

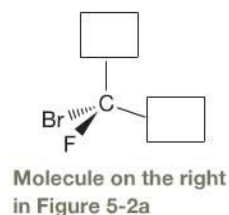
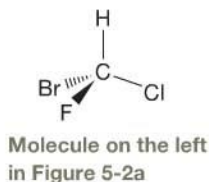
Chapter 5 Worksheets

Organic Chemistry

Isomerism 2: Chirality, Enantiomers, and Diastereomers

YOUR TURN 5.1

The molecule on the left in Figure 5-2a is redrawn on the left below. Only part of the other molecule is redrawn on the right. Using a molecular modeling kit, construct the molecule on the right in Figure 5-2a and orient it so that the C, Br, and F atoms occupy the positions shown on the right below. Complete the drawing of the molecule by adding the H and Cl atoms in the positions where they appear in your model. Comparing these two structures, are the molecules superimposable?

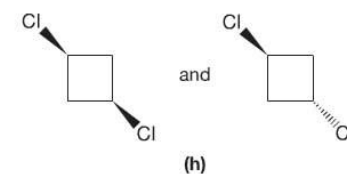
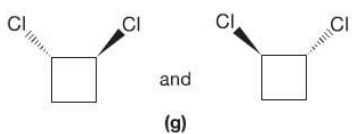
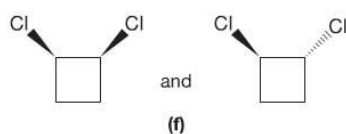
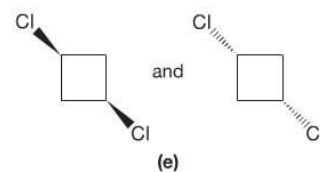
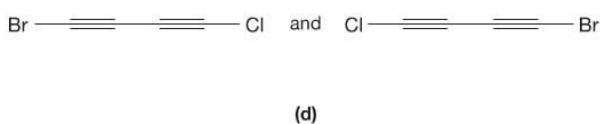
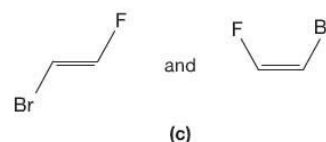
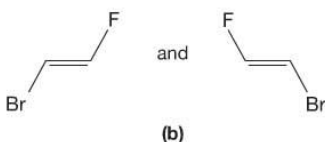
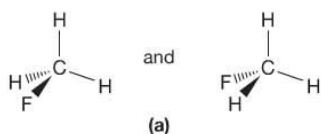


Answers to Your Turns are in the back of the book.

Use a molecular modeling kit to construct both the original molecule and the mirror image shown in Figure 5-3a. Rotate the mirror image structure as indicated in Figure 5-3b to verify that the two molecules are superimposable.

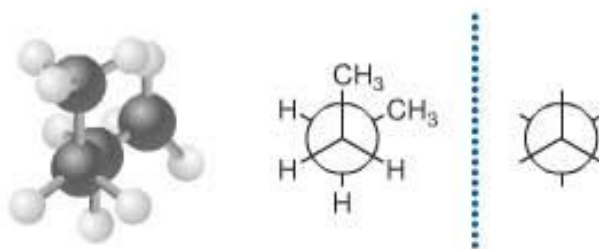
5.2 YOUR TURN

problem 5.1 For each pair of molecules given, determine whether they are *superimposable* or *nonsuperimposable*. (Hint: It may help to build a model of each molecule.)



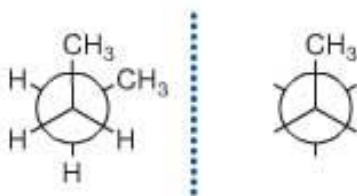
- (a) (b) (c) (d)
(e) (f) (g) (h)

SOLVED problem 5.2 Given the following Newman projection of butane in a gauche conformation, draw the Newman projection of its mirror image. The blue dotted line next to the molecule represents a mirror.

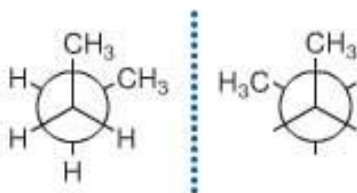


Think For each atom or group in the original molecule, where should its mirror image be with respect to the mirror?

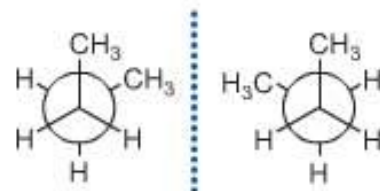
Solve Six substituents must be added to the Newman projection on the right to complete the mirror image—two CH₃ groups and four H atoms. Begin by drawing the mirror image of the topmost CH₃ group, which must be directly opposite the original CH₃ group and must also be the same distance from the mirror.



Next, add the second CH₃ group to the mirror image so that it is directly opposite the second CH₃ group in the original molecule and the two CH₃ groups are the same distance from the mirror.

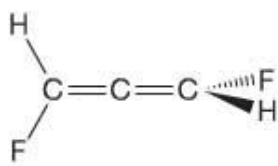


To complete the mirror image, add the remaining four H atoms.

