

**TABLE 7.1** Heats of Formation per —CH<sub>2</sub>— for Some Cycloalkanes

(*n* = number of carbon atoms)

<i>n</i>	Compound	$\Delta H_f^\circ/n$		<i>n</i>	Compound	$\Delta H_f^\circ/n$	
		$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$			$\text{kJ mol}^{-1}$	$\text{kcal mol}^{-1}$
3	cyclopropane	+17.8	+4.25	9	cyclononane	-14.8	-3.5
4	cyclobutane	+7.1	+1.7	10	cyclodecane	-15.4	-3.7
5	cyclopentane	-15.7	-3.7	11	cycloundecane	-16.3	-3.9
6	cyclohexane	-20.55	-4.95	12	cyclododecane	-19.2	-4.6
7	cycloheptane	-16.9	-4.0	13	cyclotridecane	-18.95	-4.5
8	cyclooctane	-15.55	-3.7	14	cyclotetradecane	-17.1	-4.1

exactly the same contribution to its heat of formation ( $-20.7 \text{ kJ mol}^{-1}$  or  $-4.95 \text{ kcal mol}^{-1}$ ). This means that *cyclohexane has the same stability as a typical unbranched alkane*.

Cyclohexane is the most widely occurring ring in compounds of natural origin. Its prevalence, undoubtedly a consequence of its stability, makes it the most important of the cycloalkanes. The stability of cyclohexane is due to its conformation, which is the subject of Section 7.2. The stabilities and conformations of other cycloalkanes are discussed in Sec. 7.5.

