

Lecture 15

Organic Chemistry 1

Professor Duncan Wardrop

March 2, 2010

Stereochemistry

Section 7.1 - 7.8

Historical Importance of Stereochemistry

Once a molecule is asymmetric, its extension proceeds also in an asymmetrical sense. This concept completely eliminates the difference between natural and artificial synthesis. The advance of science has removed the last chemical hiding place for the once so highly esteemed *vis vitalis*.

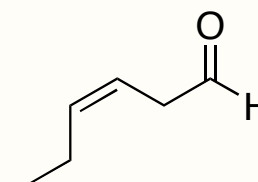
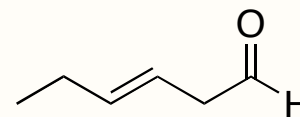
Emil Fischer, 1894

Self Test Question

Which pair of molecules below are not stereoisomers?

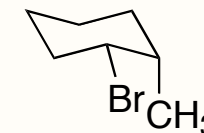
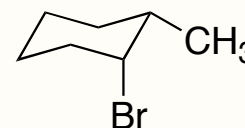
geometrical
stereoisomers

A



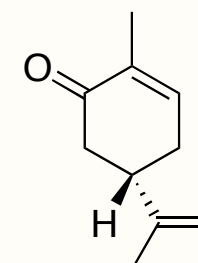
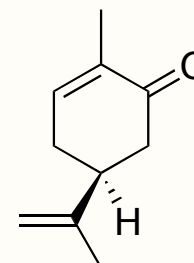
conformational
stereoisomers

B



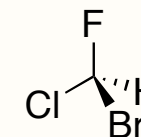
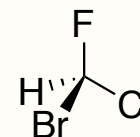
identical
molecules

C



enantiomeric
stereoisomers

D

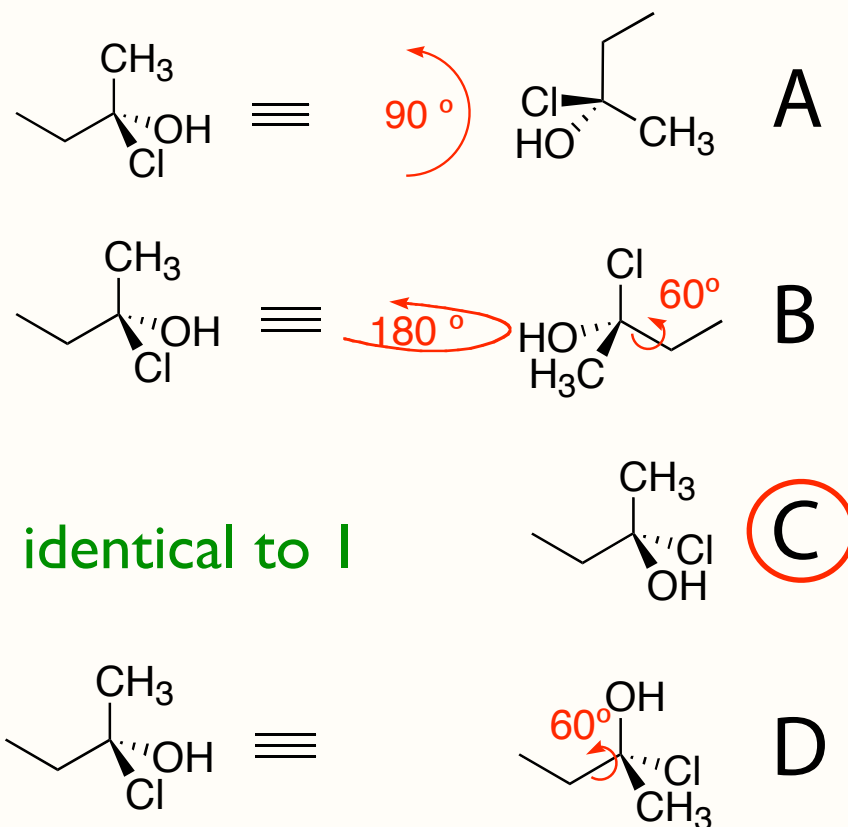
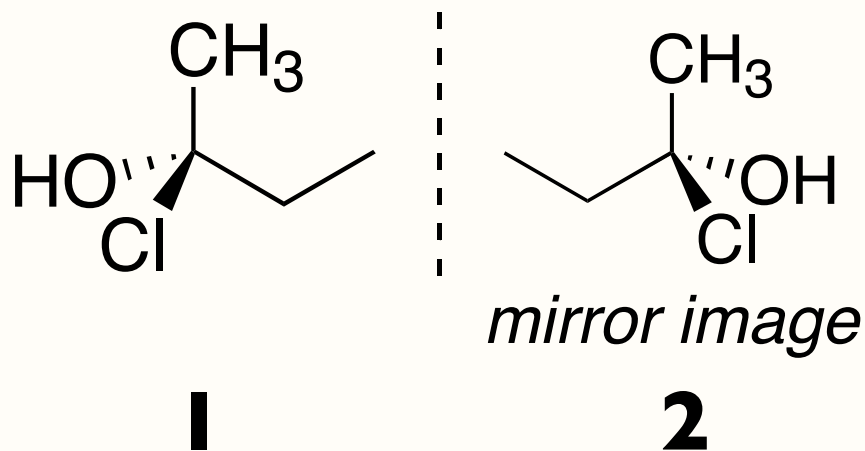


Stereoisomers:

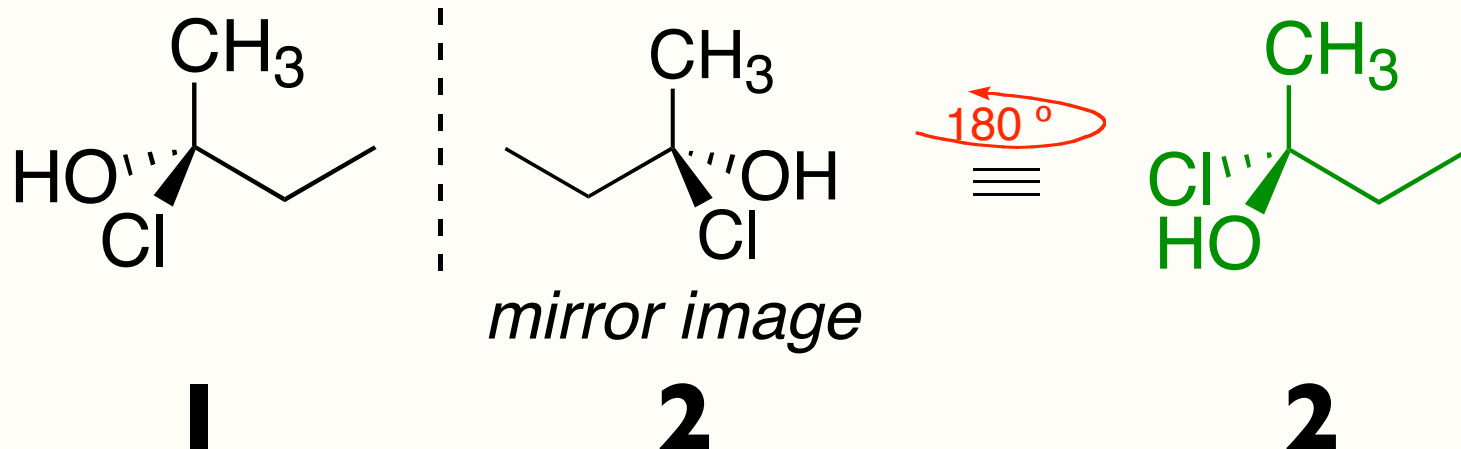
1. same connectivity
2. different arrangement of atoms in space

Self Test Question

Which structure cannot be moved in space (translation) or undergo rotation around single bonds to obtain a *mirror image* of the molecule (1) below?



