CHAPTER 26

STEREOISOMERISM

SOLUTIONS TO REVIEW QUESTIONS

1. A chiral carbon atom is one to which four different atoms or groups are attached and is a center of asymmetry in a molecule. In the following three compounds, the chiral carbon atoms are marked with an asterisk. (These are merely three examples; there are an infinite number of compounds which contain one chiral carbon atom.)

\[
\begin{align*}
\text{Cl} & \quad \text{C}^* \quad \text{C} \quad \text{H} \\
\text{Br} & \quad \text{Br}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{Cl} \\
\text{H} & \quad \text{C} - \text{C}^* - \text{C} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

\[
\text{CH}_3\text{CH(OH)CH}_2\text{OH}
\]

2. When the axes of two pieces of polaroid film are parallel, you have maximum brightness of the light passing through both. When one piece has been rotated by 90° the polaroid appears black, indicating very little light passing through.

3. A necessary and sufficient condition for a compound to show enantiomerism is that the compound not be superimposable on its mirror image.

4. Enantiomers are nonsuperimposable mirror image isomers. Diastereomers are stereoisomers that are not enantiomers (not mirror image isomers).

5. Two enantiomers of the amino acid, alanine:

\[
\begin{align*}
\text{COOH} & \quad \text{COOH} \\
\text{H} & \quad \text{H} \\
\text{H}_2\text{N} & \quad \text{H}_2\text{N} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]
6. \((\pm)-\text{tartaric acid}\) is an equal mixture of the two enantiomers, \((+)-\text{tartaric acid}\) and \((-)-\text{tartaric acid}\) and, so, has no net optical activity.

\[
\begin{array}{c}
\text{COOH} \\
\text{HO} \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{COOH}
\end{array} \quad \begin{array}{c}
\text{COOH} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{HO} \quad \text{C} \quad \text{H} \\
\text{COOH}
\end{array}
\]

\((-)-\text{tartaric acid} \quad (+)-\text{tartaric acid}

\text{Meso}-\text{tartaric acid} is a structure that is superimposable on its own mirror image and, thus, has no optical activity.

\[
\begin{array}{c}
\text{COOH} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{H} \quad \text{C} \quad \text{OH} \\
\text{COOH}
\end{array}
\]

\text{meso}-\text{tartaric acid}

7. Each chiral carbon allows for two stereoisomers. The compound has three chiral carbons (marked with *) as follows:

\[
\text{CH}_3\text{CHClCHBrCH}_2\text{CCl}_2\text{CHClCH}_3
\]

The number of stereoisomers = \(2^n\), where \(n = \) number of chiral carbons.

For this compound, number of stereoisomers = \(2^3 = 8\).

8. Physical properties of a pair of enantiomers

\[
\begin{array}{c|c|c}
\text{specific rotation} & (+) 2\text{-methyl-l-butanol} & (-) 2\text{-methyl-l-butanol} \\
\hline
+5.76^\circ & \text{129}^\circ\text{C} & \text{129}^\circ\text{C} \\
\text{density} & 0.819 \text{ g/mL} & 0.819 \text{ g/mL}
\end{array}
\]

9. Most chiral molecules are stereospecific in their biological activity. Therefore a racemic mixture of a drug provides only half the bioactive material prescribed. By using a single isomer of a compound, the dosage can be cut in half and possible side effects can be avoided from its enantiomer.

10. The specific rotation for the racemic mixture will be zero.

11. Run a sample of each compound in a polarimeter, which will show you which is \((+\) and which is \((-\) lactic acid.
12. If the following compound were meso it would not show optical rotation.

\[
\begin{array}{c}
\text{CH}_3 \\
H \quad \text{OH} \\
\text{HO} \quad H \\
\text{CH}_3
\end{array}
\]

13. Glucose has four chiral carbon atoms.

\[2^n = 2^4 = 16\] optical isomers of glucose

14. (a) and (d) are meso compounds. For (a), make two interchanges of the groups on carbons 2 or 3 and you have a structure which is meso. (d) is meso as written. There is a horizontal plane of symmetry through H and Br.
SOLUTIONS TO EXERCISES