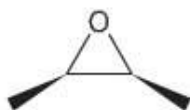


Notice that each H atom in the mirror image is directly opposite its original H atom and is the same distance from the mirror.

problem 5.3 Draw the mirror image of each of the following molecules.



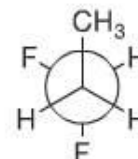
(a)



(b)



(c)



(d)

(a)

(b)

(c)

(d)

problem 5.4 For each molecule in Problem 5.3, determine whether the mirror image is superimposable on the original molecule.

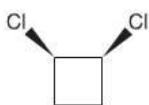
(a)

(b)

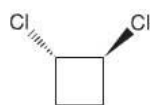
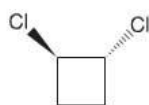
(c)

(d)

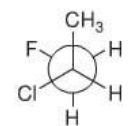
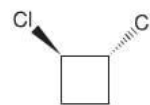
problem 5.5 Determine which pairs of molecules are mirror images.



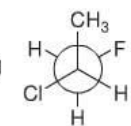
and
(a)



and
(b)



and
(c)

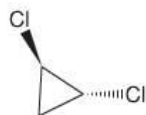


(a)

(b)

(c)

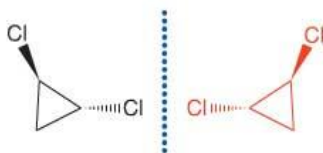
SOLVED problem 5.6 Determine whether *trans*-1,2-dichlorocyclopropane is chiral or achiral.



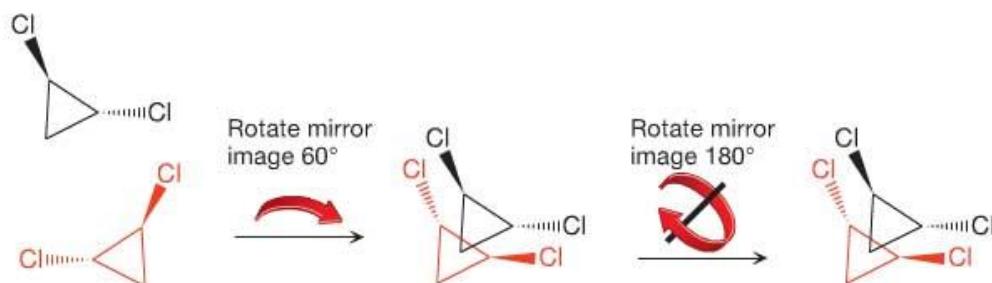
trans-1,2-Dichlorocyclopropane

Think Are *trans*-1,2-dichlorocyclopropane and its mirror image superimposable or non-superimposable? How can you tell?

Solve First draw the mirror image (shown below in red).



It then becomes a matter of lining up the two molecules to see if they are superimposable:



In neither of these two cases is the mirror image superimposable on the original molecule. We can see that the Cl atoms, in particular, are in different locations with respect to the plane of the page. There are other orientations you can try, but you will find that none of them allows the mirror image to be superimposable on the original molecule. Therefore, *trans*-1,2-dichlorocyclopropane is chiral.

Determining whether a molecule is superimposable onto its mirror image is a non-trivial task. If you cannot determine on paper whether two molecules are superimposable, construct a model of each molecule and then rotate each one in space until you are convinced one way or the other (see Your Turn 5.3).

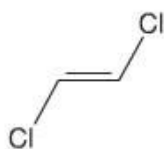
Build a molecular model of both the original molecule and the mirror image in Solved Problem 5.6. Verify that the two molecules are nonsuperimposable by performing the rotations indicated in Solved Problem 5.6. Are there other rotations you can imagine to determine whether the two molecules line up perfectly?

5.3 YOUR TURN

Is the mirror image of the molecule in Solved Problem 5.6 (i.e., the molecule in red) chiral or achiral?

5.4 YOUR TURN

problem 5.7 Is *trans*-1,2-dichloroethene chiral or achiral?

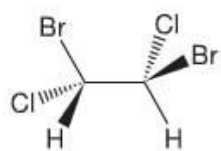


***trans*-1,2-Dichloroethene**

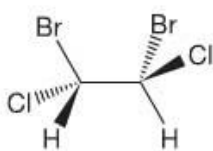
YOUR TURN 5.5

Build molecular models of the *gauche*-1,2-dibromoethane shown on the left in Figure 5-6a and its mirror image. By overlaying the two molecules, verify that they are nonsuperimposable. Next, rotate the bond as in Figure 5-6b and show that the resulting molecules are superimposable.

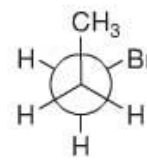
problem 5.8 Determine whether each of the following molecules is chiral or achiral.



(a)



(b)



(c)

(a)

(b)

(c)

YOUR TURN 5.6

Build molecular models of *cis*-1,2-difluorocyclohexane and its mirror image (as indicated in Fig. 5-7a). Rotate the two molecules in space to convince yourself that they are *not* superimposable. Then perform a chair flip on the mirror image and again rotate the molecules in space to convince yourself that the resulting structure *is* superimposable with the original molecule.

