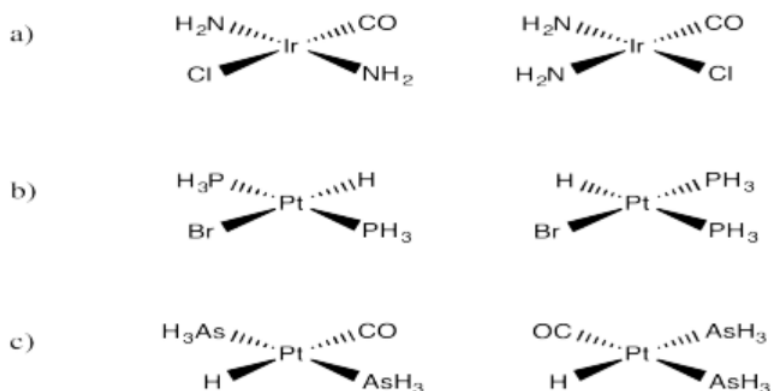
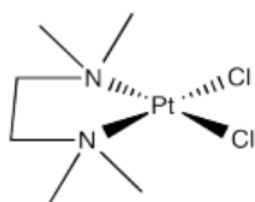


5.20: Solutions to Selected Problems

Exercise 5.2.1:



Exercise 5.2.2:



Needs to be *cis*. The tmeda group is not long enough to reach the *trans* position

Exercise 5.3.1:

Clockwise.

Exercise 5.3.2:

Counter-clockwise.

Exercise 5.3.3:

Counter-clockwise.



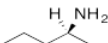
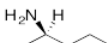




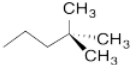
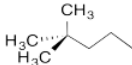
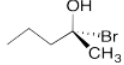
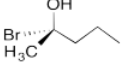
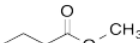
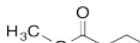
Exercise 5.3.4:

Clockwise.

Exercise 5.3.5:

Enantiomer B has a molecular weight of 126 g/mol, a density of 0.995 g/mL, an optical rotation of $[\alpha] = -26^\circ$, a melting point of 65°C and a boiling point of 225°C .

Exercise 5.3.6:

	Mirror Image	Superimposable	Chiral?
		Yes	No
		No	Yes
		Yes	No
		Yes	No
		Yes	No
		No	Yes
		Yes	No

Exercise 5.3.7:

- The plane of the page is a mirror plane. There is also one perpendicular to the page that reflects one H into the other.
- The plane of the page contains one P-Cl bond and bisects the other Cl's.
- The plane of the page is a mirror plane.
- Mirror plane contains P-Br bond and bisects the Cl's.
- There is no lone pair on the B. Therefore all atoms lie in a mirror plane.
- No mirror planes--the molecule is therefore chiral.
- There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.
- No mirror planes--the molecule is therefore chiral.
- There is a plane perpendicular to the page that contains the Br and Cl and bisects the cyclopropane ring.
- The C-C bond can be rotated by 60 degrees so that there is a plane perpendicular to the C-C bond axis.
- The C-C bond in one of the chlorine-containing arms can be rotated so that there is a mirror plane that goes through the ethyl group (with no Cl's) and the P, and one chlorine containing arm is the reflection of the other.
- Since a double bond is planar, there is a mirror plane that contains all six atoms.
- There is a mirror plane that contains two C's and bisects the two Cls.
- No mirror planes--the molecule is therefore chiral. The rings are not in the same plane due to the CH₃ and NH₂ groups, which bump into each other. They also prevent rotation around the C-C bond between the rings.

Exercise 5.3.8

Picture (a)

Exercise 5.3.9:

Picture (b)

Exercise 5.3.10:

Picture (d)

Exercise 5.3.11:

Picture (c)

Exercise 5.4.1:

Priority of groups:

1 Br (red)

2 Cl (bright green)

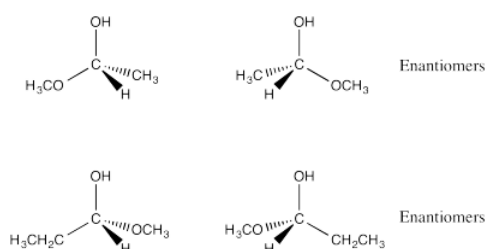
3 F (pale green)

4 H (white)

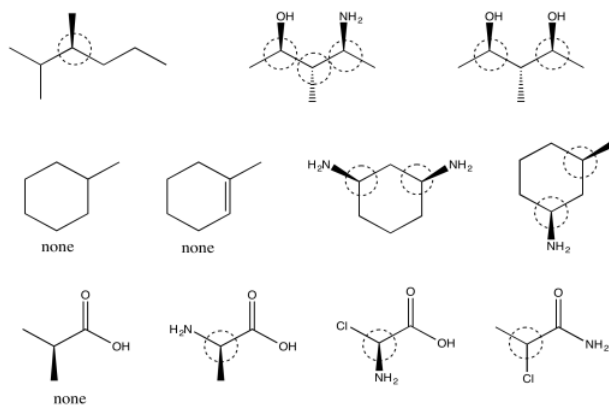
In the molecule in figure 5.4.2, with the low-priority hydrogen pointed away, bromine is at the top, chlorine is clockwise from the bromine, and fluorine is clockwise from the chlorine. It therefore has an assigned configuration of *R*.