1. specific rotation \([\alpha] = \frac{\text{observed rotation in degrees}}{\left(\frac{\text{length of sample tube in decimeters}}{\text{sample concentration in grams per milliliter}}\right)}\)

\[\alpha = \frac{+156^{\circ}}{(20 \text{ dm})(0.55 \text{ g/mole})} = 14^{\circ}\]

2. specific rotation \([\alpha] = \frac{\text{observed rotation in degrees}}{\left(\frac{\text{length of sample tube in decimeters}}{\text{sample concentration in grams per milliliter}}\right)}\)

\[\alpha = \frac{-216^{\circ}}{(1 \text{ dm})(2.35 \text{ g/mole})} = -92^{\circ}\]

3. Chiral objects can’t be superimposed on their mirror image. The following are chiral: (a) the letter \(p\); (c) a spiral staircase; (d) a left foot.

4. Chiral objects can’t be superimposed on their mirror image. The following are chiral: (b) a human body; (c) a 1/4” bolt; (d) the letter \(n\).

5. Chiral carbons are bonded to four different groups. (a) one chiral carbon; (b) two chiral carbons; (c) two chiral carbons; (d) two chiral carbons.

6. Chiral carbons are bonded to four different groups. (a) no chiral carbons; (b) two chiral carbons; (c) one chiral carbon; (d) three chiral carbons.

7. (a) 2,4-Dibromohexane has two chiral carbons and is optically active.

\[
\begin{array}{c}
\text{Br} \\
\text{CH}_3\text{CHCH}_2\text{CHCH}_2\text{CH}_3
\end{array}
\]

(b) 2,3-Dimethylhexane has one chiral carbon and is optically active.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3
\end{array}
\]

(c) 3-chlorohexane has one chiral carbon and is optically active.

\[
\begin{array}{c}
\text{Cl} \\
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_3
\end{array}
\]
(d) 2,5-Dimethylhexane has no chiral carbons and is not optically active.

```
CH3
CH3
CH3CHCH2CH2CHCH3
```

8. (a) 2,3,5-Trimethylhexane has one chiral carbon and is optically active.

```
CH3
CH3
CH3CHCHCH2CH2CH3
```

(b) 1-Iodohexane has no chiral carbons and is not optically active.

```
CH2ICH2CH2CH2CH2CH3
```

(c) 3-Ethylhexane has no chiral carbons and is not optically active.

```
CH3CH2
CH3CH2CHCH2CH2CH3
```

(d) 3-Chloro-2-iodohexane has two chiral carbons and is optically active.

```
CH3CHICHClCH2CH2CH3
```

9. (a) The sugar ribose has three chiral carbons (marked with *).

```
O
CH
*CHOH
*CHOH
*CHOH
CH2OH
```

(b) The metabolite oxaloacetic acid has no chiral carbons.

(c) The amino acid threonine has two chiral carbons (marked with *).

```
CH3
*CHOH
H2N—*CH—COOH
```
10. (a) The sugar 2-deoxyribose has two chiral carbons (marked with *).

\[
\begin{align*}
&\text{O} \\
&\quad\text{CH} \\
&\quad\text{CH}_2 \\
&\quad\text{\*CHOH} \\
&\quad\text{\*CHOH} \\
&\quad\text{CH}_2\text{OH}
\end{align*}
\]

(b) The metabolite malic acid has one chiral carbon (marked with *).

\[
\begin{align*}
&\text{COOH} \\
&\quad\text{\*CHOH} \\
&\quad\text{CH}_2 \\
&\quad\text{COOH}
\end{align*}
\]

(c) The amino acid isoleucine has two chiral carbons (marked with *).

\[
\begin{align*}
&\text{CH}_3 \\
&\quad\text{CH}_2 \\
&\quad\text{\*CHCH}_3 \\
&\quad\text{H}_2\text{N-CH-COOH}
\end{align*}
\]

11. (a) The compound has one chiral carbon (marked with *).

\[
\begin{align*}
&\text{CH}_3 \\
&\quad\text{\*NH}_2 \\
&\quad\text{CH}_2\text{CH}_3
\end{align*}
\]

(b) The compound has two chiral carbons (marked with *).

\[
\begin{align*}
&\text{COOH} \\
&\quad\text{COOH} \\
&\quad\text{H}
\end{align*}
\]