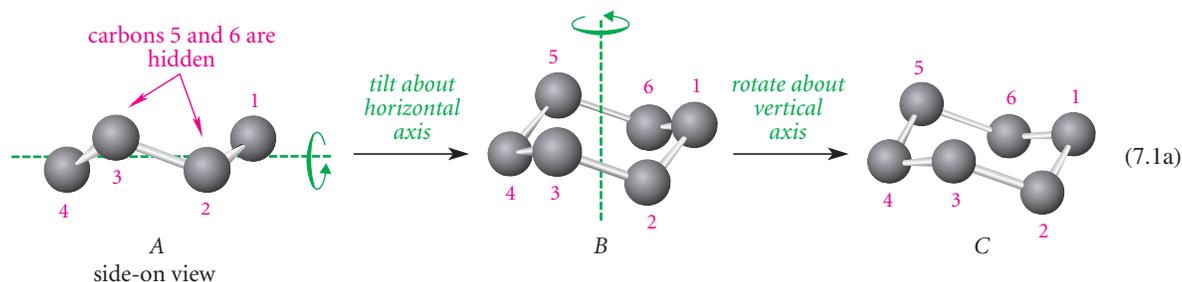
## 7.2 CONFORMATIONS OF CYCLOHEXANE

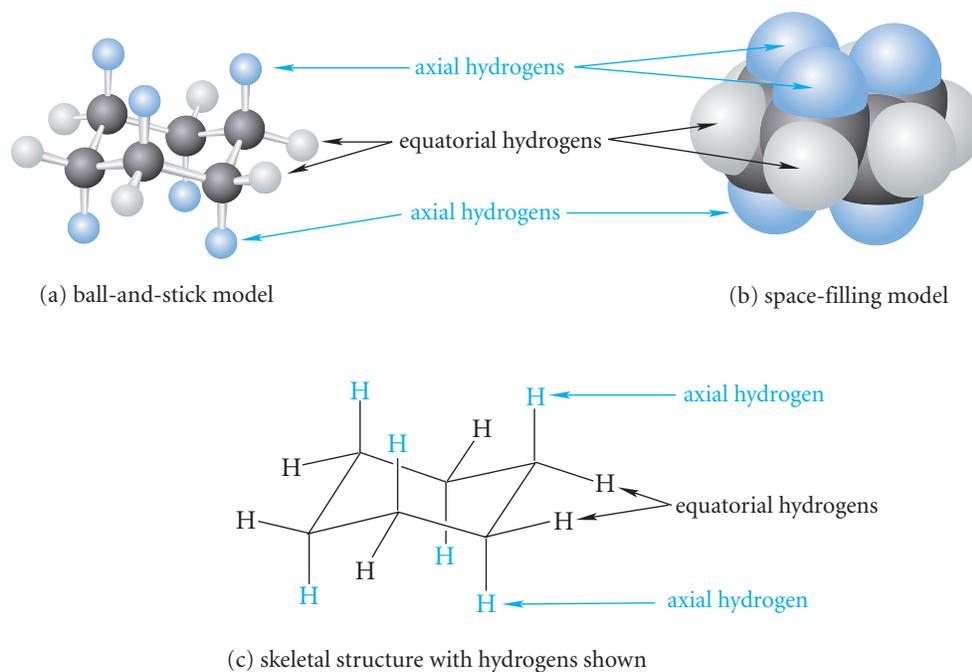
### A. The Chair Conformation

The stability data in Table 7.1 require that the bond angles in cyclohexane must be essentially the same as the bond angles in an alkane—very close to the ideal  $109.5^\circ$  tetrahedral angle. If the bond angles were significantly distorted from tetrahedral, we would expect to see a greater heat of formation. Likewise, cyclohexane must have a staggered conformation about each carbon–carbon bond, because eclipsing interactions (*torsional strain*; Sec. 2.3) would also increase the heat of formation. These two geometrical constraints can only be met if the carbon skeleton of cyclohexane assumes a nonplanar, “puckered” conformation.

The most stable conformation of cyclohexane is shown in Fig. 7.1 (p. 270). In this conformation of cyclohexane, the carbons do *not* lie in a single plane; rather, the carbon skeleton is puckered. This conformation of cyclohexane is called the **chair conformation** because of its resemblance to a lawn chair. If you have not already done so, you should construct a model of cyclohexane *now* and use it to follow the subsequent discussion. Notice the following four points about the cyclohexane molecule and how to draw it.

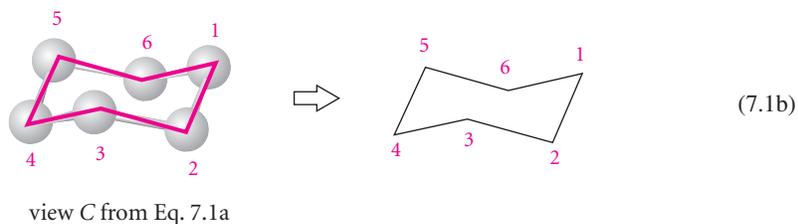
1. To draw the cyclohexane ring, we use a “tilt-and-turn” technique similar to the one used for drawing line-and-wedge structures (Eq. 6.10, p. 258).



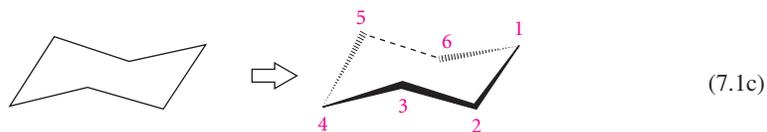


**Figure 7.1** Chair conformation of cyclohexane shown as (a) a ball-and-stick model, (b) a space-filling model, and (c) a skeletal structure. In parts (a) and (b), the axial hydrogens are blue, and in part (c), they are shown in blue type.

First, we view the model side-on (view *A* in Eq. 7.1a). In this view, carbons 5 and 6 are obscured behind carbons 2 and 3. Then, we tilt the model about a horizontal axis to give view *B*. Finally, we turn the model slightly about a vertical axis to give the view used to draw the skeletal structure, as shown in Eq. 7.1b.

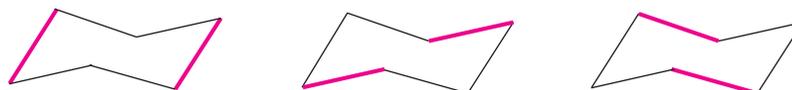


If we imagine carbons 1 and 4 to be in the plane of the page, then carbons 2 and 3 are in front of the page, and carbons 5 and 6 are behind the page.



Remembering that the lower part of the ring is in front of the page is essential to avoiding an optical illusion.

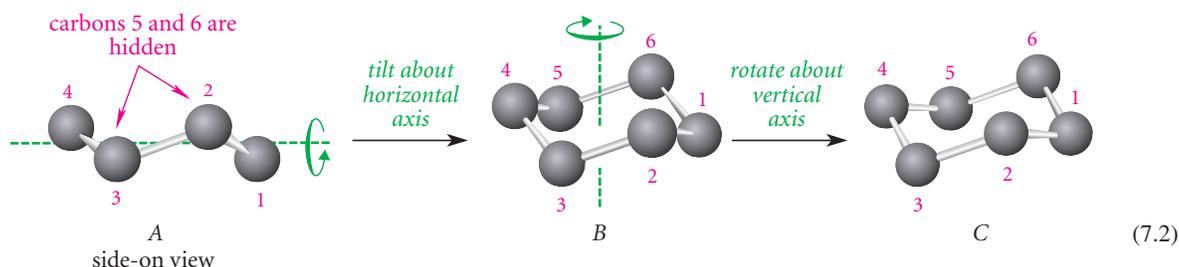
2. Bonds on opposite sides of the ring are parallel:



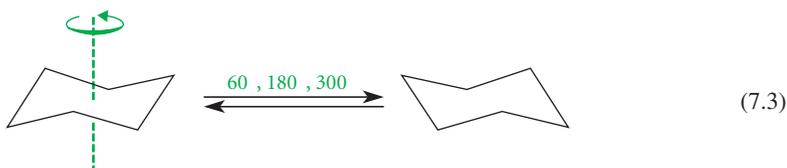
3. Two perspectives are commonly used for cyclohexane rings. In one, the leftmost carbon is below the rightmost carbon; and in the other, the leftmost carbon is above the rightmost carbon:



These two perspectives are mirror images. (However, they are not enantiomeric.) As shown in Eqs. 7.1a–c, the perspective on the left is based on a view of the model from above and to the left of the model. The perspective on the right is based on a view of the model from above and to the right. The “tilt-and-turn” procedure for producing this structure is the same except that the rotation is in the opposite direction.



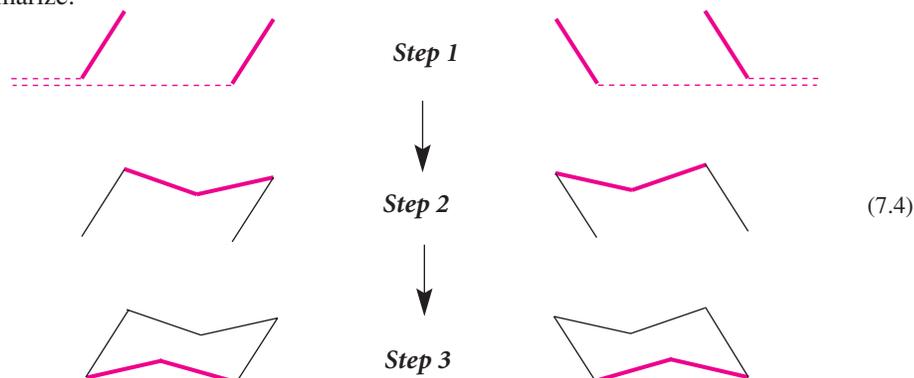
4. A rotation of either perspective by an odd multiple of  $60^\circ$  (that is,  $60^\circ$ ,  $180^\circ$ , and so on), followed by the slight shift in viewing direction, gives the other perspective. *Be sure to verify this with models!*



It is important for you to be able to draw a cyclohexane chair conformation. Once you’ve examined the preceding points, practice drawing some cyclohexane rings in the two perspectives. Use the following three steps:

- Step 1** Begin by drawing two parallel bonds slanted to the left for one perspective, and slanted to the right for the other. Notice that one slanted line is somewhat lower than the other in each case.
- Step 2** Connect the tops of the slanted bonds with two more bonds in a “V” arrangement.
- Step 3** Connect the bottoms of the slanted bonds with the remaining two bonds in an inverted “V” arrangement.

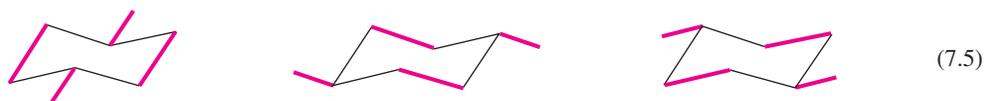
To summarize:



Now let's consider the hydrogens of cyclohexane, which are of two types. If you place your model of cyclohexane on a tabletop (you did build it, didn't you?), you'll find that six C—H bonds are perpendicular to the plane of the table. (Your model should be resting on three such hydrogens.) These hydrogens, shown in blue in Fig. 7.1a–b, are called **axial** hydrogens. The remaining C—H bonds point outward along the periphery of the ring. These hydrogens, shown in white in Fig. 7.1a, are called **equatorial** hydrogens. As we might expect, other groups can be substituted for the hydrogens, and these groups also can exist in either axial or equatorial arrangements.