In the molecule in figure 5.4.3, with the low-priority hydrogen pointed away, bromine is at the top, chlorine is counterclockwise from the bromine, and fluorine is counterclockwise from the chlorine. Thus, it has an assigned configuration of *S*.

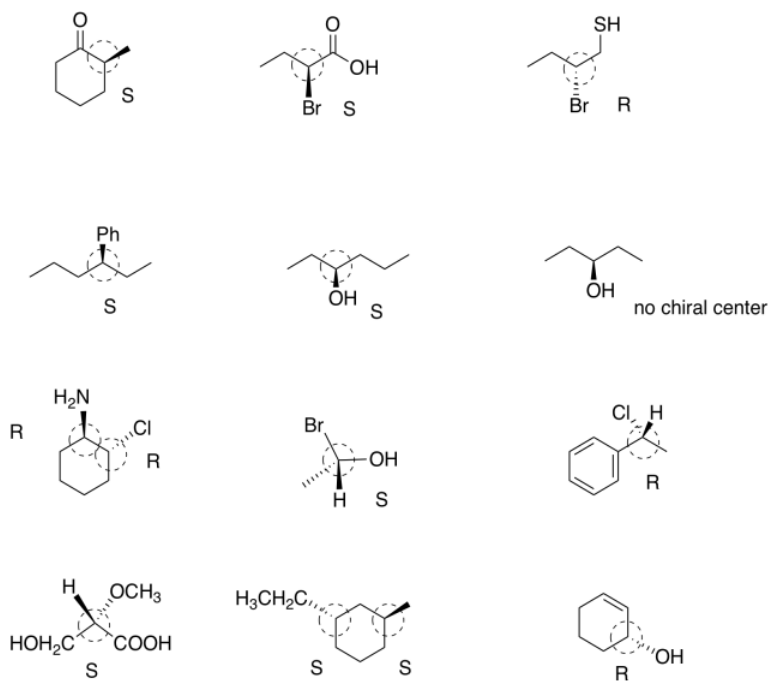
Exercise 5.4.2



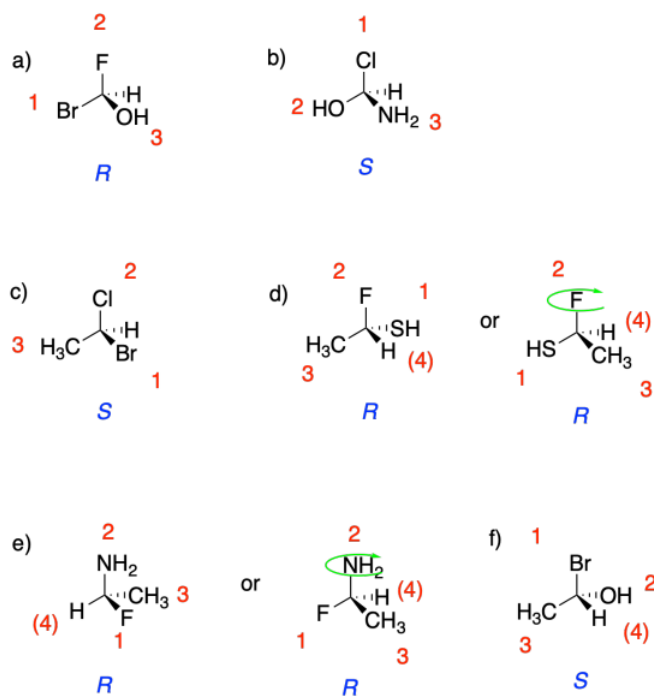
Exercise 5.4.3:



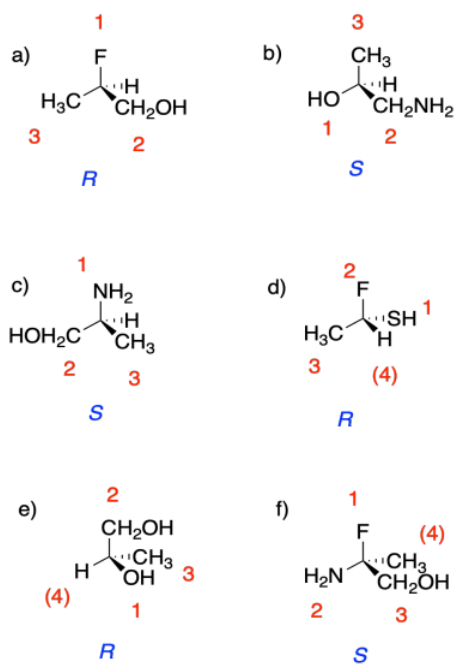
Exercise 5.4.4:



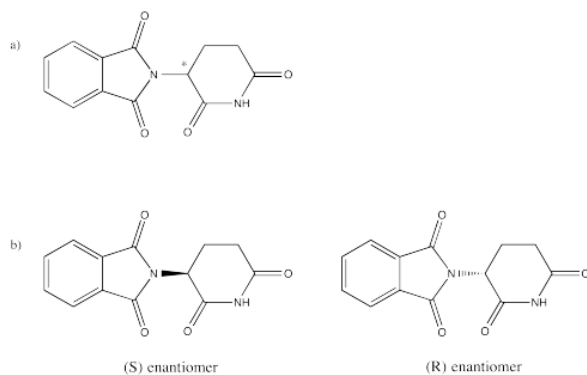
Exercise 5.4.5:



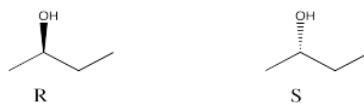
Exercise 5.4.6:



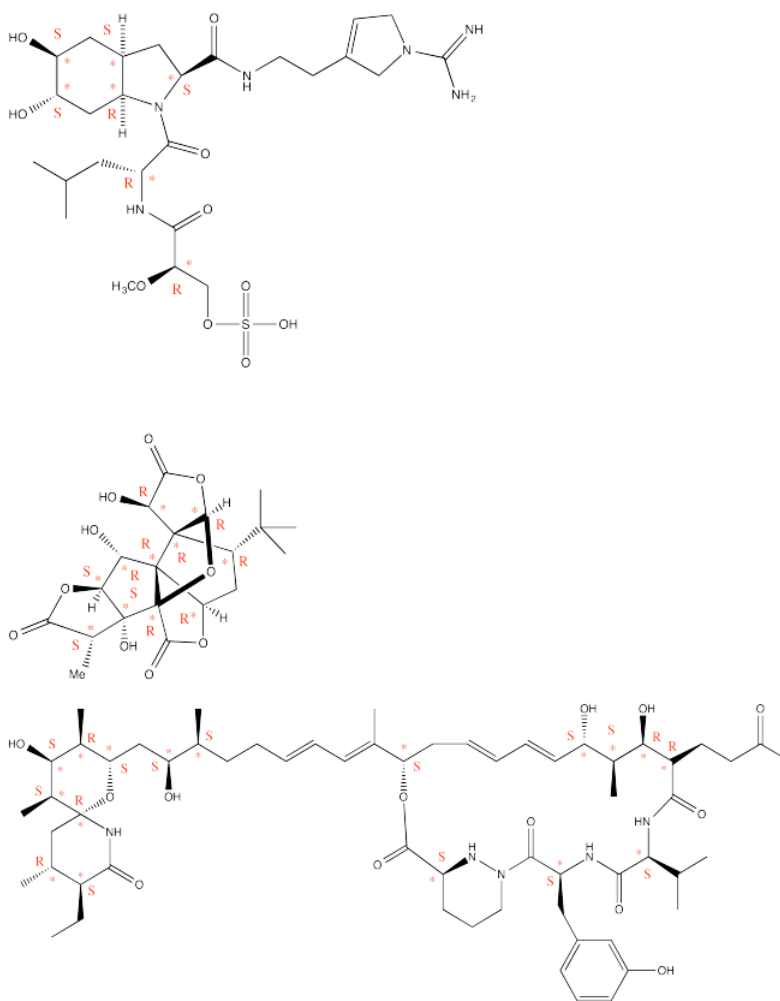
Exercise 5.5.1:



Exercise 5.5.2:



Exercise 5.5.3:



Exercise 5.6.1:

A pure sample of A would have $[\alpha] = 75^\circ$

Optical purity or enantiomeric excess = $\frac{50}{75} = 66\%$

% major enantiomer = $66 + \frac{34}{2} = 83\%$

% minor enantiomer = $100 - 83 = 17\%$

Exercise 5.6.2

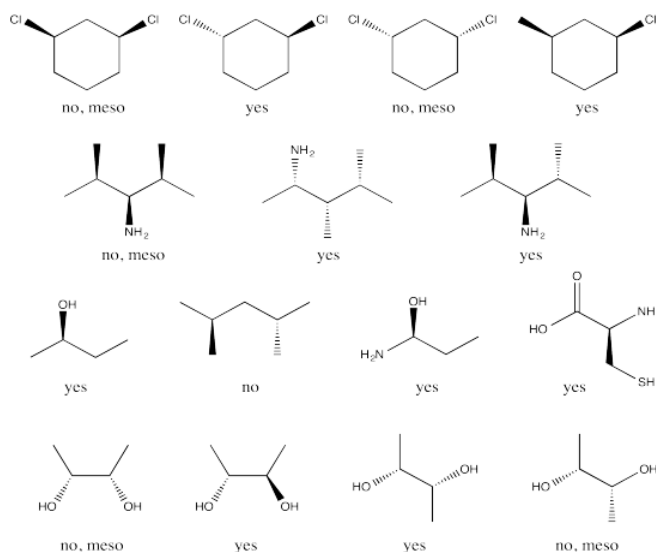
% *major* = 90%

% *major* = 10%

Optical purity or enantiomeric excess = $\frac{X}{-50} = 90 - 10 = 80\%$

Solve for X. $X = -40^\circ$

Exercise 5.6.4:



Exercise 5.7.1:

$$a) [\alpha] = \frac{\alpha}{(c)(l)}$$

$$c = \left(\frac{0.250g}{2mL}\right)\left(\frac{10mL}{1dL}\right) = 1.25 \frac{g}{dL}$$

$$\alpha = \frac{(0.775^\circ + 0.806^\circ + 0.682^\circ)}{3} = 0.754^\circ$$

$$[\alpha] = \frac{\alpha}{(c)(l)} = \frac{(0.754^\circ)}{(1.25 \frac{g}{dL})(0.5dm)} = +1.21^\circ$$

b)

$$-1.21^\circ$$

Exercise 5.7.2:

$$[\alpha] = \frac{\alpha}{(c)(l)}$$

$$[\alpha] = 32^\circ$$

$$c = \left(\frac{0.150g}{1mL}\right)\left(\frac{10mL}{1dL}\right) = 1.5 \frac{g}{dL}$$

$$c = (0.150g / 1 mL)(10 mL / 1 dL) = 1.5g/dL$$

$$[\alpha] = \frac{\alpha}{(c)(l)} = 32^\circ = \frac{\alpha}{(1.5 \frac{g}{dL})(0.5dm)}$$

