Chapter 7
STEREOCHEMISTRY II
CHIRAL MOLECULES

7.1 Try to see if the object is identical to its mirror image or not.
   a) Achiral  b) Chiral  c) Chiral  d) Achiral  e) Chiral  f) Chiral

7.2 Carbon atoms in a compound that are attached to four different groups are chirality centers. Carbons that are doubly bonded or triply bonded are not chirality centers. The presence of chirality centers in a molecule does not necessarily mean that the molecule is chiral. However, any compound with a single chirality center is chiral.
   a) This compound has no chirality center, so it is achiral.
   b) This compound has no chirality center, so it is achiral.
   c) This molecule has one chirality center, so it is chiral.

   d) This molecule has one chirality center, so it is chiral.

   e) The carbon bonded to the chlorine is bonded to a hydrogen and to two other carbons that are part of the ring. Proceeding around the ring in one direction, the second carbon encountered is attached to two methyl groups, while in the other direction the second carbon is bonded to two hydrogens. Therefore these groups are not identical. This molecule is chiral.

   f) This molecule has no chirality center because identical substituents are encountered as one proceeds in either direction around the ring.

7.3 a) Has a plane of symmetry
    b) Has a plane of symmetry
    c) No plane of symmetry
d) Has a plane of symmetry passing through Cl and bisecting the bond on
the opposite side of the ring connecting the two quaternary carbons
e) No plane of symmetry
f) Has a plane of symmetry passing through C=O perpendicular to plane
of H₃C-C-CH₃
g) Has a plane of symmetry passing through H-C-CH₃ and bisecting the
Cl-C-Cl angle
h) No plane of symmetry

First assign priorities from 1 through 4 to the four groups bonded to the
chirality center using the Cahn-Ingold-Prelog sequence rules outlined in
Section 6.2 in the text. The group with the highest priority gets number 1
and the lowest priority group gets number 4. View the molecule at the
chirality center with group number 4 pointed directly away from you. If the
priority numbers of the remaining groups cycle in a clockwise direction
(1 → 2 → 3 → 1), the chirality center has the R configuration. If the cycle is
in a counterclockwise direction then the chirality center has the S
configuration.

7.5

Draw the structure without stereochemistry and identify the chirality
center. Assign priorities to the groups attached to the chirality center.
Draw a tetrahedral carbon and place the lowest priority group on the bond
pointed away from you. Place group number 1 on any one of the other
three bonds. If the configuration is R at the chiral center, place groups 2
and 3 in a clockwise direction from group 1. If the configuration is S, place
groups 2 and 3 in a counterclockwise direction from group 1.
7.6 a) False. Enantiomeric molecules exhibit different properties only in a chiral environment.
b) False. Enantiomers have identical physical properties.
c) True. Water is not chiral.
d) Cannot be determined. The direction of rotation of plane polarized light by a chiral molecule has no relationship to the assigned configuration of the molecule and can only be determined by experiment.
e) True. The assignment of d to a chiral molecule denotes that the compound rotates plane polarized light in the clockwise or + direction.

7.7 Enantiomers are nonsuperimposable mirror images of a molecule. Diastereomers are non-mirror image stereoisomers of a molecule.
The meso stereoisomer does not rotate plane polarized light because it has a plane of symmetry. The other two stereoisomers do rotate plane polarized light.

The cis-diastereomer of 1,2-dimethylcyclopropane is meso and does not rotate plane polarized light because it has a plane of symmetry bisecting the ring. The trans-isomer exists as a pair of enantiomers that do rotate plane polarized light.