Chirality



A molecule is **chiral** if its two mirror image forms are not superimposable on one another

Superimposable molecules can be laid on top of one another so that all equivalent atoms (points) line up

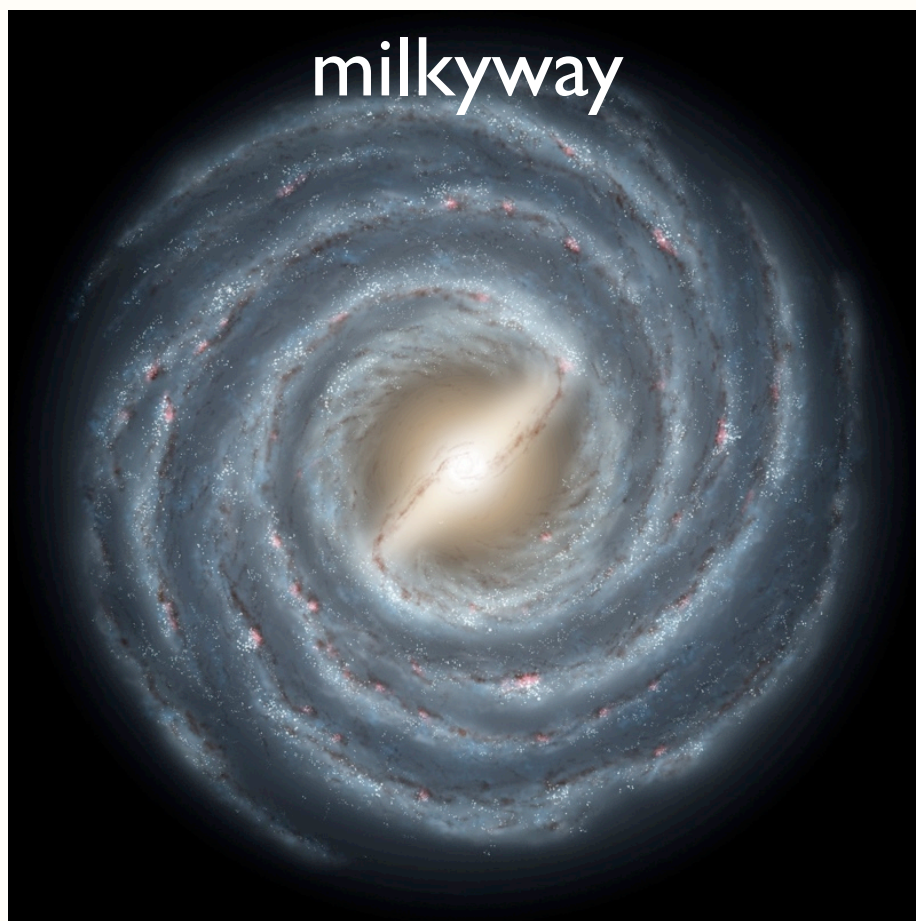
Chiral Objects

chiral: non-superimposable mirror images



Chiral Objects

chiral: non-superimposable mirror images



Chirality

chiral: non-superimposable mirror images

fingerprint



mirror image



Chirality

chiral: non-superimposable mirror images

DNA double helix



mirror image



Chirality

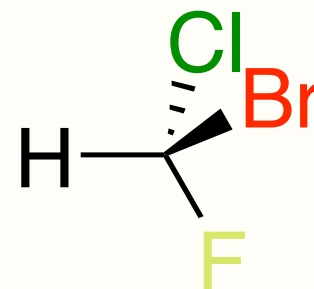
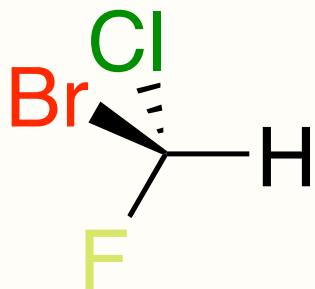
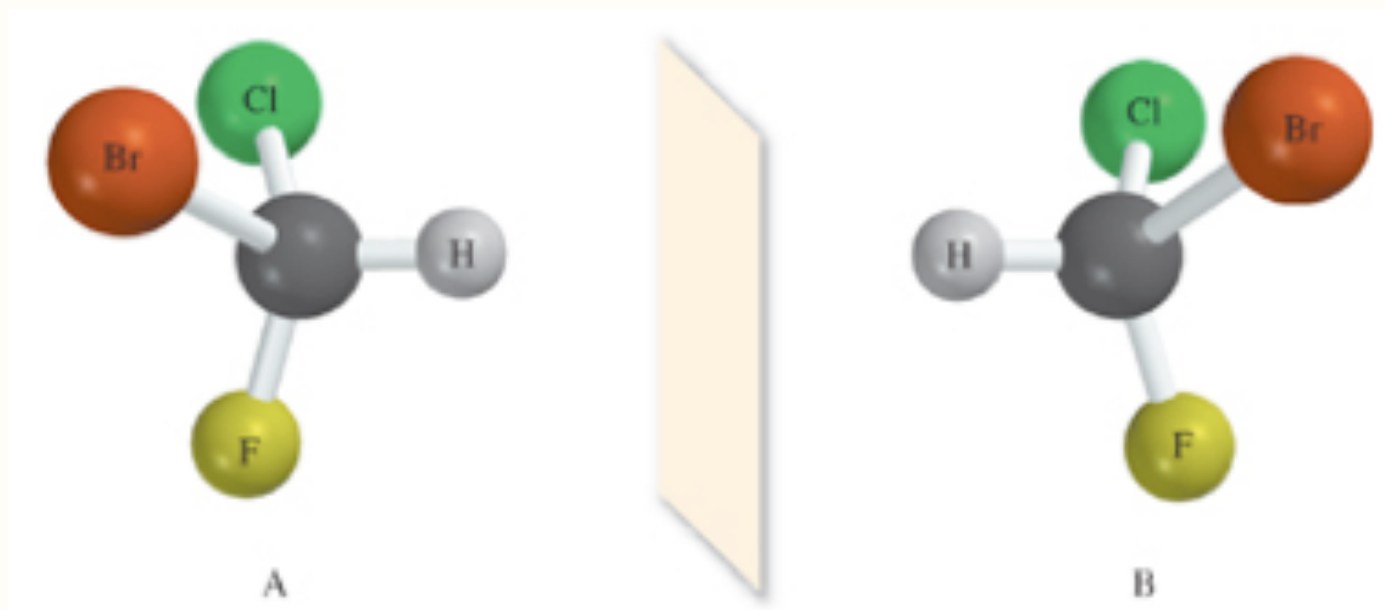
chiral: non-superimposable mirror images
cheir (Greek) = hand



chirality is synonymous with “handedness”

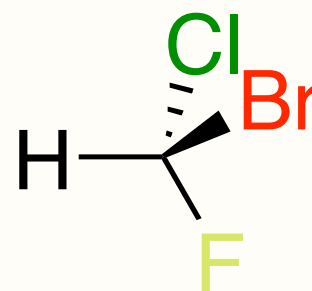
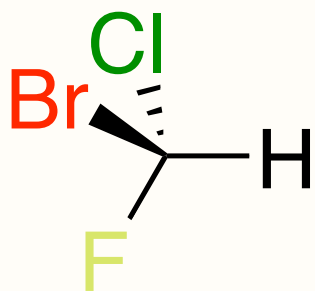
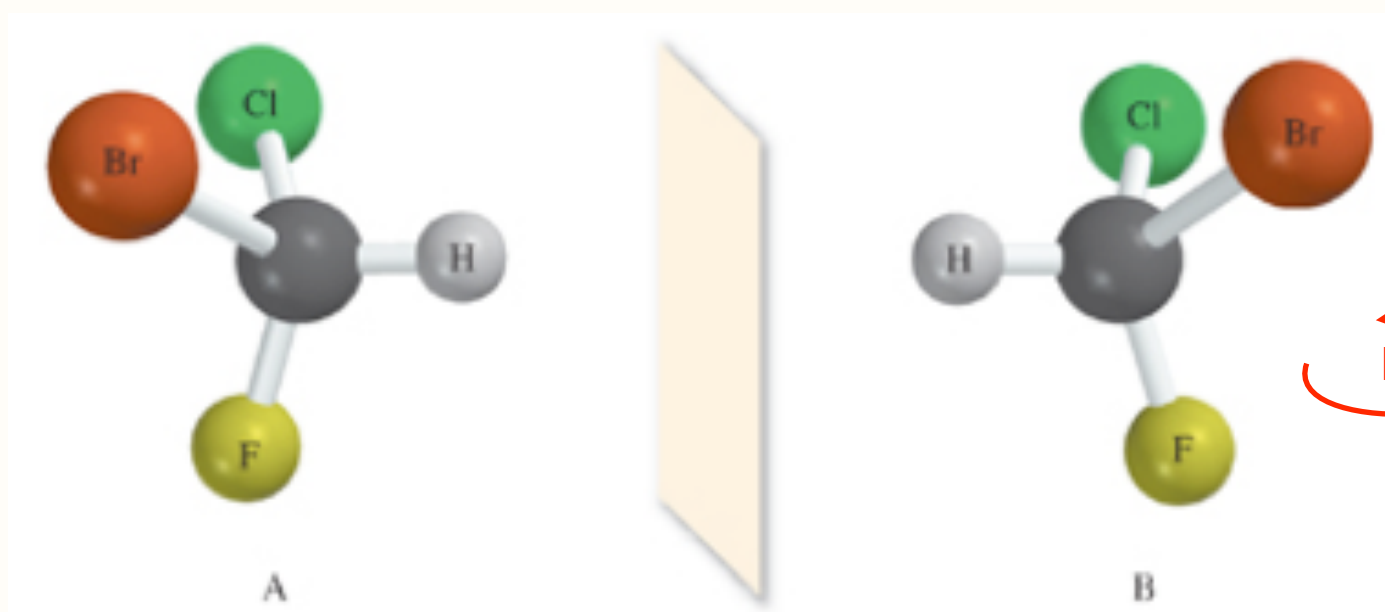
Molecules can Also Be Chiral

chiral: non-superimposable mirror images



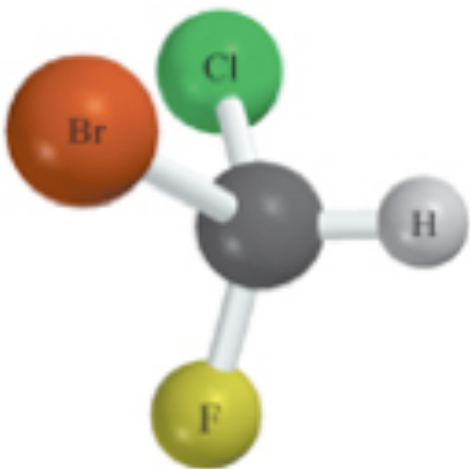
Superimposibility

to check for superimposibility, rotate mirror image 180° along a plane perpendicular to the mirror plane