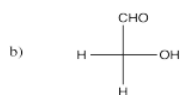
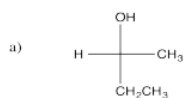
Solve for α . $\alpha = +24^\circ$

Exercise 5.8.1:

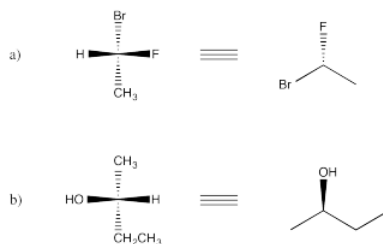
D-glyceraldehyde is R

L-glyceraldehyde is S

Exercise 5.8.2:



Exercise 5.8.3:



Exercise 5.9.1:

a) left b) right

Exercise 5.9.2:

a) right b) left

Exercise 5.9.1:

a) right b) right

Exercise 5.9.2:

a) left b) left

Exercise 5.9.5:

D-threose

2S, 3R

Exercise 5.9.6:

L-threose

2R, 3S

D- and L-threose are enantiomers of one another

Exercise 5.9.7:

L-erythrose

2S, 3S

L-erythrose and L-threose are diastereomers of one another.

Exercise 5.9.8:

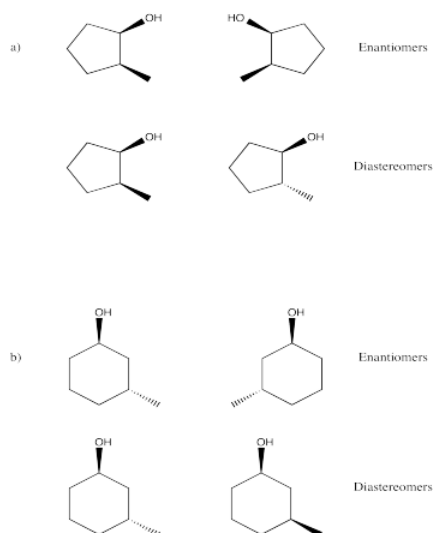
a) $(2)^3 = 8$ possible stereoisomers

RRR; SSS; RRS; SSR; RSS; SRR; SRS; RSR

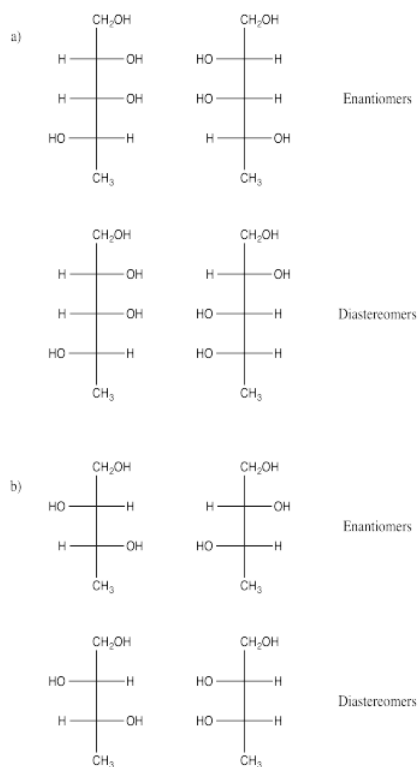
b) 4 pairs

c) 12 different possible pairs of diastereomers

Exercise 5.9.9:



Exercise 5.9.10:



Exercise 5.10.1:

a) D-threitol → 2R, 3S

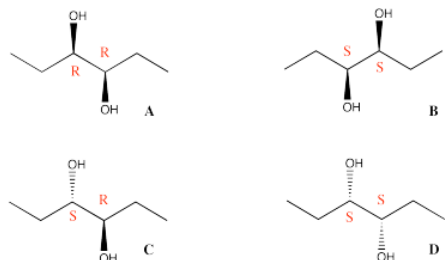
b) L-threitol → 2S, 3S

c) erythritol \rightarrow 2S, 3R or 2R, 3S (a meso compound)

Exercise 5.10.2:

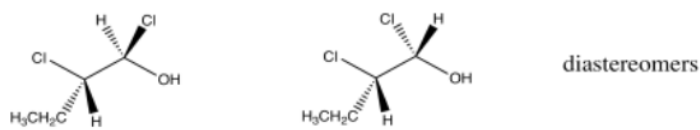
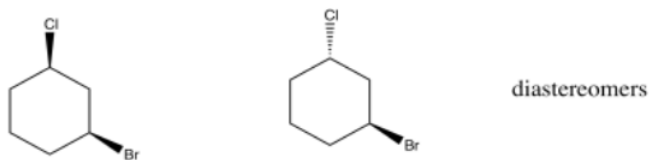
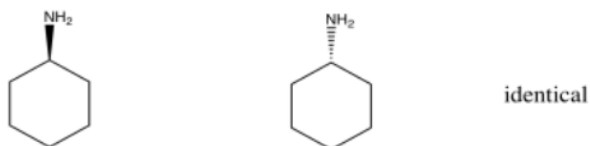
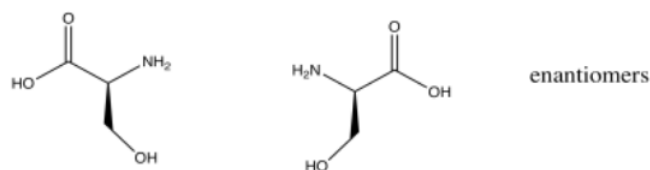
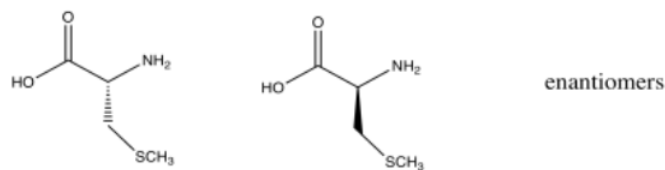
It does not matter which end you start counting from on these compounds since they are constituted the same.

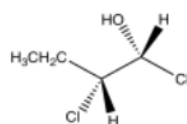
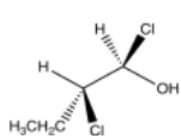
Exercise 5.10.3:



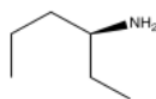
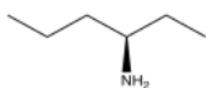
- B and D
- A and D or A and B
- A and C or B and C or D and C
- C

Exercise 5.10.4:

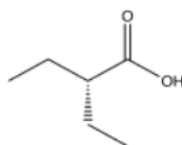
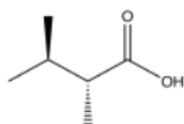




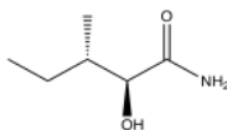
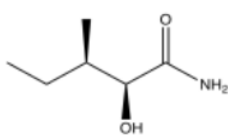
identical



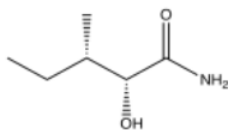
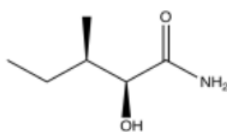
enantiomers



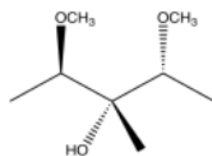
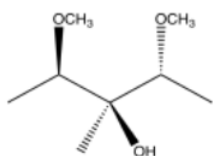
constitutional isome



diastereomers

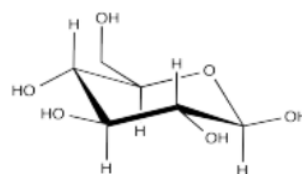
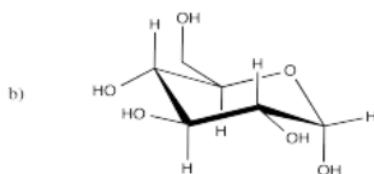
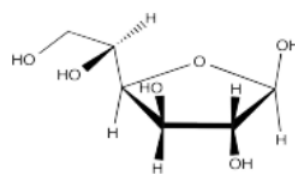
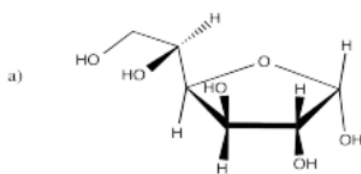


enantiomers

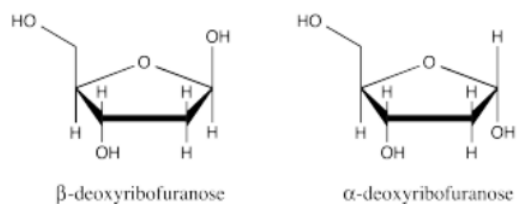


identical

Exercise 5.11.1:



Exercise 5.11.2:



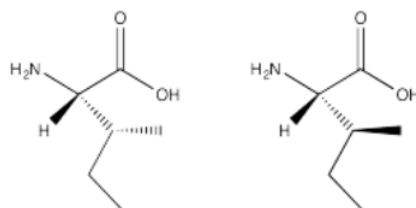
- a) Trans
b) Cis

Exercise 5.12.1:

Glycine

Exercise 5.12.2:

Isoleucine



Exercise 5.12.3:

Proline

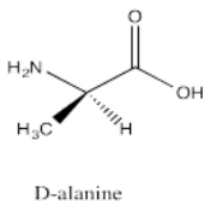
Exercise 5.12.4:

Glutamic acid and aspartic acid

Exercise 5.12.5:

Arginine, asparagine, glutamine, lysine; also tryptophan contains an aromatic heterocycle, although it is not basic.