YOUR TURN 5.7

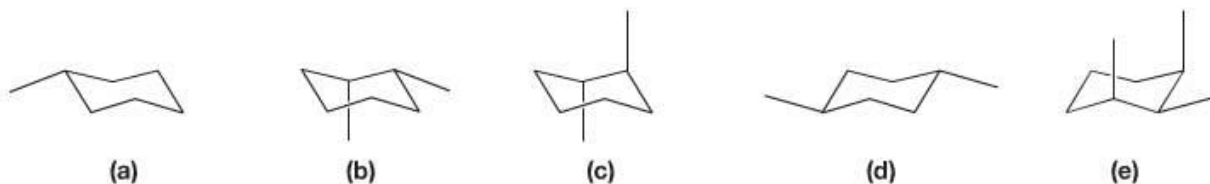
Use molecular models to prove to yourself that *trans*-1,2-difluorocyclohexane is chiral, as predicted using Haworth projections in Figure 5-8. The molecule and its mirror image are as follows:



***trans*-1,2-Difluorocyclohexane**

- Build a model of the original molecule and a model of its mirror image.
- Rotate the two molecules in space to show that they are *not* superimposable.
- Carry out a chair flip on the model of the mirror image and once again rotate the molecules in space to show that they are *not* superimposable.

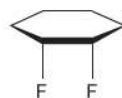
problem 5.9 Determine whether each of the following molecules is chiral or achiral.



(a) (b) (c) (d) (e)

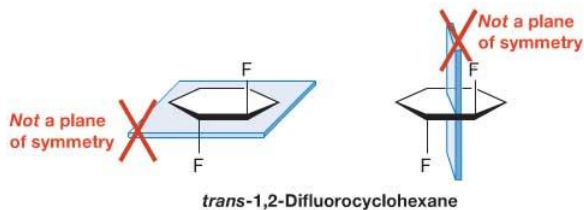
YOUR TURN 5.8

Recall from Figure 5-8 that *cis*-1,2-difluorocyclohexane is achiral. Find the plane of symmetry in the following Haworth projection and indicate where it is, using a dashed line.



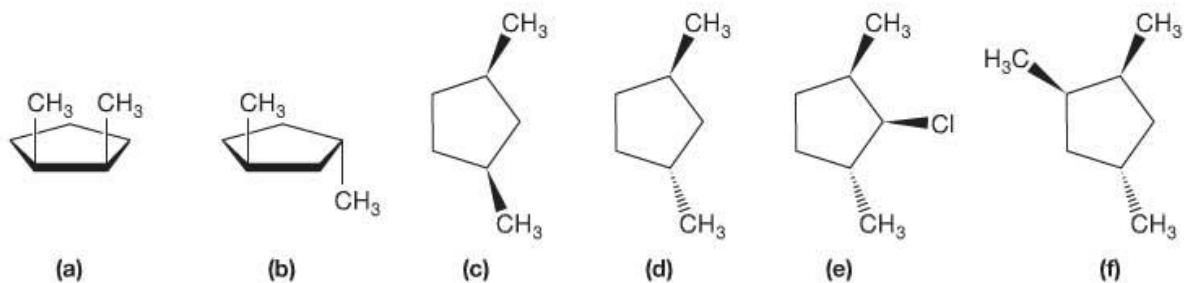
cis-1,2-Difluorocyclohexane

Recall, too, that *trans*-1,2-difluorocyclohexane is chiral, in which case it does *not* have a plane of symmetry. Convince yourself that each plane in the following diagrams is *not* a plane of symmetry. Write an "O" at the position where each F's mirror image would be. Is there an F already at each "O" you drew?

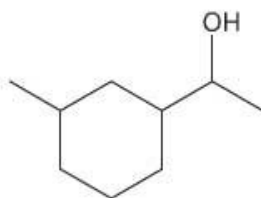


5.9 YOUR TURN

problem 5.10 Determine whether each of the following molecules possesses a plane of symmetry. If it does, indicate that plane of symmetry using a dashed line.

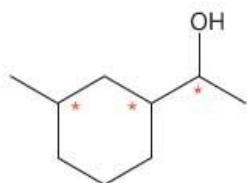


SOLVED problem 5.11 How many stereocenters are in the following molecule?

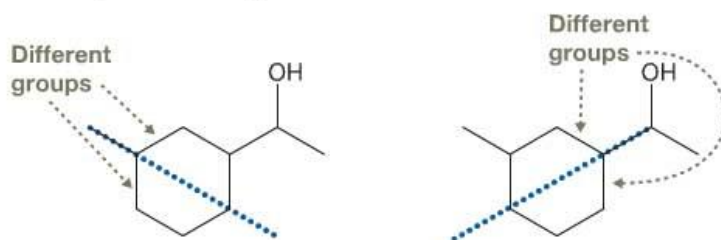


Think Which atoms are bonded to four *different* groups? How can you determine whether groups that are part of a ring are different from each other?

Solve The three C atoms indicated by an asterisk are bonded to four different groups and are, therefore, stereocenters.