7.11  a) Yes  b) No, meso  c) Yes  d) No, no chirality center
To construct a Fisher projection, the molecule is first arranged with the horizontal bonds to its chirality center projecting out of the page and the vertical bonds projecting into the page. In the Fisher projection a tetrahedral carbon is represented by a cross. The horizontal line of the cross represent bonds projecting above the page and the vertical line represent the bonds projecting into the page.

\[
\begin{align*}
\text{a) } & \quad \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{CH}_3
\end{array} & \quad \text{b) } & \quad \begin{array}{c}
\text{CO}_2\text{H} \\
\text{CH}_3
\end{array} & \quad \text{c) } & \quad \begin{array}{c}
\text{H}_3\text{C} \\
\text{CH}_2\text{CH}_3
\end{array}
\end{align*}
\]

\[\begin{array}{c}
\text{O} \\
\text{CH}
\end{array}\]

**7.13**

\[
\begin{align*}
\text{a) } & \quad \begin{array}{c}
\text{H}_2\text{N} \\
\text{H} \\
\text{OH}_2\text{OH}
\end{array} & \quad \begin{array}{c}
\text{CO}_2\text{H} \\
\text{H}_2\text{C} \quad \text{CH}_2\text{CH}_3
\end{array}
\end{align*}
\]

**7.14**

a) This compound is chiral because it is an allene with two different groups on each end.

b) This compound is not chiral. The N is bonded to two ethyl groups.

c) This allene is not chiral because two groups on one end, the H’s, are the same.

d) The silicon is a chirality center because it is bonded to four different groups, so this compound is chiral.

e) This biphenyl is not chiral because one ring is symmetrically substituted with two methyl groups. The plane of the lower ring, which bisects the plane of the upper ring, is a plane of symmetry.

f) This biphenyl is chiral. The CO₂H group on the upper ring destroys the symmetry plane that is present in example (e).

**7.15**

The compound does not have a symmetry plane, so it is chiral. However, because it has only hydrogens in the ortho positions, the two enantiomers interconvert rapidly by rotation about the bond connecting the rings, and the compound cannot be resolved.
7.16
a) R  
b) R  
c) R  
d) R  
e) S  
f) S  
g) R  
h) S  
i) S

7.17
a)  
b)  

7.18
a) 8  
b) 3 (one is meso)  
c) 8  
d) none (not chiral)

7.19
a)  

b)  

7.20
a) This compound has a plane of symmetry passing through the C between the C's bonded to the OH groups and the C on the opposite side of the ring, so it is a meso compound and it will not rotate plane polarized light.
b) This is a chiral compound, so it will rotate plane polarized light.
c) This compound does not have a chirality center, so it will not rotate plane polarized light.
d) This is a chiral compound, so it will rotate plane polarized light.
e) This has two planes of symmetry (horizontal and vertical), so it will not rotate plane polarized light.
f) This has one plane of symmetry (horizontal), so it will not rotate plane polarized light.
g) This has no plane of symmetry, so it will rotate plane polarized light.
h) This has a plane of symmetry passing horizontally through the center of the molecule. It is a meso compound and it will not rotate plane polarized light.
i) This does not have a plane of symmetry, so it will rotate plane polarized light.

Enantiomers exhibit different properties only when they are in a chiral environment.

a) True 

b) True 

c) True (Water is achiral.)

d) True (They rotate plane polarized light the same magnitude but in opposite directions.)

e) False 

f) True 

g) True (Methanol is achiral.)

h) True 

i) False [(S)-2-Butanol is chiral.]

j) Cannot be determined (There is no relationship between the direction of rotation of plane polarized light and the absolute configuration.)

k) False (The reagents are achiral, so a 50:50 mixture of enantiomers must be produced.)

7.22 

a) Identical 

b) Identical 

c) Identical 

d) Enantiomers 

e) Diastereomers 

f) Diastereomers 

g) Enantiomers 

h) Diastereomers 

i) Identical 

7.23 

a) Diastereomers 

b) Diastereomers 

c) Enantiomers 

d) Enantiomers 

e) Identical 

f) Enantiomers 

g) Enantiomers 

7.24 

a) +66.5 

b) +0.7°

c) The observed rotation is directly proportional to the concentration. For example, if the concentration of the solution is halved, the observed rotation will be one half that of the rotation observed for the concentrated solution. The results can be distinguished for each case: one half of +160° is + 80°; one half of -200° is -100°; and one half of +520° is + 260°.

7.25 

The resolution of this amine using one enantiomer of a chiral carboxylic acid is similar to the scheme described in Section 7.7 of the text.
The mixture of the R and S enantiomers of the amine is reacted with the S enantiomer of 2-chloropropanoic acid to produce a mixture of diastereomers of the salt.