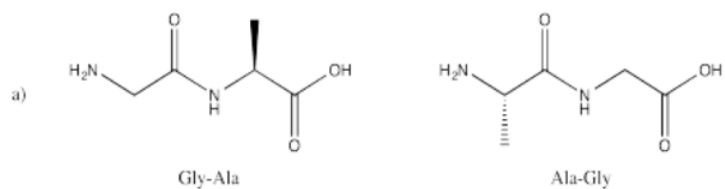
Exercise 5.12.6:



Exercise 5.12.7:

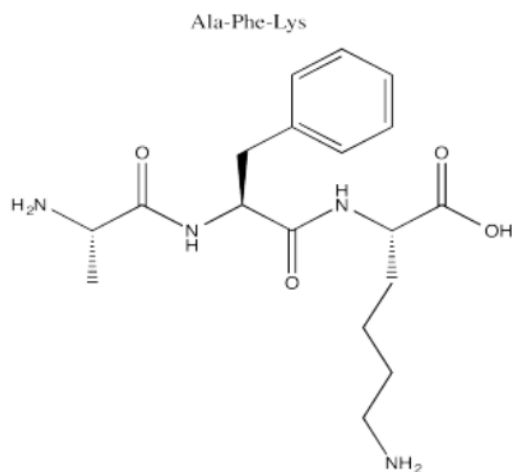
Cysteine

Exercise 5.13.1:

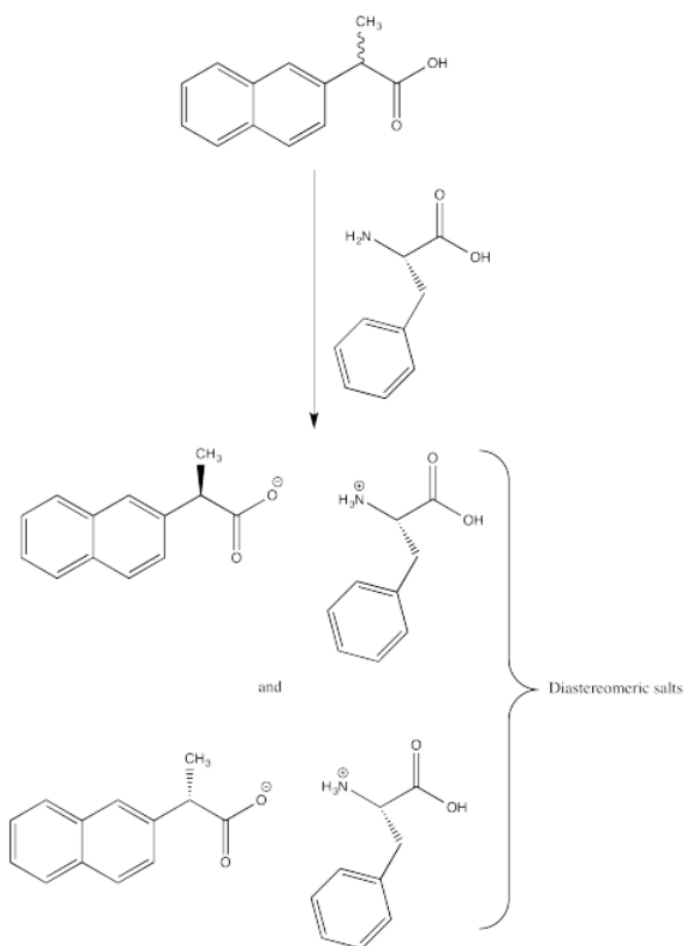


b) No. They are constitutional isomers of one another.

Exercise 5.13.2:



Exercise 5.14.1:



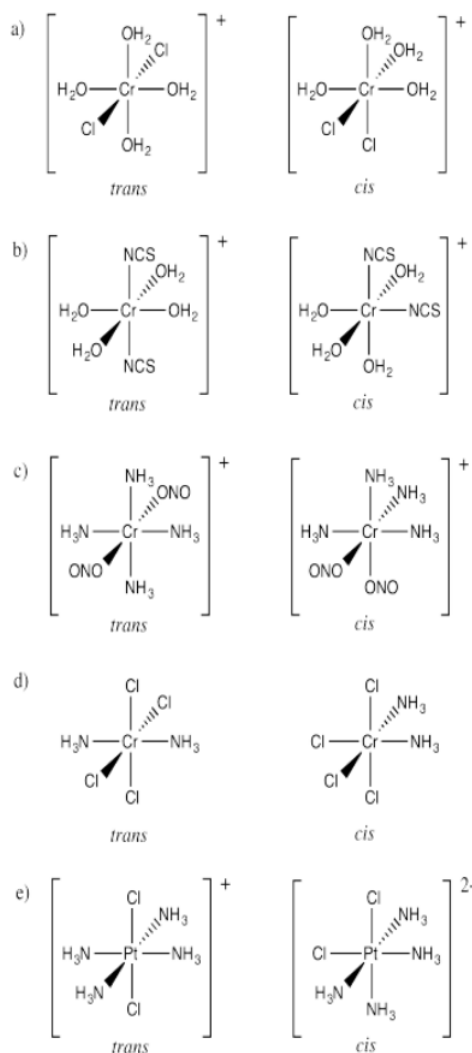
Exercise 5.15.1:

- A. Cis
- B. Trans
- C. Trans
- D. Neither (There is free rotation around the C-C single bond.)
- E. Neither (C-C triple bonds have substituents at 180 degrees to each other (linear).)
- F. cis