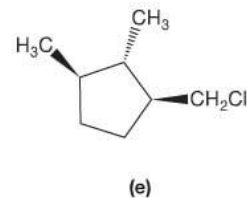
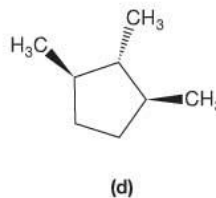
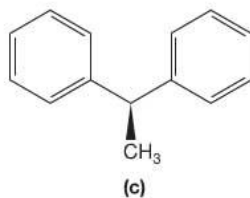
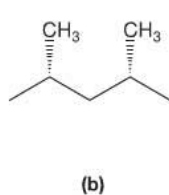
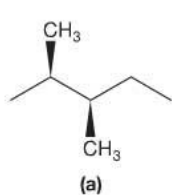


The right-most C is bonded to H, OH, CH₃, and the ring. Each of the other stereocenters is bonded to H, a group that is not part of the ring, and two groups that are part of the ring. For those C atoms, we can apply the plane of symmetry test to determine whether the groups that are part of the ring are different from each other:



In each case, the plane indicated by the dotted line is *not* a plane of symmetry, so the two groups that are part of the ring are, indeed, different from each other.

problem 5.12 Determine how many stereocenters exist in each of the following molecules.



(a)

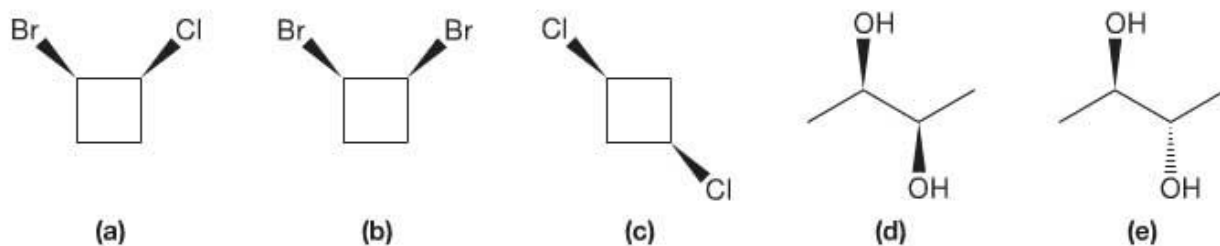
(b)

(c)

(d)

(e)

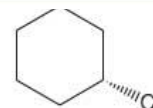
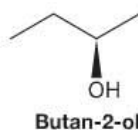
problem 5.13 Which of the following molecules are *meso*? (Hint: Consider rotations about single bonds.)



YOUR TURN 5.10

Place an asterisk at the stereocenter in butan-2-ol and 3-chloro-1,1-dimethylcyclohexane in Figure 5-14.

FIGURE 5-14 Tetrahedral stereocenters and chirality Each molecule has exactly one tetrahedral stereocenter and is therefore chiral.

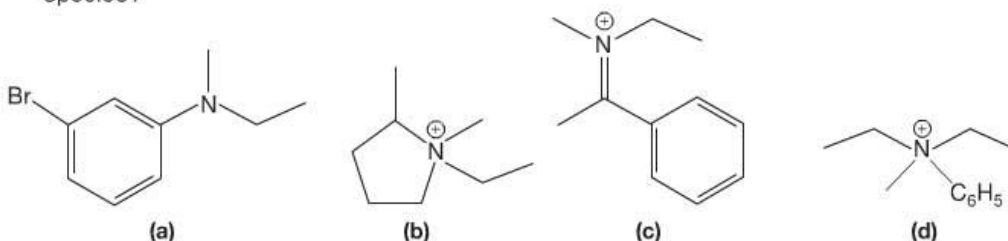


YOUR TURN 5.11

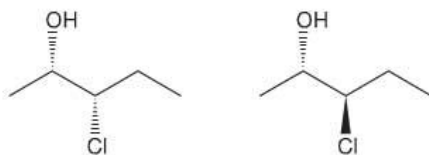
Prove to yourself that butan-2-ol is chiral by (1) drawing the mirror image, (2) building models of both the original molecule and the mirror image, and (3) lining the models up to determine whether they are superimposable or nonsuperimposable.

problem 5.14 Figure 5-15b shows the result of exchanging groups W and X on the black structure, giving the blue structure. Repeat this exercise, but instead, exchange groups W and Y on the black structure and determine whether or not the resulting structure is superimposable on the blue structure in Figure 5-15.

problem 5.15 How many tetrahedral stereocenters are in each of the following species?

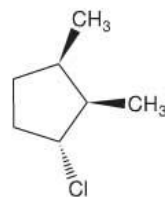


Confirm that the following compounds are different by building a model of each, and rotating one to determine if it is superimposable on the other.

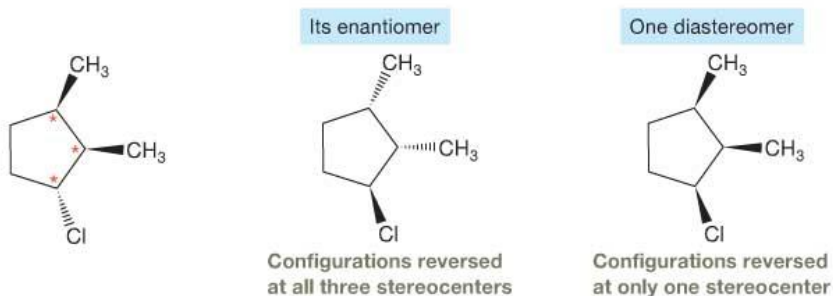


SOLVED problem 5.16 Given the following configurational isomer of 1-chloro-2,3-dimethylcyclopentane, draw its enantiomer and one of its diastereomers.