(c) The compound has one chiral carbon (marked with *).

\[
\begin{align*}
&\text{CH}_3 \\
&\quad\text{\*NHCH}_3 \\
&\quad\text{CH}_3
\end{align*}
\]

(d) The compound has one chiral carbon (marked with *).

\[
\begin{align*}
&\text{CH}_3 \\
&\quad\text{\*Cl} \\
&\quad\text{CH}_3
\end{align*}
\]
12. (a) $\text{H} - \text{CH}_3$  
(b) $\text{H}_2\text{NCH}_3$  
(c) $\text{CH}_3 - \text{OH}$  
(d) $\text{CH}_2\text{CH}_2\text{CH}_3$  

13. The two projection formulas (A) and (B) are the same compound, for it takes two changes to make (B) identical to (A).

\[
\begin{array}{cccc}
\text{Cl} & \text{Br} & \text{H} & \text{Cl} \\
\text{Br} & \text{C} & \text{H} & \text{Br} \\
\text{F} & \text{F} & \text{F} & \text{F} \\
\text{(A)} & \text{(B)} & \text{1st change in (B)} & \text{2nd change in (B)}
\end{array}
\]

\[
\begin{array}{cccc}
\text{Cl} & \text{Br} & \text{H} & \text{Cl} \\
\text{Br} & \text{C} & \text{H} & \text{Br} \\
\text{F} & \text{F} & \text{F} & \text{F} \\
\text{(A)} & \text{(B)} & \text{1st change in (B)} & \text{2nd change in (B)}
\end{array}
\]

14. The two projection formulas (A) and (B) are the same compound, for it takes two changes to make (B) identical to (A).

\[
\begin{array}{cccc}
\text{H} & \text{CH}_3 & \text{H} & \text{H} \\
\text{Br} & \text{C} & \text{F} & \text{Br} & \text{C} & \text{F} \\
\text{F} & \text{CH}_3 & \text{F} & \text{CH}_3 \\
\text{(A)} & \text{(B)} & \text{1st change in (B)} & \text{2nd change in (B)}
\end{array}
\]

\[
\begin{array}{cccc}
\text{COOH} & \text{COOH} \\
\text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 \\
\text{(a), (e), and (f) are (−)-lactic acid} & \text{(b), (c), and (d) are (+)-lactic acid}
\end{array}
\]

16. (+)-alanine is $\text{H}_2\text{N} - \text{H}$  
(b), (c), and (d) are (+)-alanine  
(-)-alanine is $\text{H} - \text{NH}_2$  
(a), (e), and (f) are (−)-alanine
17. Diastereomers are all stereoisomers that are not mirror images of.

18. Diastereomers are all stereoisomers that are not mirror images of.

19. Diastereomers are all stereoisomers that are not mirror images of.

20. Each chiral carbon allows for two stereoisomers. Galactose has four chiral carbons. number of stereoisomers = \( 2^n \) where \( n \) = number of chiral carbons

number of stereoisomers for galactose = \( 2^4 = 16 \) stereoisomers
22. Each chiral carbon allows for two stereoisomers. Ribose has three chiral carbons. 

\[
\text{number of stereoisomers} = 2^n \quad \text{where} \quad n = \text{number of chiral carbons}
\]

\[
\text{number of stereoisomers for ribose} = 2^3 = 8 \text{ stereoisomers}
\]

23. All possible stereoisomers of the following compounds, with enantiomers and meso compounds labeled.

(a) 1,2-dibromopropane

\[
\begin{array}{c}
\text{CH}_2\text{Br} \\
\text{H} \\
\text{Br} \\
\text{CH}_3 \\
\text{Br} \\
\text{CH}_3
\end{array}
\]

enantiomers

(b) 2-butanol

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{OH} \\
\text{CH}_2\text{CH}_3 \\
\text{HO} \\
\text{CH}_2\text{CH}_3
\end{array}
\]

enantiomers

(c) 3-chlorohexane

\[
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{H} \\
\text{Cl} \\
\text{CH}_2\text{CH}_3 \\
\text{Cl} \\
\text{CH}_3\text{CH}_2\text{CH}_2
\end{array}
\]

enantiomers

There are no meso compounds in 24(a), (b), or (c).