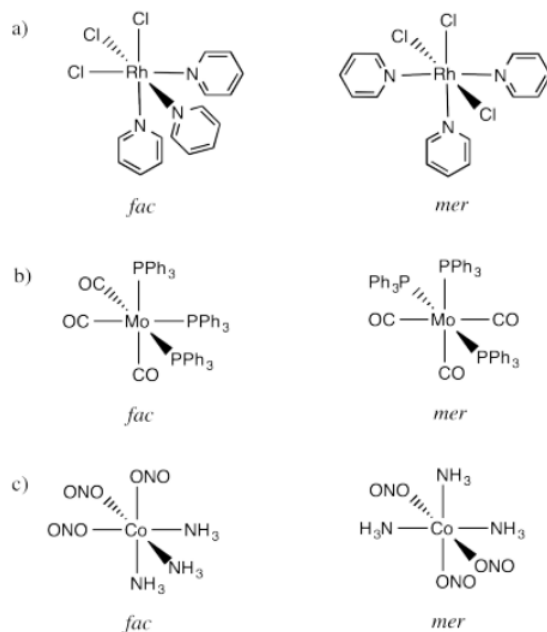
Exercise 5.16.1:

- A. Z
- B. E
- C. E
- D. Z
- E. E
- F. E
- G. Z
- H. E

Exercise 5.17.1:



Exercise 5.17.2:



Exercise 5.18.1:

- a) Enantiomers
- b) Enantiomers
- c) Identical
- d) Identical
- e) Enantiomers
- f) Identical

- g) Enantiomers

Exercise 5.18.2:

- a) Δ b) Λ c) Δ d) Λ e) Δ f) Δ g) Λ h) Λ

Exercise 5.20.1:

Pure = 125°

$$\text{Optical purity} = \frac{100}{125} = 0.80$$

$$\% \text{ Major} = 80 + \frac{20}{2} = 90\%$$

$$\% \text{ Minor} = 100 - 90 = 10\%$$

Exercise 5.20.2

Pure = 100°

$$\text{Optical purity} = \frac{95}{100} = 0.95$$

$$\% \text{ Major} = 95 + \frac{5}{2} = 97.5\%$$

$$\% \text{ Minor} = 100 - 97.5 = 2.5\%$$

Exercise 5.20.3

$$\text{Pure} = 18^\circ$$

$$\% \text{ Major} = 60\%$$

$$\% \text{ Minor} = 40\%$$

$$\text{Optical purity} = \frac{X}{18} = 20\%$$

Solve for X:

$$X = 3.6^\circ$$

Exercise 5.20.4:

$$\text{Pure} = 25^\circ$$

$$\% \text{ Major} = 80\%$$

$$\%Minor = 20\%$$

$$\text{Optical purity} = \frac{X}{25} = 80 - 20 = 60\%$$

Solve for X:

$$X = 15^\circ$$

Exercise 5.20.5

$$[\alpha] = \frac{\text{observed rotation}}{(l)(c)}$$

$$c = \frac{0.050g}{2.0mL} = 0.025 \frac{g}{mL}$$

$$\text{Average observed rotation} = \frac{(0.625 + 0.706 + 0.682)}{3} = 0.671^\circ$$

$$[\alpha] = \frac{0.671^\circ}{(0.025 \frac{g}{mL})(0.5dm)} = 53.68^\circ$$

Exercise 5.20.6:

$$[\alpha] = \frac{\text{observed rotation}}{(l)(c)}$$

$$c = \frac{0.540g}{2.0mL} = 0.27 \frac{g}{mL}$$

$$\text{Average observed rotation} = \frac{(1.225 + 1.106 + 1.182)}{3} = 1.171^\circ$$

$$[\alpha] = \frac{1.171^\circ}{(0.27 \frac{g}{mL})(1.0dm)} = 4.34^\circ$$

Exercise 5.20.7:

$$[\alpha] = \frac{\text{observed rotation}}{(l)(c)}$$

$$c = \frac{0.250g}{2.0mL} = 0.125 \frac{g}{mL}$$

$$42^\circ = \frac{\text{observed rotation}}{(0.125 \frac{g}{mL})(0.5dm)}$$

$$\text{observed rotation} = 2.625^\circ$$

Exercise 5.20.8

$$\text{a) } [\alpha] = \frac{\text{observed rotation}}{(l)(c)}$$

$$c = \frac{0.10g}{2.0mL} = 0.05 \frac{g}{mL}$$

$$c = \frac{0.10g}{2.0mL} = 0.05 \frac{g}{mL}$$

$$\text{Average observed rotation} = \frac{(0.995 + 0.904 + 0.936)}{3} = 0.945^\circ$$

$$[\alpha] = \frac{0.945^\circ}{(0.05 \frac{g}{mL})(1.0dm)} = 18.9^\circ$$

$$\text{b) \% optical purity} = \frac{(100)(18.9)}{25} = 75.6\%$$

c) enantiomeric excess = 75.6%

$$d) \frac{(100-75.6)}{2} = 12.2\%$$

12.2 % one enantiomer

87.8% other enantiomer

e) Enantiomers differ in how they interact with plane polarized light, but not in other physical analyses.