Think How many tetrahedral stereocenters exist? To obtain its enantiomer, how many of those configurations must be reversed? To obtain one of its diastereomers, how many of those configurations must be reversed?



Solve There are three tetrahedral stereocenters, indicated by asterisks below. To obtain its enantiomer, we must reverse *all* three of those configurations. To obtain a diastereomer, we must reverse at least one configuration, but not all of them. The enantiomer and one diastereomer are shown.

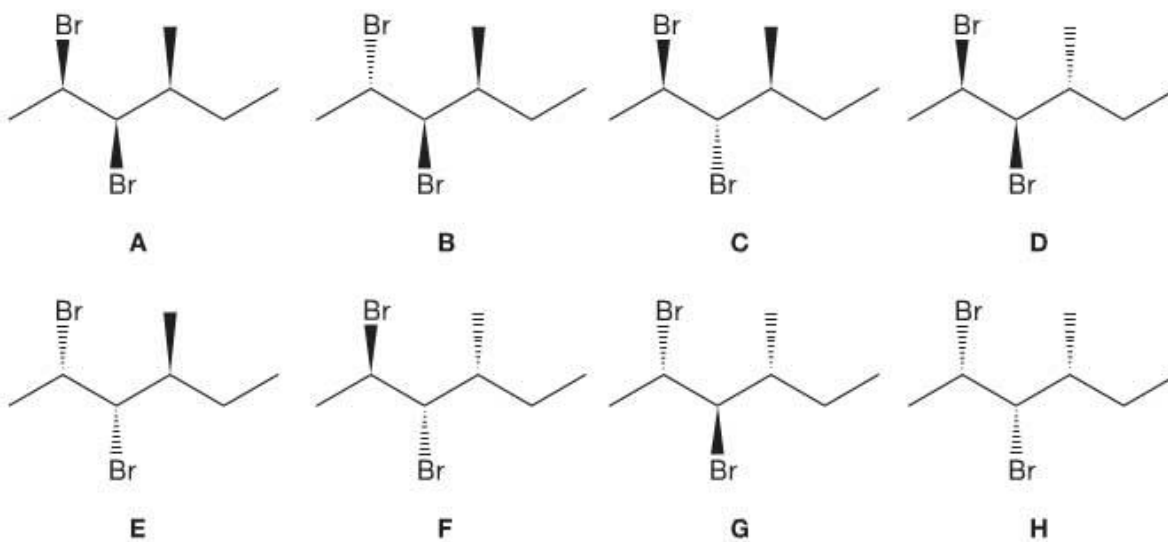


problem 5.17 Draw two more diastereomers of the molecule given in Solved Problem 5.16.

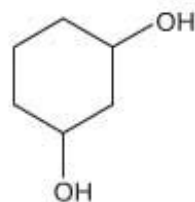
YOUR TURN 5.13

In molecule A in Figure 5-20, indicate each stereocenter with an asterisk.

problem 5.18 Which molecules in Figure 5-20 are enantiomers of molecule A? Which molecules are diastereomers? (*Hint*: How many stereocenters are there? In each structure, how many stereocenters are inverted relative to those in molecule A?)



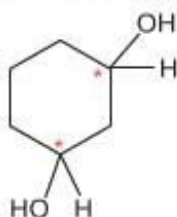
SOLVED problem 5.19 Draw all configurational isomers of cyclohexane-1,3-diol. Does the total number of configurational isomers equal 2^n ? Explain.



Cyclohexane-1,3-diol

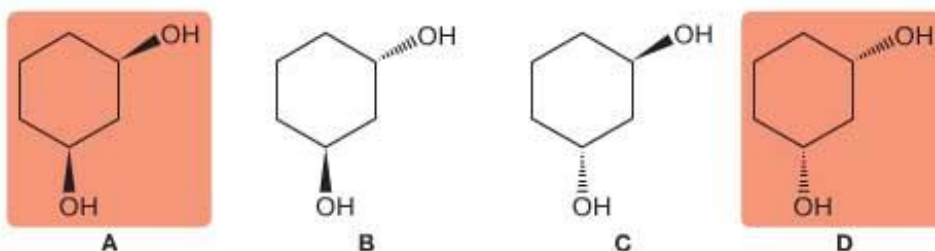
Think How many stereocenters are there? How can we change each stereocenter to convert from one configurational isomer to another?

Solve There are two stereocenters, indicated by the asterisks.