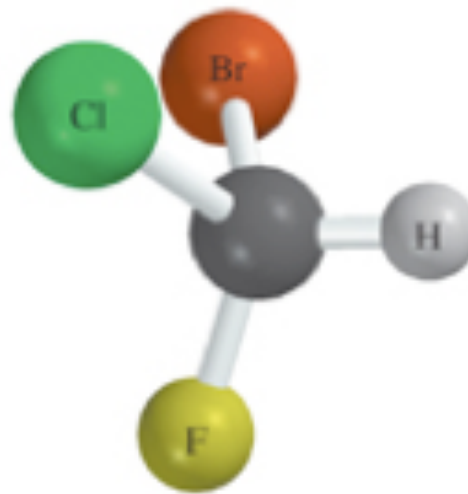


Non-superimposable

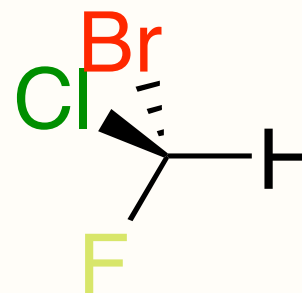
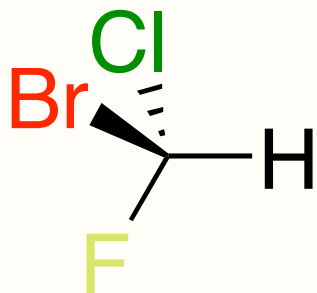
if the images are not identical, they are non superimposable; not all points (atoms) line up



A



B'



Not Everything is Chiral!

achiral: not chiral; mirror images are superimposable



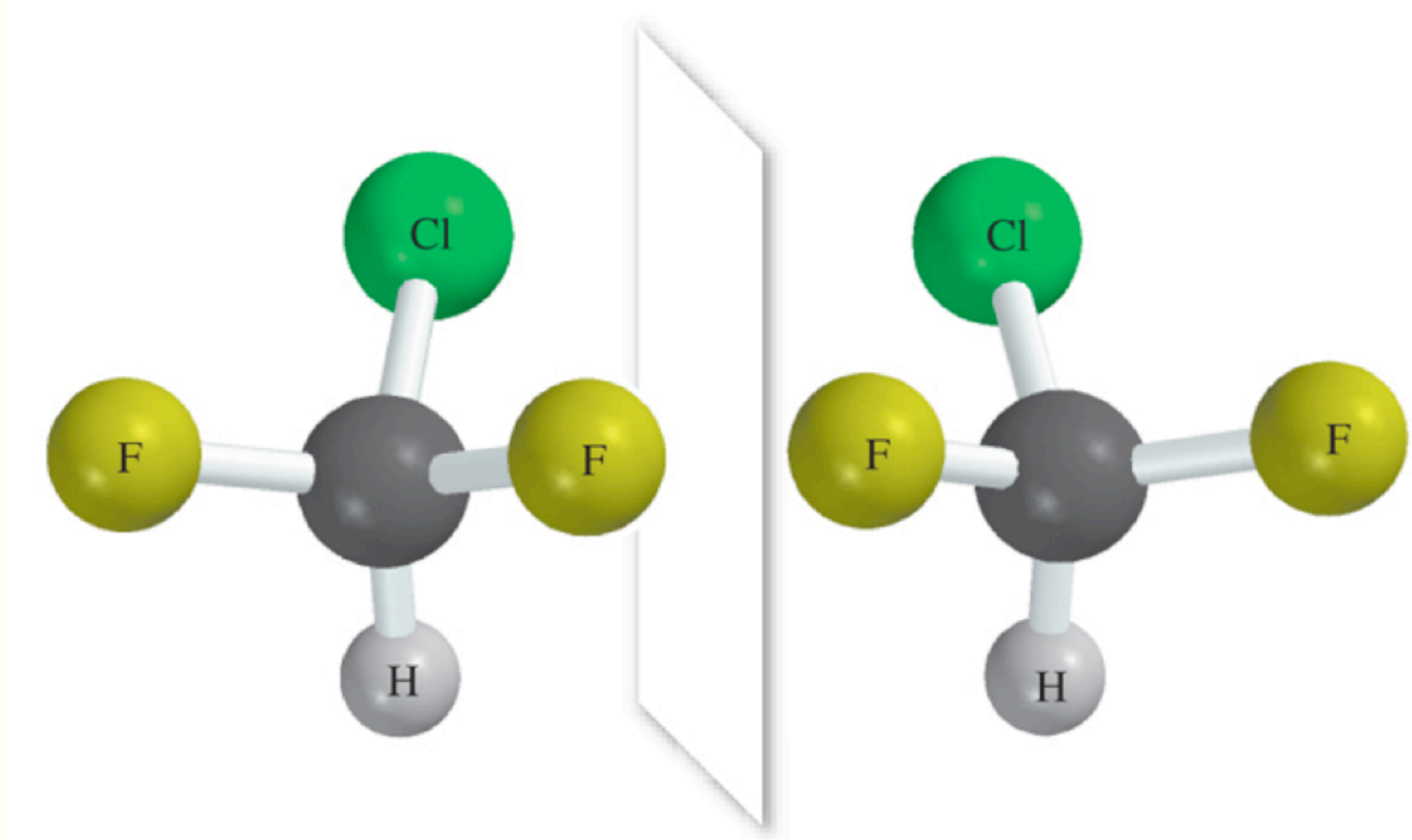
Not Everything is Chiral!

achiral: not chiral; mirror images are superimposable



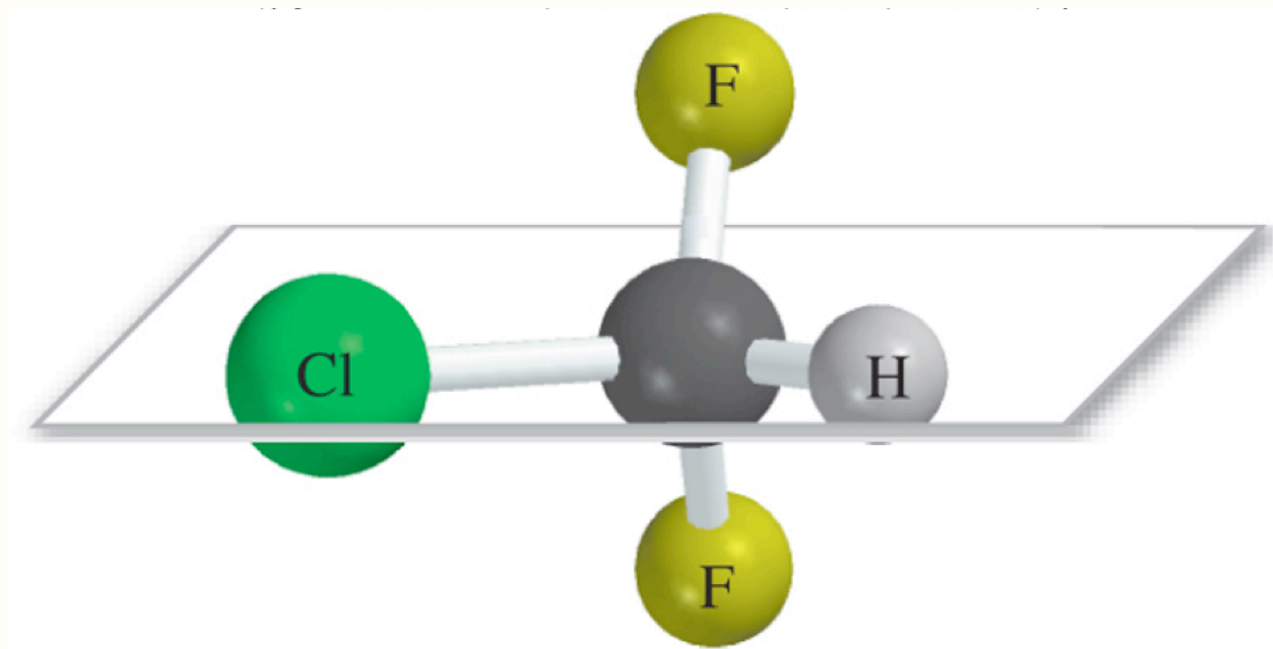
Not Everything is Chiral!