24. All possible stereoisomers of the following compounds with enantiomers and meso compounds labeled.

(a) 2,3-dichlorobutane

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H} \\
\text{Cl} \\
\text{CH}_3
\end{array}
\]

enantiomers

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{H} \\
\text{CH}_3
\end{array}
\]

enantiomers

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{H} \\
\text{CH}_3
\end{array}
\]

meso

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\text{H} \\
\text{CH}_3
\end{array}
\]

meso
25. All the stereoisomers of 1,2,3-trihydroxybutane:

Compounds A and B, and C and D are pairs of enantiomers. There are no meso compounds. Pairs of diastereomers are A and C, A and D, B and C, and B and D.
26. All the stereoisomers of 3,4-dichloro-2-methylpentane:

Compounds A and B, and C and D are pairs of enantiomers. There are no meso compounds. Pairs of diastereomers are A and C, A and D, B and C, and B and D.

27. The four stereoisomers of 2-hydroxy-3-pentene:

The two cis compounds are enantiomers and the two trans compounds are enantiomers.

28. The four stereoisomers of 2-chloro-3-hexene.

The two cis compounds are enantiomers and the two trans compounds are enantiomers.
29. Assume (+)-2-bromopentane is

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H} - \text{C} - \text{Br} \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_3 \\
\end{array}
\]

All possible isomers formed when (+)-2-bromopentane is further brominated to dibromopentanes:

\[
\begin{array}{c|c|c|c|c}
\text{CH}_2\text{Br} & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{H} - \text{C} - \text{Br} & \text{Br} - \text{C} - \text{Br} & \text{H} - \text{C} - \text{Br} & \text{H} - \text{C} - \text{Br} \\
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{A} & \text{B} & \text{C} & \text{D} \\
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
\text{H} - \text{C} - \text{Br} & \text{H} - \text{C} - \text{Br} & \text{H} - \text{C} - \text{Br} & \text{H} - \text{C} - \text{Br} \\
\text{CH}_2 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\
\text{H} - \text{C} - \text{Br} & \text{Br} - \text{C} - \text{H} & \text{CH}_2 & \text{CH}_2 \\
\text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2\text{Br} \\
\text{E} & \text{F} & \text{G} & \\
\end{array}
\]

Compounds A, C, D, F, G are optically active; B has no chiral carbon atom; E is a meso compound.

30. Assume (+)-2-chlorobutane is

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2 \\
\text{H} - \text{C} - \text{Cl} \\
\text{CH}_3 \\
\end{array}
\]
All possible isomers formed when (+)-2-chlorobutane is further chlorinated to dichlorobutane:

<table>
<thead>
<tr>
<th>CH₃</th>
<th>CH₂Cl</th>
<th>CH₃</th>
<th>CH₃</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂</td>
<td>CH₂</td>
<td>CH₂</td>
<td>H—C—Cl</td>
<td>Cl—C—H</td>
</tr>
<tr>
<td>H—C—Cl</td>
<td>Cl—C—Cl</td>
<td>H—C—Cl</td>
<td>Cl—C—Cl</td>
<td>Cl—C—Cl</td>
</tr>
<tr>
<td>CH₂Cl</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
</tr>
</tbody>
</table>

Compounds A, B, and E are optically active; C does not have a chiral carbon atom; D is a meso compound.

31. Neither of the products, 1-chloropropane or 2-chloropropane, has a chiral carbon atom so neither product would rotate polarized light.

32. If 1-chlorobutane and 2-chlorobutane were obtained by chlorinating butane, and then distilled, they would be separated into the two fractions, because their boiling points are different. 1-chlorobutane has no chiral carbon, so would not be optically active. 2-chlorobutane would exist as a racemic mixture (equal quantities of enantiomers) because substitution of Cl for H on carbon-2 gives equal amounts of the two enantiomers. Distillation would not separate the enantiomers because their boiling points are identical. The optical rotation of the two enantiomers of the 2-chlorobutane fraction would exactly cancel, and thus would not show optical activity.