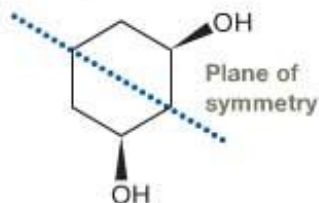


To obtain all possible configurational isomers, we can systematically reverse the configurations at the different stereocenters. Begin with the isomer in which both OH groups point toward us (Structure A):

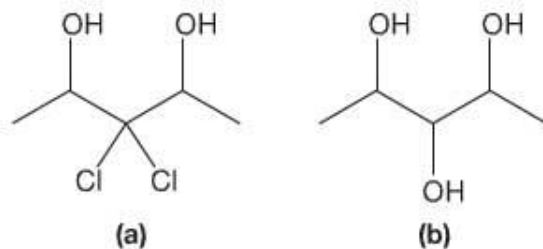
Structures A and D are the same molecule.



It may appear that there are four total isomers, which does equal 2^n with n (the number of stereocenters) being two. Structures A and D are exactly the same, however, so there are only three total isomers. There are fewer than 2^n isomers because one of the isomers is meso. Although it has two stereocenters, it has a plane of symmetry, too, and is therefore achiral—its mirror image is no different from itself.



problem 5.20 Draw all possible configurational isomers of each molecule. How many stereocenters are there? Does the number of configurational isomers equal 2^n ? Explain.



YOUR TURN 5.14

Build a model of the molecule represented by the Fischer projection in Figure 5-21 (shown again on the left below). Use different colored balls to represent the four different substituents. View the molecule from the vantage point indicated on the right below and fill in the atoms in the boxes provided.

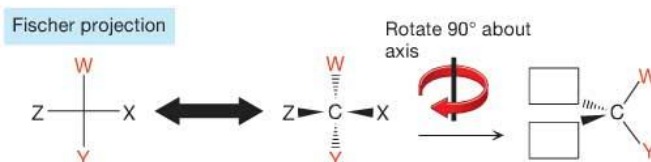
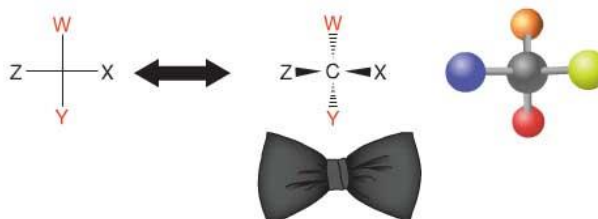


FIGURE 5-21 Fischer projections

(Left) A generic Fischer projection of a carbon stereocenter, where W, X, Y, and Z are different substituents. (Middle) The dash-wedge structure that corresponds to the Fischer projection. The substituents on the horizontal point toward you, reminiscent of a bow tie, whereas the substituents on the vertical point away from you. (Right) A ball-and-stick model of the molecule.

Fischer projection



YOUR TURN 5.15

Identify the C atoms at which the stereochemical configurations are different in D-allose and D-glucose.

problem 5.21 What is the stereochemical relationship between D-allose and L-glucose? Explain.

problem 5.22 Draw the enantiomer of D-allose as a Fischer projection.

YOUR TURN 5.16

Complete the Fischer projection in Figure 5-25b by placing the H and OH substituents appropriately on C5 and C6.

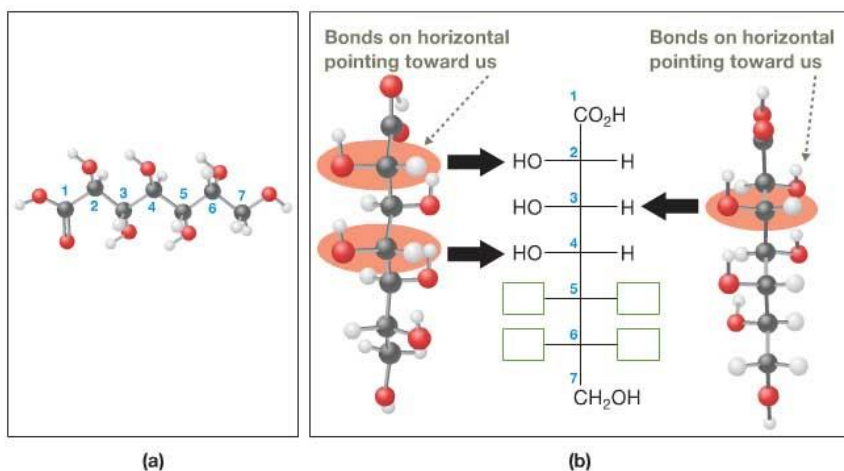
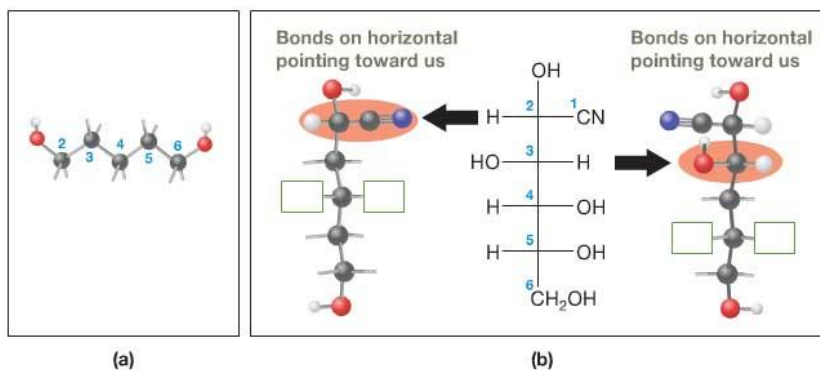


FIGURE 5-25 Converting a zigzag conformation to a Fischer projection (a) Ball-and-stick model of the molecule in question in its zigzag conformation. (b) On the left, the molecule is oriented such that the stereocenters at C2, C4, and C6 have the horizontal bonds pointing toward us. This allows us to complete the Fischer projection at C2, C4, and C6. On the right, the molecule is oriented such that the horizontal substituents at C3 and C5 are pointing toward us, allowing us to complete the Fischer projection at C3 and C5.