achiral: not chiral; mirror images are superimposable



Symmetry Tests for Achiral Molecules

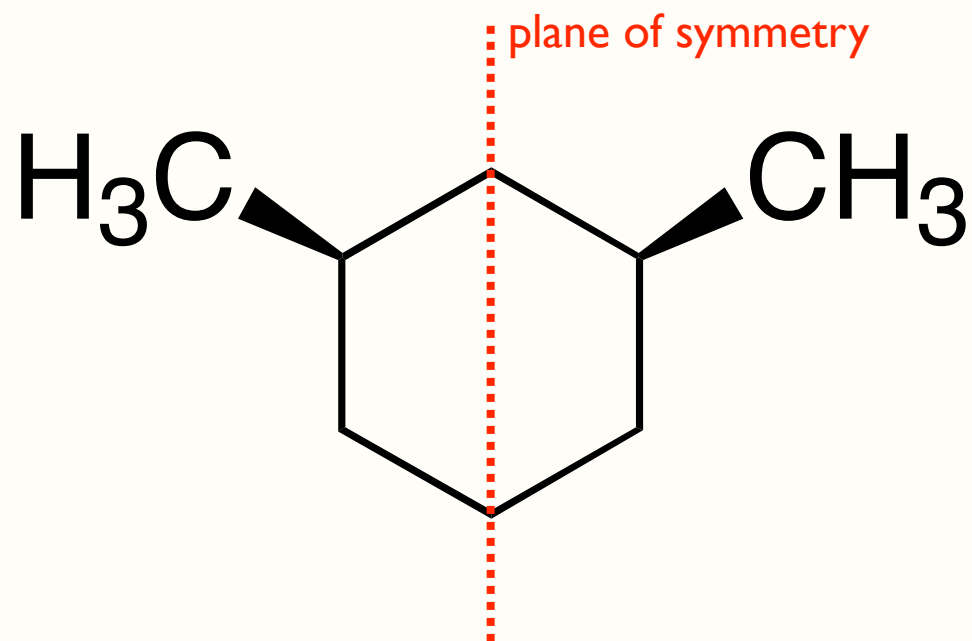
Any molecule with a plane of symmetry or a center of symmetry is achiral (not chiral)



A plane of symmetry bisects a molecule into two mirror image halves

Symmetry Tests for Achiral Molecules

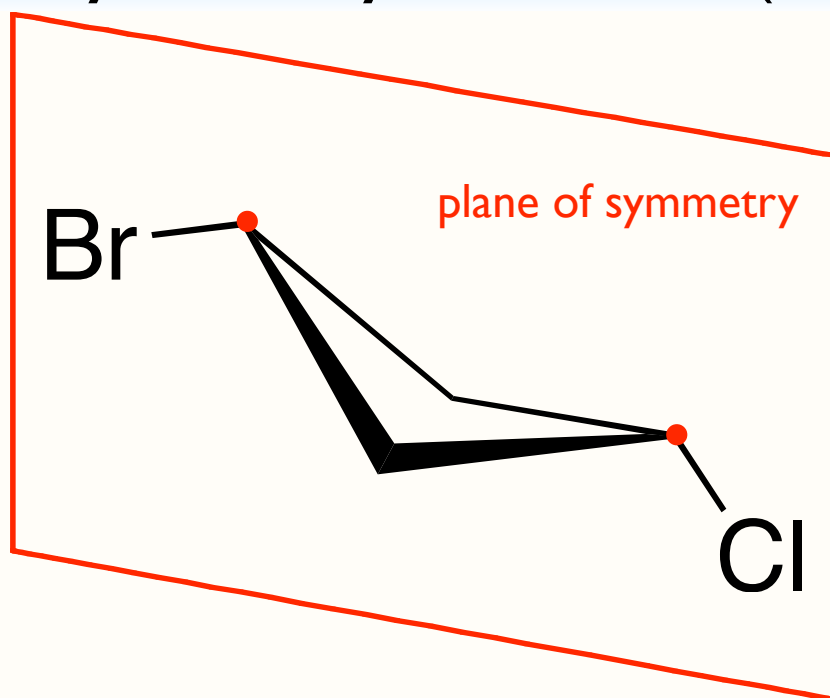
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Symmetry Tests for Achiral Molecules

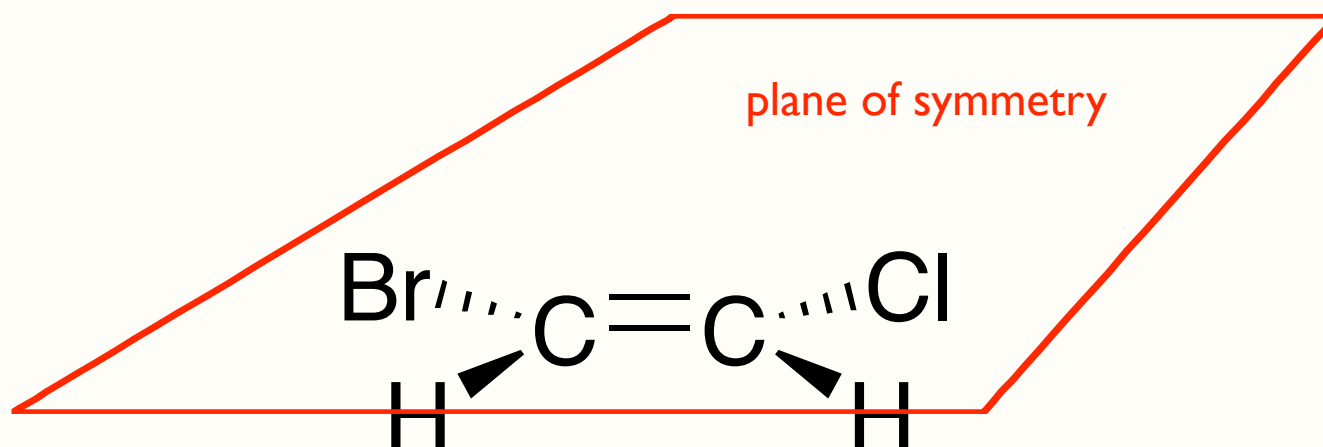
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Symmetry Tests for Achiral Molecules

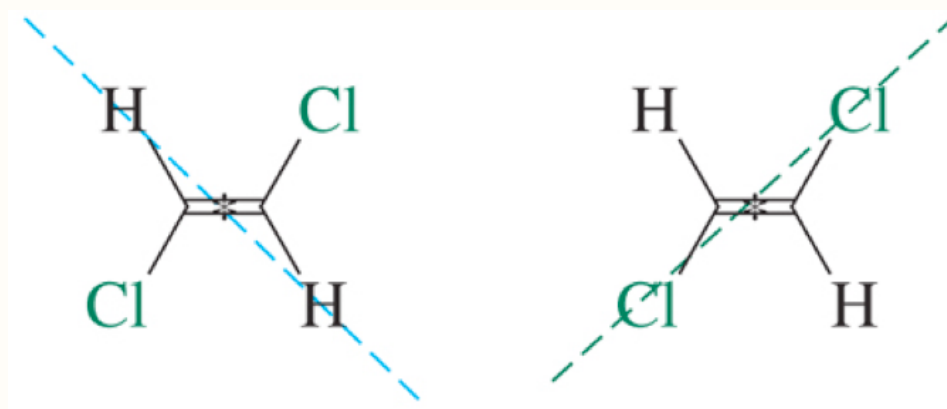
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Symmetry Tests for Achiral Molecules

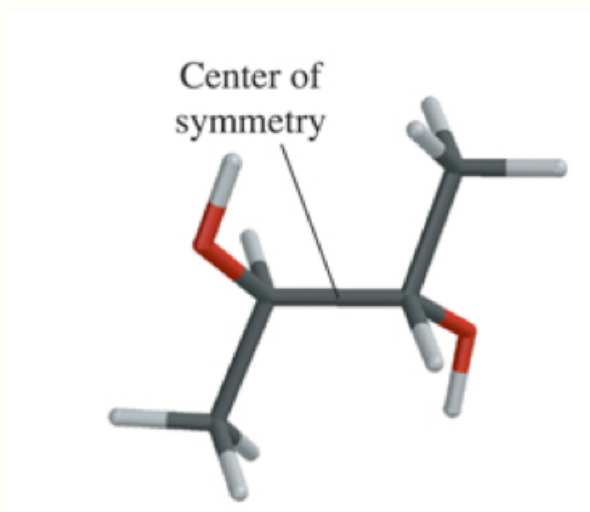
Any molecule with a plane of symmetry or a center of symmetry is achiral (not chiral)



center of symmetry: a line drawn from center of molecule to an element extends in opposite direction to an identical element