33. Compounds (a) and (d) are meso. Make two changes on C-3 in compound (a) to prove that it is meso.

34. Compound (d) is meso.
35. (a) enantiomers  
(b) nonisomers  
(c) diastereomers  

36. (a) nonisomers  
(b) enantiomers  
(c) diastereomers  

37. If four different groups were attached to a central carbon atom in a planar arrangement, it would not rotate polarized light because there would be a plane of symmetry in the molecule. No such plane of symmetry is possible when the four different groups are arranged in a tetrahedral structure.  

38. (a) and (b)  

39. (a) A chiral primary alcohol of formula C₅H₁₀O.  

(b) A compound with three primary alcohol groups is chiral, and has the formula C₆H₁₄O₃.  

40. (a)  

(b) The spearmint molecule is the optical isomer of the caraway molecule and differs from it in structure at the chiral carbon atom.
41. Ephedrine has two chiral carbons and can have four stereoisomers. This number is calculated using
\[2^n = 2^2 = 4.\]

42. A chiral carbon is bonded to four different groups. Tyrosine has one chiral carbon.

43. Based on its name, dextromethorphan, this drug is probably the dextrorotatory isomer. It rotates plane-polarized light in a clockwise direction. The symbol, (+), would be used to indicate this drug’s optical activity.

44. Stereoisomer structures

(a) 2-bromo-3-chlorobutane

There are no meso compounds.
There are no meso compounds.

45. Meso structures for alkanes
   (a) C₈H₁₈
   (b) C₉H₂₀
(c) $C_{10}H_{22}$

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{H} & \quad \text{H} & \quad \text{H} \\
& \quad \text{H} & \quad \text{H} & \quad \text{H} \\
& \quad \text{H} & \quad \text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{H} & \quad \text{CH}_3 & \quad \text{CH}_3 \\
& \quad \text{H} & \quad \text{H} & \quad \text{H} \\
& \quad \text{H} & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
46. Optically active alcohols of \(\text{C}_6\text{H}_{14}\text{O}\) (one enantiomer of each structure).

   \[
   \begin{align*}
   \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CCH}_2\text{CH}_3 \\
   \text{CH}_3 & \quad \text{CH}_3 \\
   \text{CH}_3\text{CH}_2\text{CH}_2\text{CCH}_2\text{OH} & \quad \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_2\text{OH} \\
   \text{H} & \quad \text{H} \\
   \text{CH}_3\text{CH}_2\text{CCH}_2\text{CCH}_3 & \quad \text{CH}_3\text{CH}_2\text{CCH}_2\text{CCH}_3 \\
   \text{H} & \quad \text{OH} \\
   \text{CH}_3 & \quad \text{CH}_3 \\
   \text{CH}_3\text{CH} & \quad \text{CH}_3\text{C} \\
   \text{CCH}_2\text{OH} & \quad \text{CCH}_3 \\
   \text{CH}_3 & \quad \text{CH}_3
   \end{align*}
   \]

47. A compound of formula \(\text{C}_3\text{H}_8\text{O}_2\):

   \[
   \begin{align*}
   \text{COOH} & \quad C\text{-NH}_2 & \quad \text{COOH} \\
   \text{H}_2\text{N} & \quad \text{C} & \quad \text{H}_2\text{N} \\
   \text{CH}_3 & \quad \text{NH}_2 & \quad \text{OH} \\
   \text{CH}_3 & \quad \text{COOH} & \quad \text{CH}_3
   \end{align*}
   \]

The similarity is that the chiral carbon in each compound is bonded to an \(\text{NH}_2\), a \(\text{COOH}\), and an \(\text{H}\) group.

48. A compound of formula \(\text{C}_3\text{H}_8\text{O}_2\):

   (a) is chiral; contains two OH groups \(\text{CH}_3\text{CHCH}_2\text{OH}\)

   \[
   \begin{align*}
   \text{CH}_3\text{CHCH}_2\text{OH} & \\
   \end{align*}
   \]

   (b) is chiral; contains one OH group \(\text{CH}_3\text{-O-CHCH}_3\)

   \[
   \begin{align*}
   \text{CH}_3\text{-O-CHCH}_3 & \\
   \end{align*}
   \]

   (c) is achiral; contains two OH groups \(\text{CH}_2\text{CH}_2\text{CH}_2\)

   \[
   \begin{align*}
   \text{CH}_2\text{CH}_2\text{CH}_2 & \\
   \end{align*}
   \]