Exercise 5.20.9

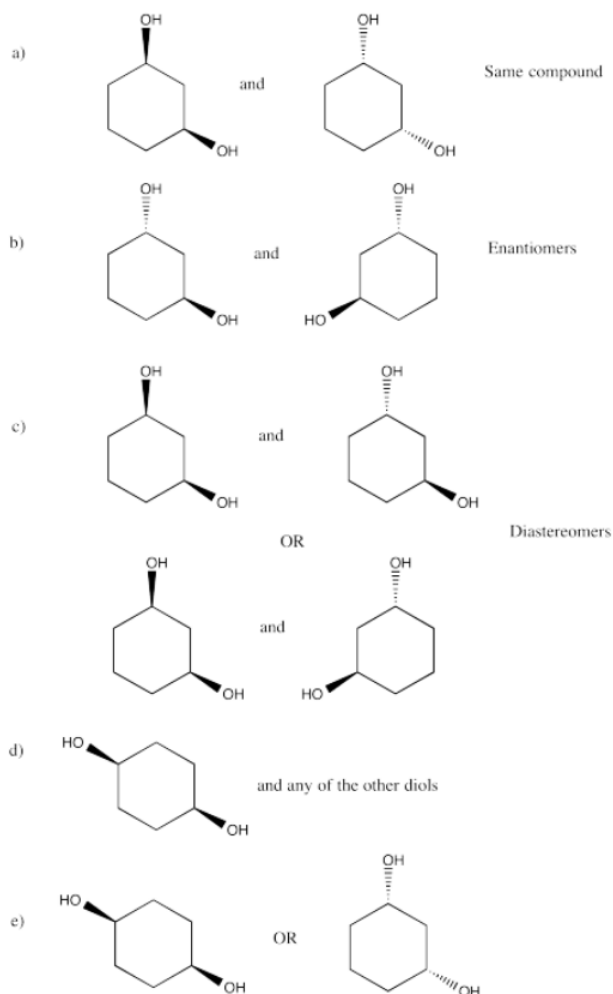
$$[\alpha] = \frac{\text{observed rotation}}{(l)(c)}$$

$$40^\circ = \frac{\text{observed rotation}}{(l)(c)}$$

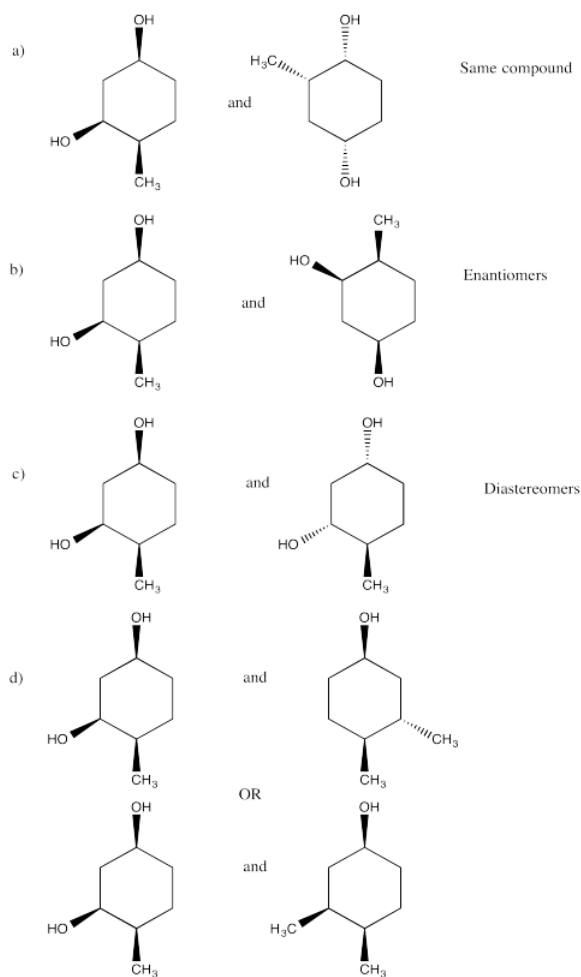
$$40^\circ = \frac{\text{observed rotation}}{(l)(1.1c)}$$

Observed rotation = 44°

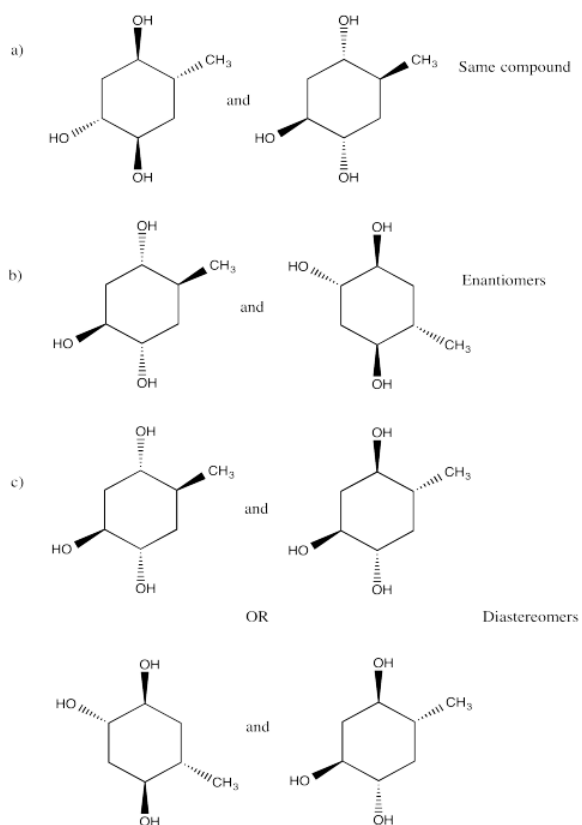
Exercise 5.20.10



Exercise 5.20.11:



Exercise 5.20.12:



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