Symmetry Tests for Achiral Molecules

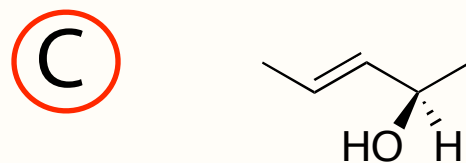
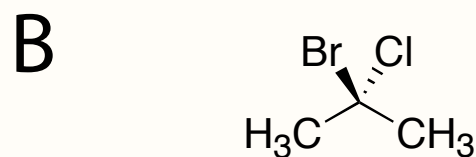
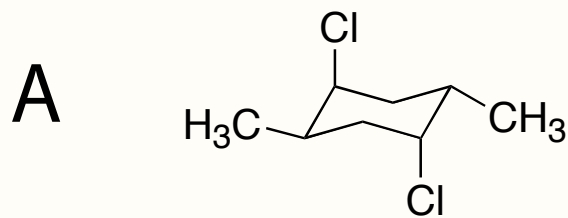
Any molecule with a plane of symmetry or a center of symmetry is achiral (not chiral)



center of symmetry: a line drawn from center of molecule to an element extends in opposite direction to an identical element

Self Test Question

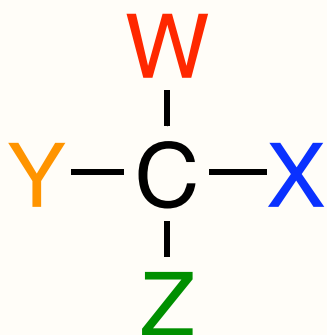
Which molecule below is chiral?



Chirality Center

Chirality center: an atom bonded to ligands in a spatial arrangement which is not superimposable on its mirror image

Asymmetric carbon: a carbon atom bonded to four different atoms or groups (a type of chirality center)



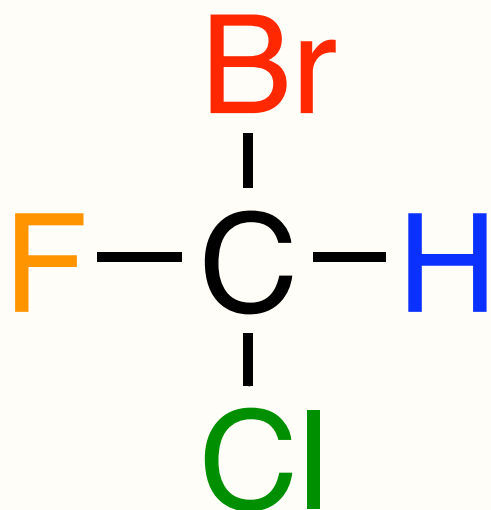
other terminology
commonly used:

- stereocenter
- stereogenic center

← avoid these terms; both have different meanings from chirality center

Chirality Center

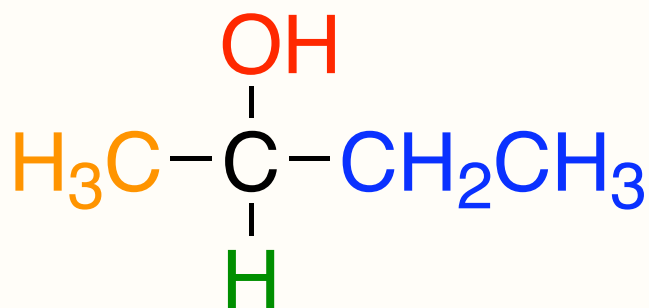
A molecule with a single chirality center is chiral



bromochlorofluoromethane is chiral

Chirality Center

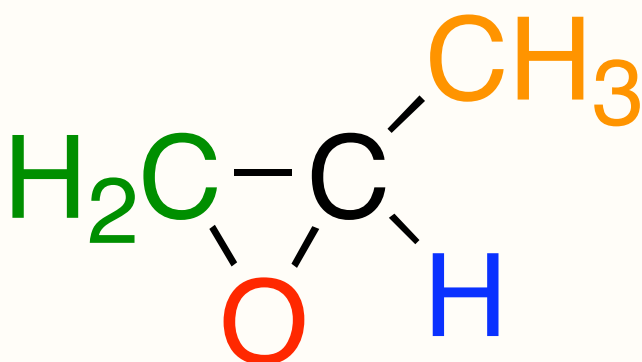
A molecule with a single chirality center is chiral



- 2-butanol is chiral
- although two carbon atoms are bonded to the chirality center, they are part of different groups

Chirality Center

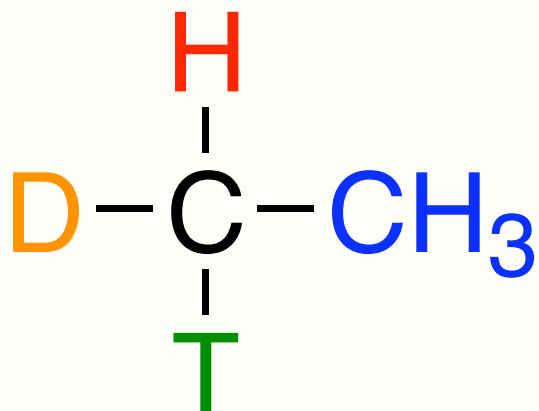
A molecule with a single chirality center is chiral



- 1,2-epoxypropane: a chirality center can be part of a ring
- attached to the chirality center are:
 - H
 - CH₃
 - CH₂O
 - OCH₂

Chirality Center

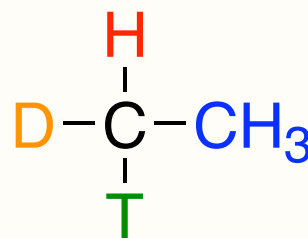
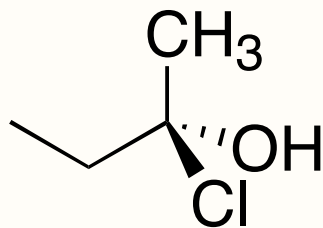
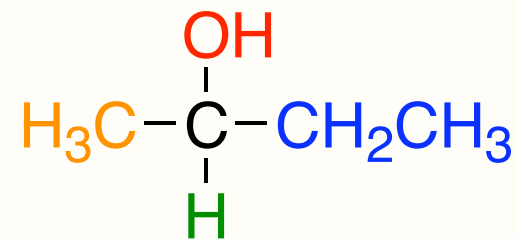
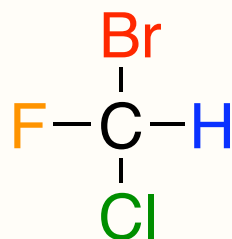
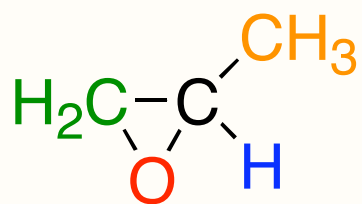
A molecule with a single chirality center is chiral



chiral as a result of isotopic substitution

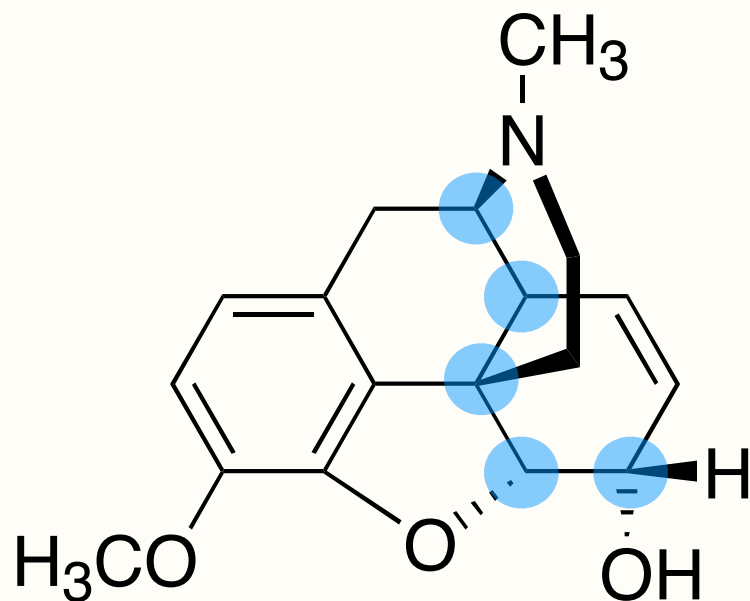
1 Chirality Center = Chiral

A molecule with a single chirality center must be chiral. But a molecule with two or more chirality centers may be chiral or it may not be chiral (Sections 7.10-7.13)



Self Test Question

How many chirality centers in a molecule of codeine?