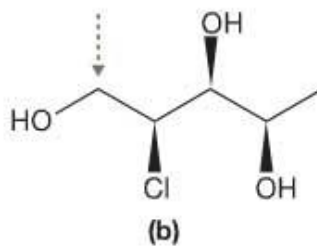
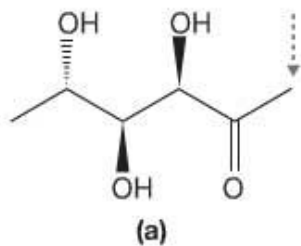
YOUR TURN 5.17

In Figure 5-26b, write the atoms in the boxes provided to match the stereochemical configurations indicated at C4 and C5 in the Fischer projection.

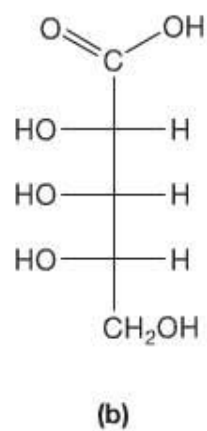
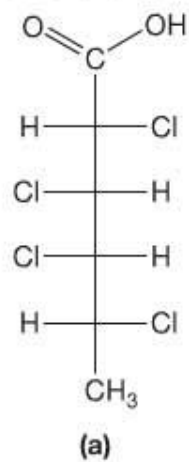
FIGURE 5-26 Converting a Fischer projection to a zigzag conformation (a) The backbone of a molecular model in the zigzag conformation showing just the carbon stereocenters and the terminal OH groups. (b) On the left, the backbone is oriented so that the substituents on the horizontal at C2 and C4 are pointed toward us. On the right, the backbone is oriented so that the substituents on C3 and C5 are pointed toward us.



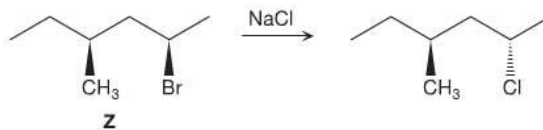
problem 5.23 Draw each of the following molecules as Fischer projections so that the carbon indicated is at the top.



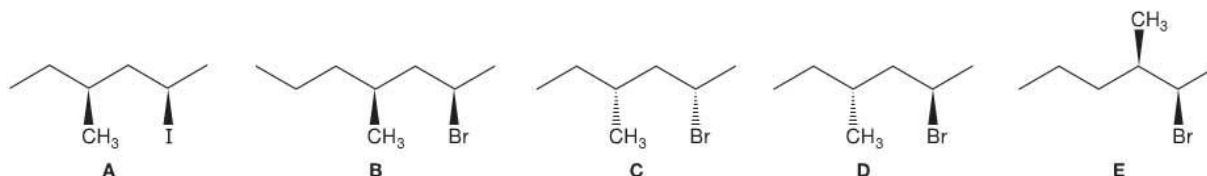
problem 5.24 Draw the following molecules in their zigzag conformations.



SOLVED problem 5.25 In Chapter 8, you will learn that 2-bromo-4-methylhexane (molecule **Z**) can undergo the following substitution reaction when treated with NaCl.



The following molecules, **A-E**, undergo a similar substitution reaction with NaCl.

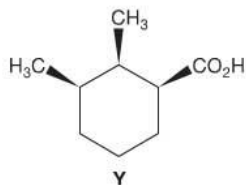


For which of these molecules will the *rate* of the reaction be precisely the same as that of the reaction involving **Z**? Explain.

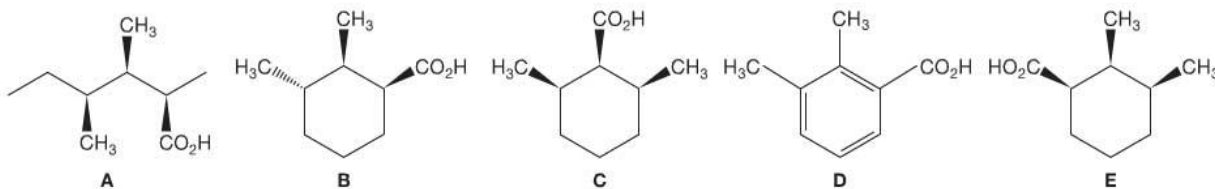
Think How is each molecule **A** through **E** related to **Z**? How do those relationships translate into relative behavior?