Since diastereomers have different physical properties, the mixture can be separated by conventional separation techniques.

Each of the pure diastereomers of the salt is then treated with a strong base to regenerate the pure enantiomers of the amine.

\[ (\text{R})\text{-RNH}_2 \quad (\text{S})\text{-RNH}_2 \]
\[ \quad \downarrow (\text{S})\text{-RCOO}^- \]
\[ (\text{R})\text{-RNH}_3 \quad (\text{S})\text{-RCOO}^- \]
\[ \quad \downarrow \text{Separate} \]
\[ (\text{R})\text{-RNH}_3 \quad (\text{S})\text{-RCOO}^- \]
\[ \quad \downarrow \text{NaOH} \quad \downarrow \text{NaOH} \]
\[ (\text{R})\text{-RNH}_2 \quad (\text{S})\text{-RNH}_2 \]

\[ \text{7.26} \]
a) The DU of X = 1. Therefore X has one ring or one pi bond.
b) Unknown X must have a double bond because it reacts with H\textsubscript{2} to form a saturated compound, Y, with DU = 0.
c) Compound X has a chirality center because it rotates plane polarized light. Compound Y is achiral, so hydrogenation of the double bond destroys the chirality center by converting the double bond group into an alkyl group that is the same as another alkyl group on the chirality center.
There are four stereoisomers of this compound.

Both enantiomers of the cis-diastereomer are of equal stability as are both enantiomers of the trans-diastereomer. The trans-diastereomer is more stable than the cis-diastereomer because it has the conformation with both substituents equatorial. The methyl group is axial in the more stable conformer of the less stable diastereomer (cis) because the axial strain energy of the phenyl group is larger than that of the methyl group.

This tripeptide has four chirality centers and 16 stereoisomers.

b) Sucrose has nine chirality centers and 512 stereoisomers.
c) Pancreatistatin has six chirality centers and 64 stereoisomers.
d) Testosterone has six chirality centers and 64 stereoisomers.
e) This prostaglandin has four chirality centers and 16 stereoisomers (without any isomers involving the double bonds).
f) Vitamin E has three chirality centers and 8 stereoisomers.
g) Vitamin D$_2$ has six chirality centers and 64 stereoisomers (without any isomers involving the double bonds).
h) Vitamin C has two chirality centers and 4 stereoisomers.
i) Apoptolidin has 25 chirality centers and 33,554,432 stereoisomers (without any isomers involving the double bonds).
7.30 In all of the amino acids, except cysteine, the CO$_2$H group has priority number 2. Because S has a higher atomic number than O, the CH$_2$SH group of cysteine has priority number 2 and the CO$_2$H group has priority number 3. This causes the configuration to change from $S$ for most amino acids to $R$ for cysteine, even though all of the groups are in the same positions.

7.31 a) This allene is not chiral because it has two identical groups on one end.
b) This allene is chiral because the groups bonded to each end are different.
c) This biphenyl is not chiral because the two methyl groups on one ring are identical. It has a plane of symmetry that bisects the ring substituted with the methyl groups.
d) This biphenyl is chiral because it does not have a plane of symmetry.
e) The N is bonded to three identical groups, so this ammonium salt is not chiral.
f) The S is pyramidal and bonded to three different groups, so this compound is chiral.

7.32 a) Enantiomers b) Identical c) Enantiomers d) Enantiomers e) Diastereomers f) Identical (These are different conformations of the meso diastereomer.)

7.33 a) S b) R c) R d) S

7.34 a) This molecule is not chiral because it has a plane of symmetry. It is meso.
b) This molecule is chiral because it does not have a plane of symmetry.
c) This molecule is chiral because it does not have a plane of symmetry after rotation so the methyl groups are aligned.
d) This molecule is not chiral because it has a plane of symmetry passing through the CH$_2$ between the two OH groups. It is meso.
e) This molecule is chiral because it does not have a plane of symmetry.

7.35 The model and the Fischer projection represent enantiomers.

7.36 Estradiol has five chirality centers and 32 stereoisomers.