A. 7

B. 6

C. 5

D. 4

E. 3

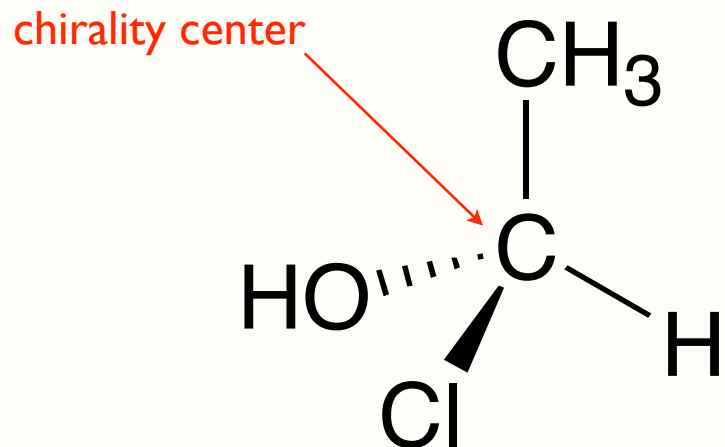
Cahn–Ingold–Prelog (CIP) Priority Rules

R-S Notation for Chirality Centers

Section: 7.6

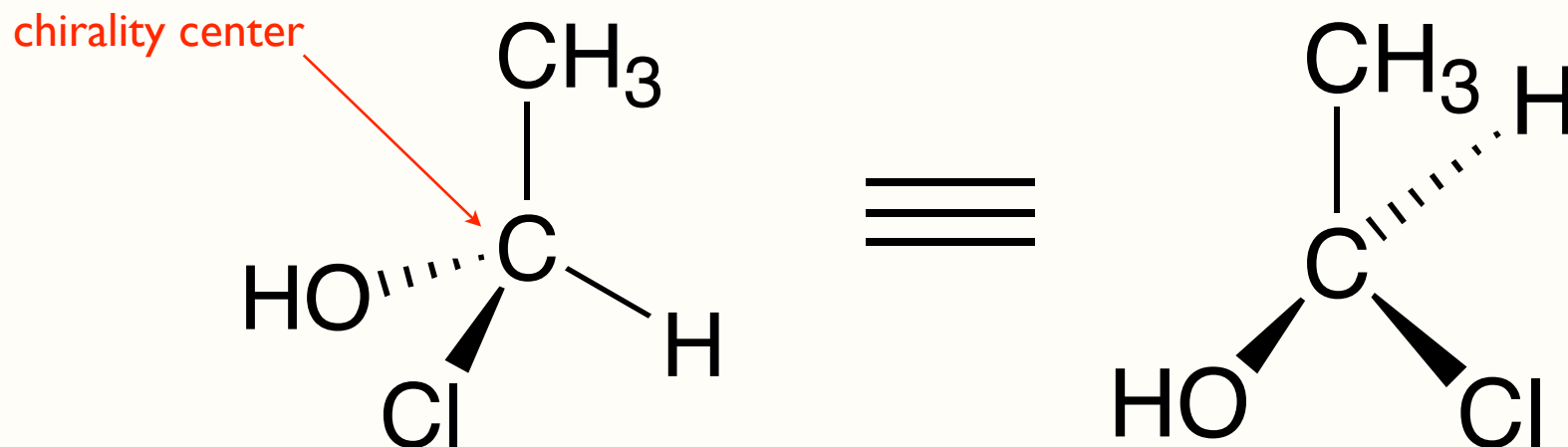
CIP R/S Notation

Step One: Locate chirality center



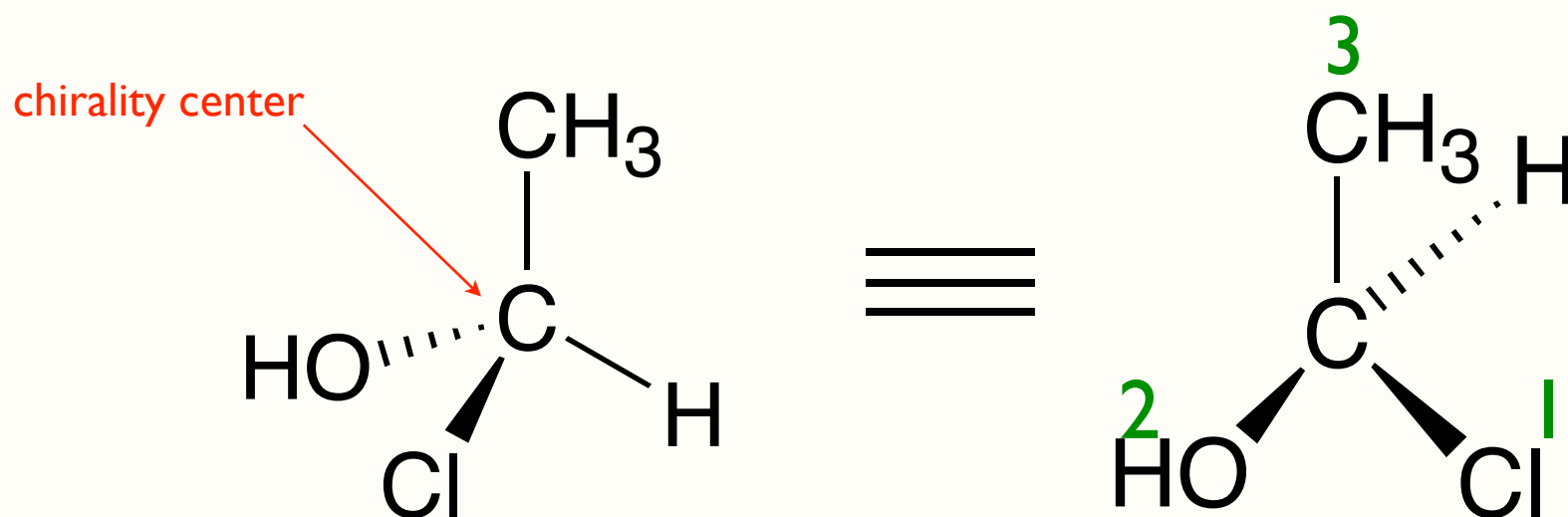
CIP R/S Notation

Step Two: Orient molecule so that lowest ranked (CIP priority) atom or group points away from you



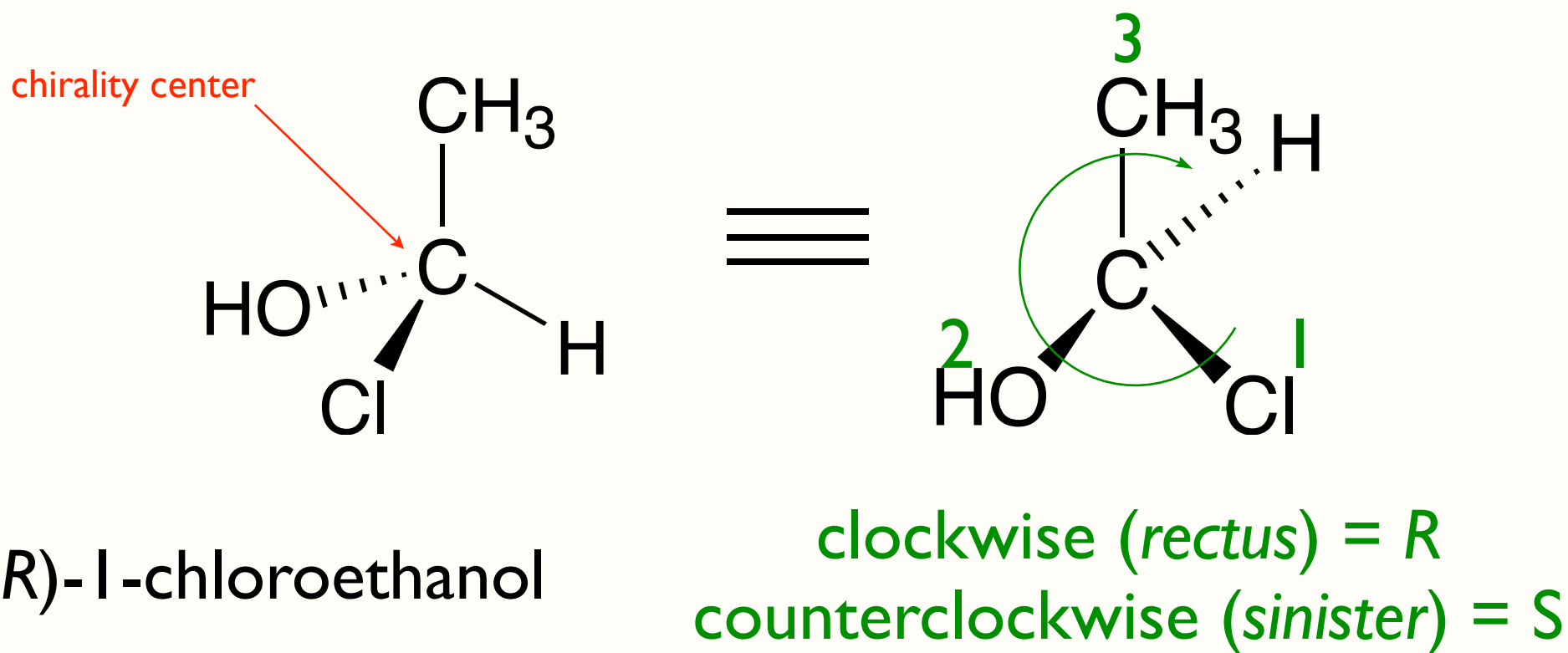
CIP R/S Notation

Step Three: Number 3 highest priority groups in order of increasing priority (CIP sequence rules)