Solve **A** and **B** are unrelated to **Z** because they have different molecular formulas. **C**, **D**, and **E** are all isomers of **Z**. **C** is its enantiomer, **D** is a diastereomer of it, and **E** is one of its constitutional isomers. Only enantiomers have precisely the same behavior, so the correct answer is **C**.

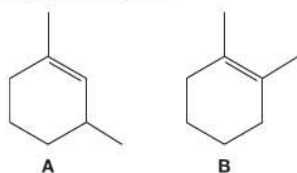
problem 5.26 As discussed in Chapter 6, the carboxylic acid functional group (CO_2H) in the following molecule, **Y**, is moderately acidic.



For which of the following molecules, **A-E**, must the carboxylic acid functional group have an acidity that is *different* from that of **Y**? Explain.



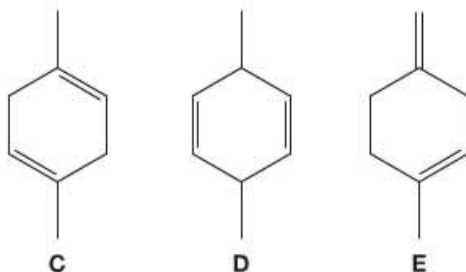
SOLVED problem 5.27 Which of the following molecules do you think will have the smaller heat of combustion? Explain.



Think Which of the C=C double bonds is more highly alkyl substituted? More stable? What is the relationship between relative stability and relative heats of combustion?

Solve The two molecules are isomers of each other, each with the formula C_8H_{14} . As a result, they have precisely the same combustion products, in which case any difference in the heat of combustion must come from differences in the stability of the reactants. The C=C double bond in molecule **A** is trisubstituted (one CH_3 group and two alkyl groups that are part of the ring), whereas the C=C double bond in molecule **B** is tetrasubstituted (two CH_3 groups and two alkyl groups that are part of the ring). Thus, **B** is more stable and will have a *smaller* heat of combustion (i.e., less heat is released).

problem 5.28 Which of the following do you think will have the greatest heat of combustion? The smallest? Explain.



SOLVED problem 5.29 Suppose that 20.00 g of a chiral compound is dissolved in 0.1000 L of solution and is placed in a tube that is 20.00 cm long. What is its specific rotation of light if the observed rotation is determined experimentally to be $+45.00^\circ$?

Think Which variable in Equation 5-2 are we solving for? The equation calls for concentration—how do we calculate it? Are the units correct for the length of the tube, l ?

Solve We are asked for $[\alpha]_D^{20}$ and are given the value for α , which is $+45.00^\circ$. Equation 5-2 must therefore be rearranged as follows:

$$[\alpha]_D^{20} = \frac{\alpha}{(l)(c)}$$

To solve this equation, we must have values for c and l in their correct units. We can calculate concentration in units of g/mL by dividing the 20.00 g of sample by the 100.0 mL of solution, to yield 0.2000 g/mL. The length of the tube, l , is given to us as 20.00 cm, but must be converted to dm. Because 1 dm = 10 cm, the length of our tube is 2.000 dm. Therefore, the specific rotation is:

$$[\alpha]_D^{20} = \frac{(+45.00^\circ)}{(2.000 \text{ dm})(0.2000 \text{ g/mL})} = 112.5^\circ$$

problem 5.30 Penicillin V has a specific rotation of $+223^\circ$. What would the measured angle of rotation be of a 0.00300 g/mL solution, if it were measured in a tube 10.0 cm long?

SOLVED problem 5.31 Suppose a solution of a pure chiral molecule has a specific rotation of -32° . What is the specific rotation of a solution that is 90% of the (+) enantiomer and 10% of the (–) enantiomer?

Think Which enantiomer is in excess and what is its ee? How does that govern the mixture's ability to rotate plane-polarized light?

Solve Because the solution is excess in the (+) enantiomer, the specific rotation of the mixture should be in the (+) direction. Realize that the 10% that is the (–) enantiomer can be combined with 10% of the solution that is the (+) enantiomer, such that 20% of the solution is effectively racemic and the other 80% is excess in the (+) enantiomer. Thus, 20% of the solution does not contribute toward the rotation of plane-polarized light and 80% contributes toward a specific rotation of $+32^\circ$ [the value for the pure (+) enantiomer]. This can be summarized by rearranging Equation 5-3 and substituting the appropriate numbers.

$$\begin{aligned}(\text{specific rotation of mixture}) &= (\% \text{ ee})(\text{specific rotation of pure enantiomer})/(100) \\ &= (80)(+32^\circ)/(100) \\ &= 25.6^\circ\end{aligned}$$

problem 5.32 Suppose that a pure compound has a specific rotation of $+49^\circ$. In the laboratory, a solution in which the compound is mixed with its enantiomer is found to have a specific rotation of $+12^\circ$. What is the ee of the mixture? What percentage of the mixture is the (+) enantiomer and what percentage is the (–) enantiomer?

problem 5.33 Name the sugar that fits each of the following descriptions. (a) The C2 epimer of D-glucose. (b) The C3 epimer of D-glucose. (c) The C4 epimer of D-talose. (d) The C3 epimer of D-xylose.
