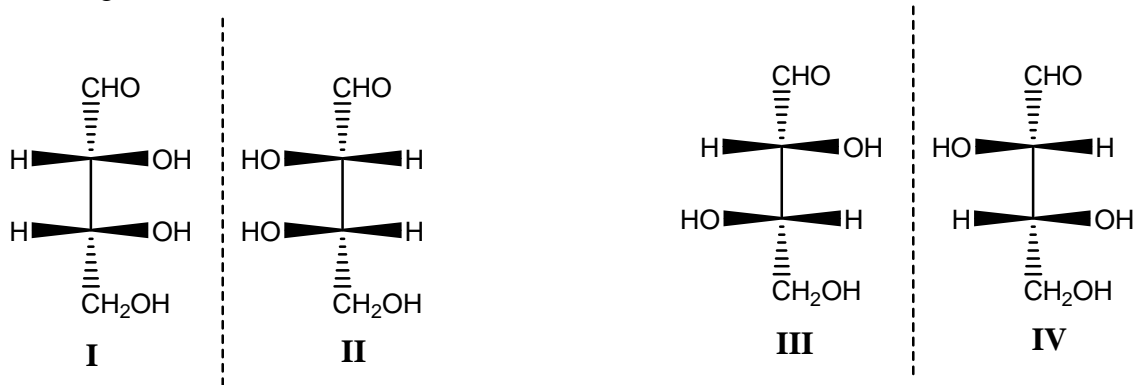
(+) and (-) have no correlation with R and S assignment.

6.9 Isomers with more than one asymmetric center

Know the difference between enantiomers and diastereomers



A. Assign R and S for identification:



Enantiomers:

Diastereomers:

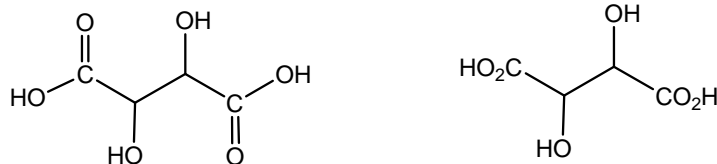
B. Racemic Mixtures: a pair of enantiomers in 1/1 ratio

Optical property is canceled intermolecularly.

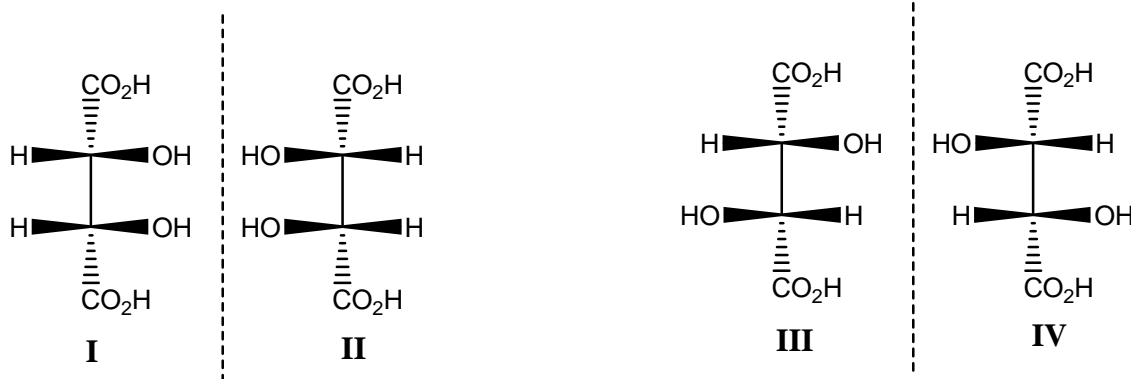
6.10 Meso compounds have asymmetric centers but are optically inactive

Meso Compounds (the presence of plane of symmetry)

Optical property is canceled intramolecularly.

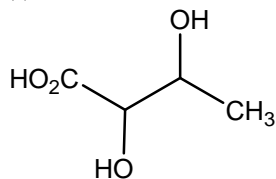


A. Assign R and S for identification and check the presence of plane of symmetry:

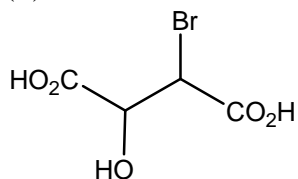


B. More examples:

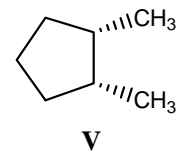
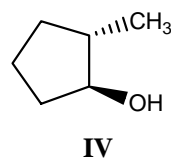
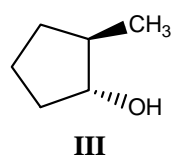
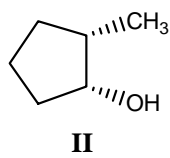
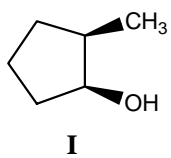
(i)



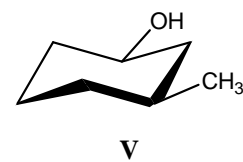
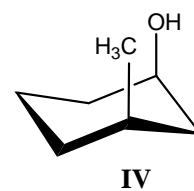
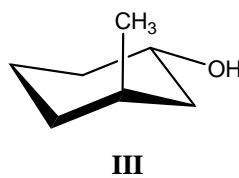
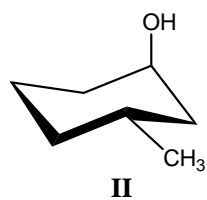
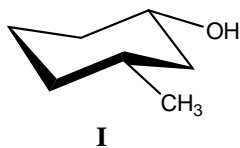
(ii)