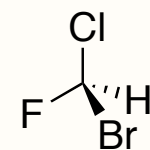
CIP R/S Notation

Step Four: Determine rotation direction of groups in decreasing priority

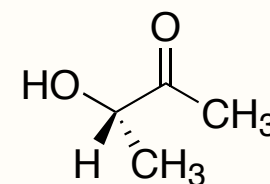
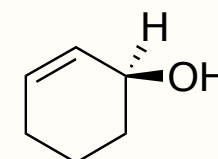
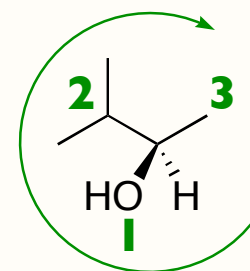


Self Test Question

Which molecule has a chirality center with an absolute configuration of *R*?

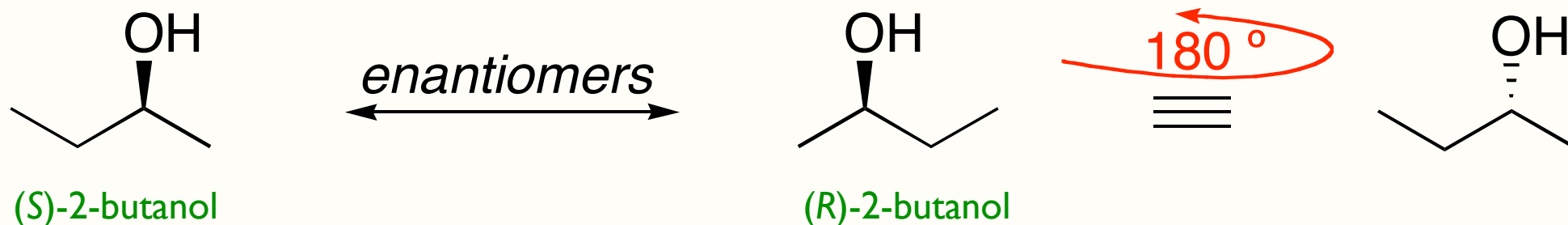


clockwise = *R*



Enantiomers

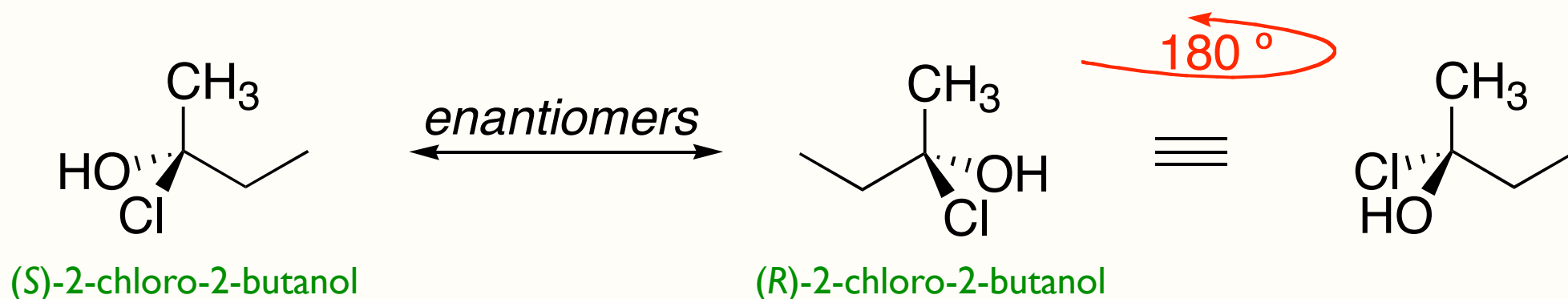
molecules which are non-superimposable mirror images are called enantiomers;
enantiomer describes a relationship between **two** molecules (*enantiomer: opposite handedness*)



enantiomers have opposite configurations
(R/S) at every chirality center

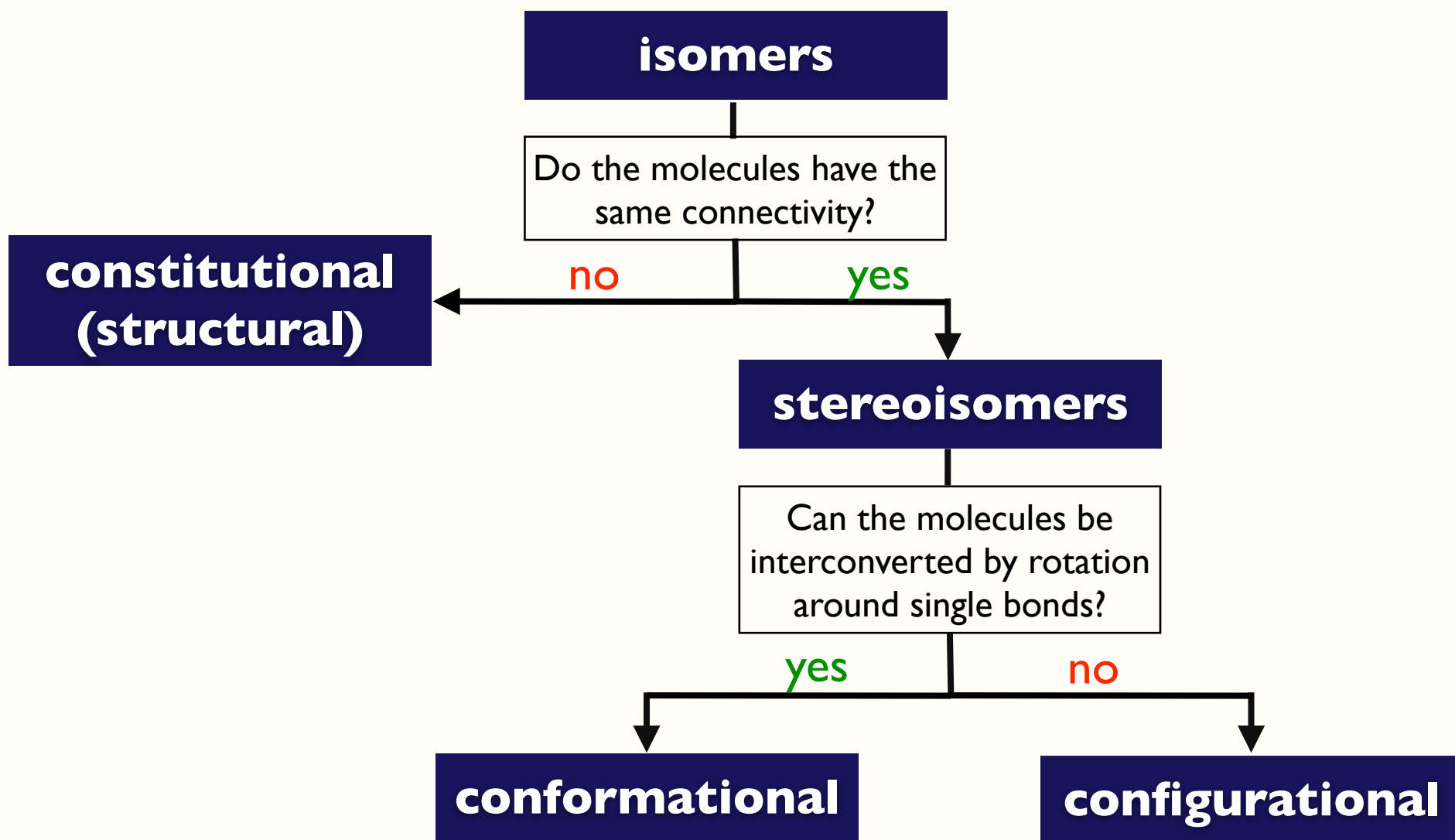
Enantiomers

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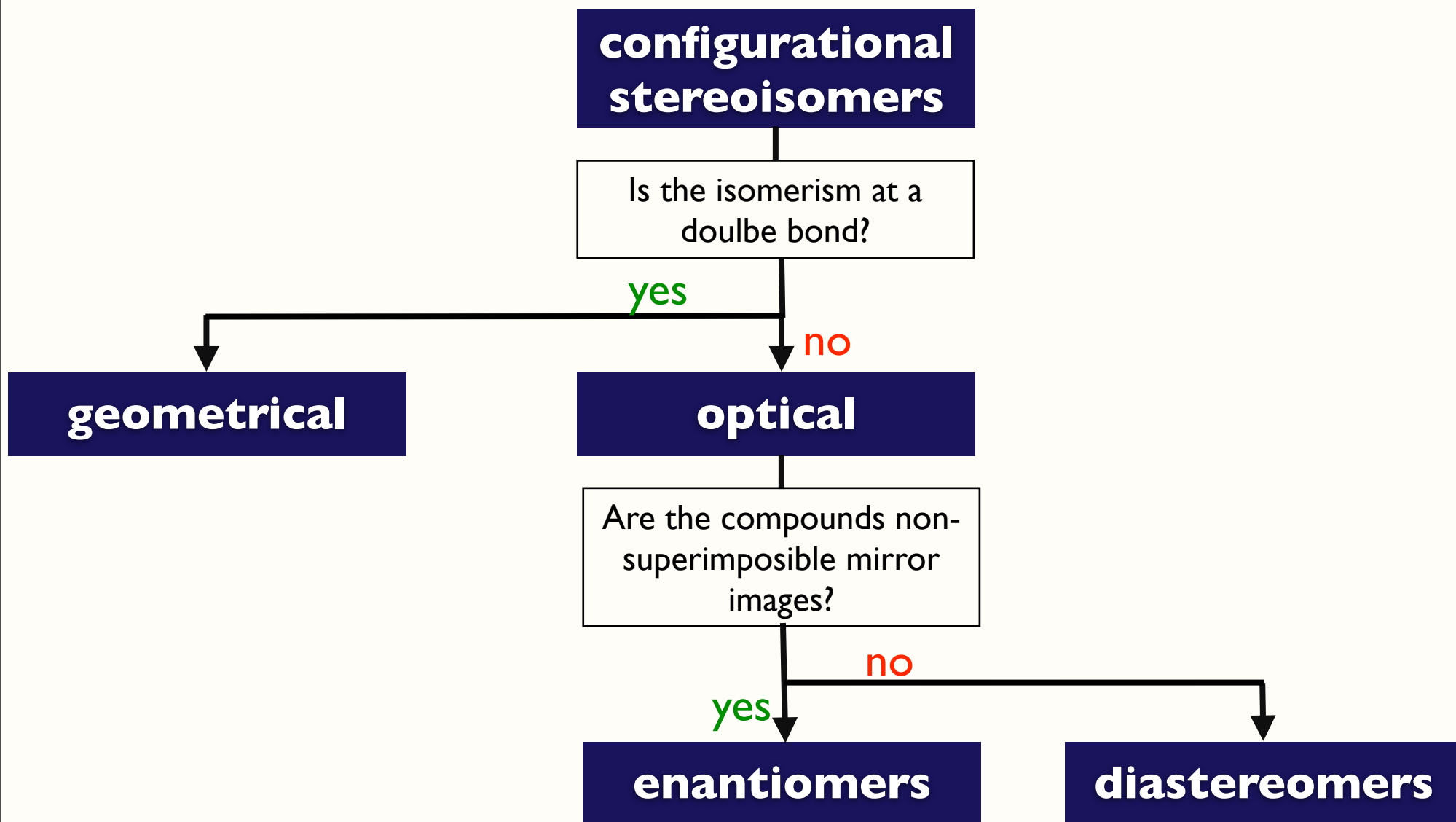


enantiomers have opposite configurations
(R/S) at every chirality center

Isomers

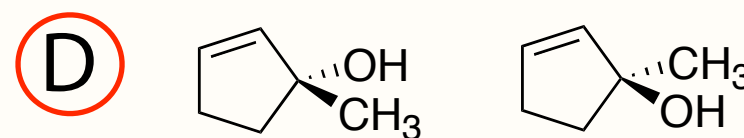
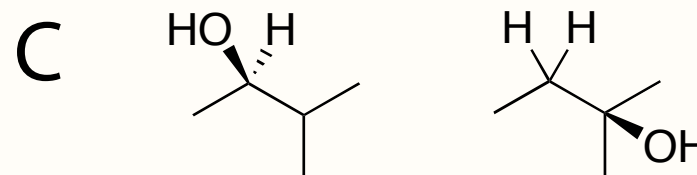
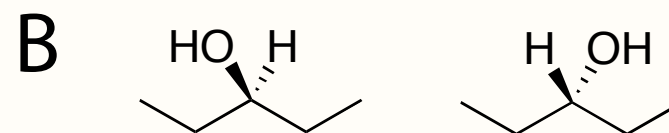
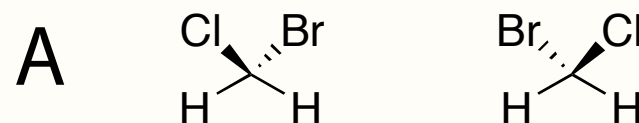


Stereoisomers



Self Test Question

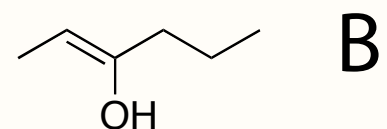
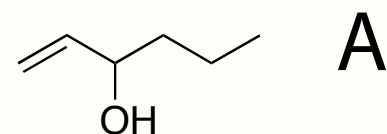
Which pair of molecules are enantiomers?



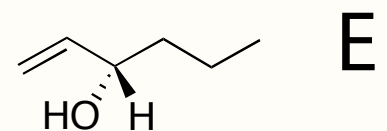
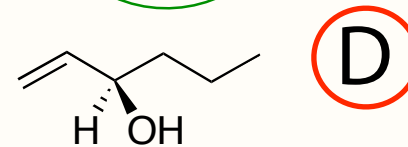
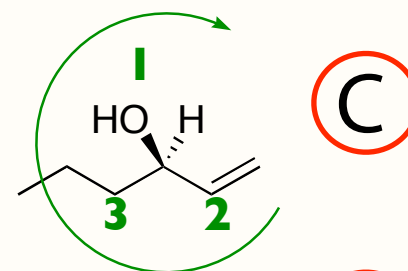
Remember: if a molecule has a plane or center of symmetry, it is not chiral and therefore has no enantiomers.

Self Test Question

Which molecule is (*R*)-1-hexen-3-ol?



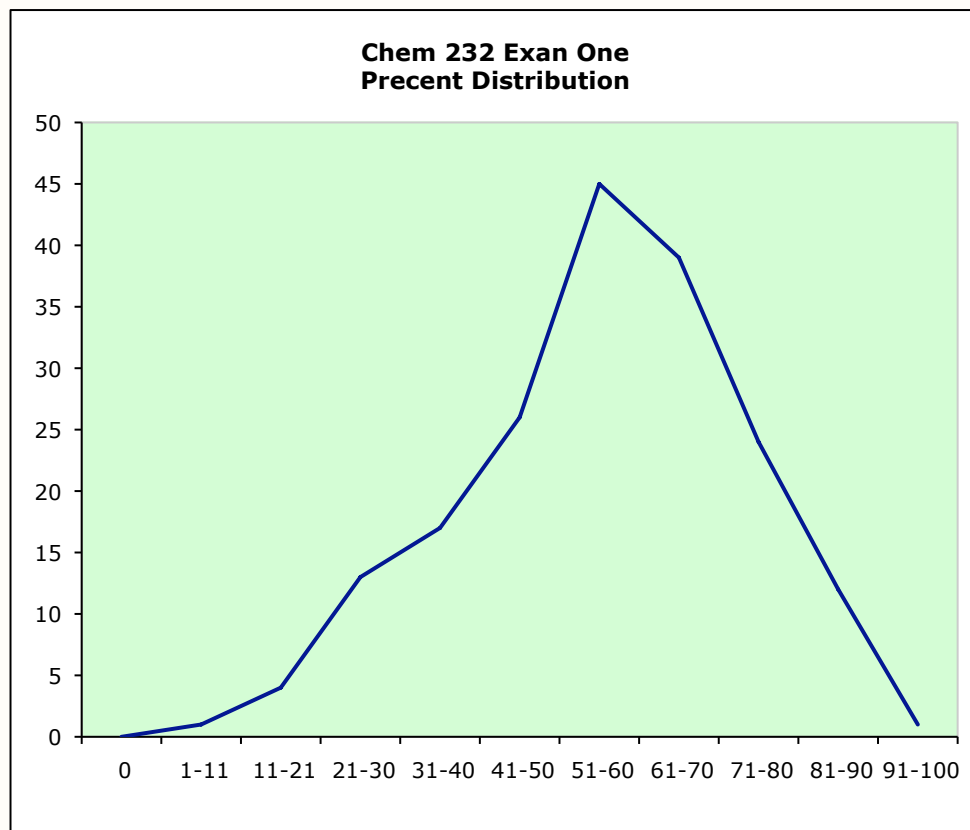
clockwise = *R*



Next Lecture...

Chapter 7: Sections 7.9 - 7.17

Projected Grades



A >77
B 66-76
C 39-65
D 24-38
F <23