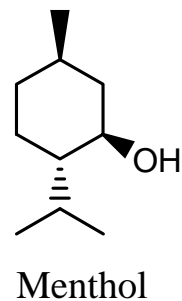
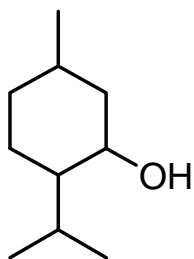
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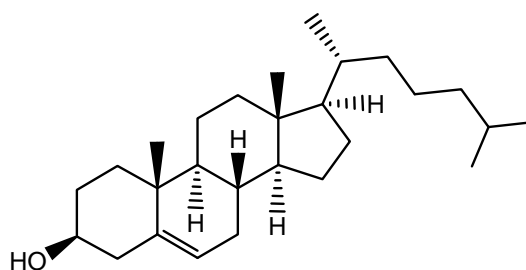
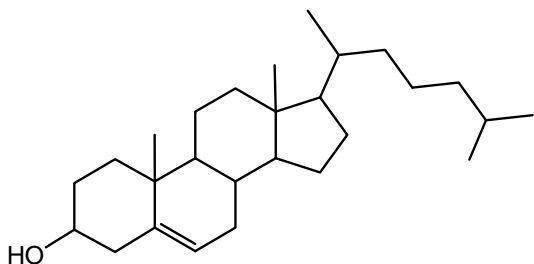
(iv)



C. Molecules with three or more stereocenters



Number of possible stereoisomers: 2^n , n = number of stereocenters



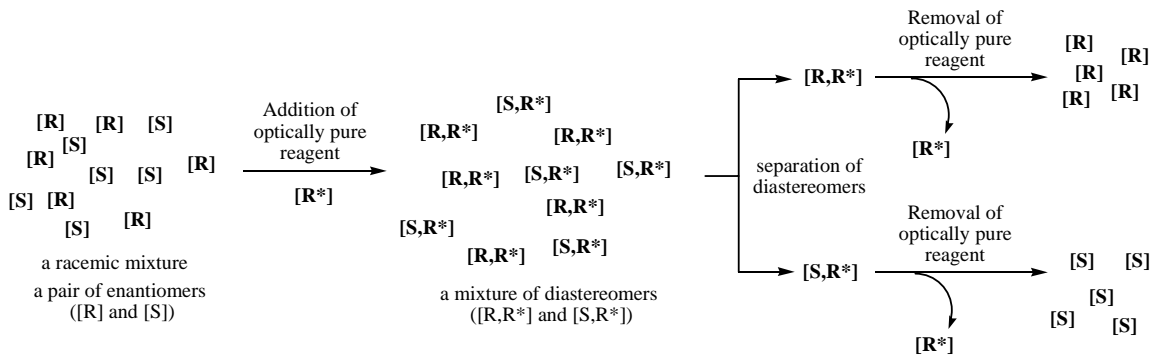
6.11 How enantiomers can be separated

A. Properties of stereoisomers

Enantiomers: same chemical properties (reactivity), same physical properties (ex. boiling point, melting point, density and pK_a) except for the **specific rotation (a pair of Enantiomers has the exact opposite direction in rotation)**.

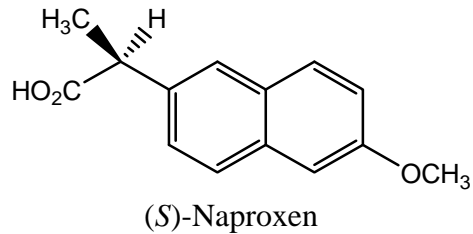
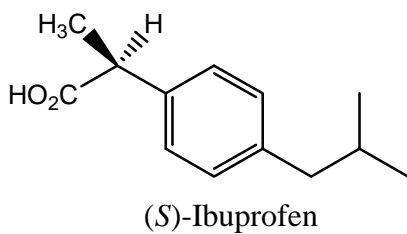
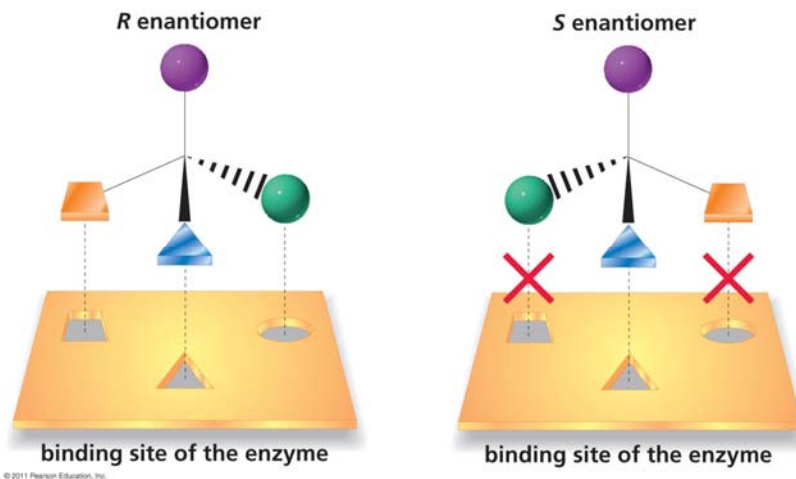
Diastereomers: different chemical and physical properties.

B. Separation of Enantiomers: Resolution



6.12 Receptors

The Significance of Chirality in the Biological World



6.13 The stereochemistry of reactions

6.14 The stereochemistry of enzyme-catalyzed reactions