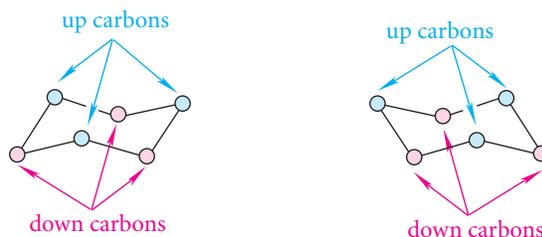
In the chair conformation, all bonds are staggered. You should be able to see this from your model by looking down any C—C bond. As you learned when you studied the conformations of ethane and butane (Sec. 2.3), staggered bonds are energetically preferred over eclipsed bonds. The stability of cyclohexane (Sec. 7.1) is a consequence of the fact that all of its bonds can be staggered without compromising the tetrahedral carbon geometry.

Once you have mastered drawing the cyclohexane ring, it's time to add the C—H bonds to the ring. Drawing the axial bonds is fairly easy: they are simply vertical lines. However, drawing the equatorial bonds can be a little tricky. Notice that pairs of equatorial bonds are parallel to pairs of ring bonds (red):



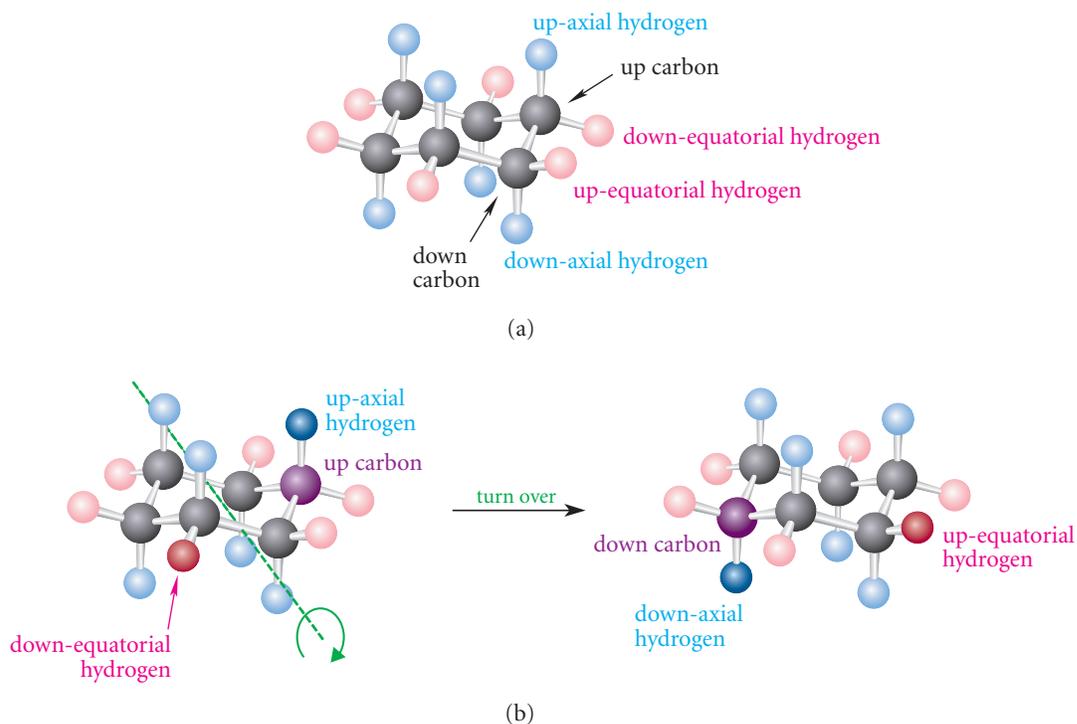
(Notice also how all the equatorial bonds in Fig. 7.1 adhere to this convention.)

You should notice a few other things about the cyclohexane ring and its bonds. First, if we make a model of the cyclohexane carbon skeleton without hydrogens and place it on a tabletop, we find that every other carbon is resting on the tabletop. We'll refer to these carbons as *down carbons*. The other three carbons lie in a plane above the tabletop. We'll refer to these carbons as *up carbons*.



Now add the hydrogens to your model, and notice that the three axial hydrogens on up carbons point up, and the three axial hydrogens on down carbons point down. In contrast, the three equatorial hydrogens on up carbons point down, and the three equatorial hydrogens on down carbons point up (Fig. 7.2a). *The up and down hydrogens of a given type are completely equivalent.* That is, the up equatorial hydrogens are equivalent to the down equatorial hydrogens, and the up axial hydrogens are equivalent to the down axial hydrogens. You can see this equivalence by turning the ring over, as shown in Fig. 7.2b. This causes the up carbons to exchange places with the down carbons, the up-axial hydrogens to exchange places with the down-axial hydrogens, and the up-equatorial hydrogens to exchange places with the down-equatorial hydrogens. Everything looks the same as it did before turning the molecule over. (Be sure to convince yourself with models that these statements are true.)

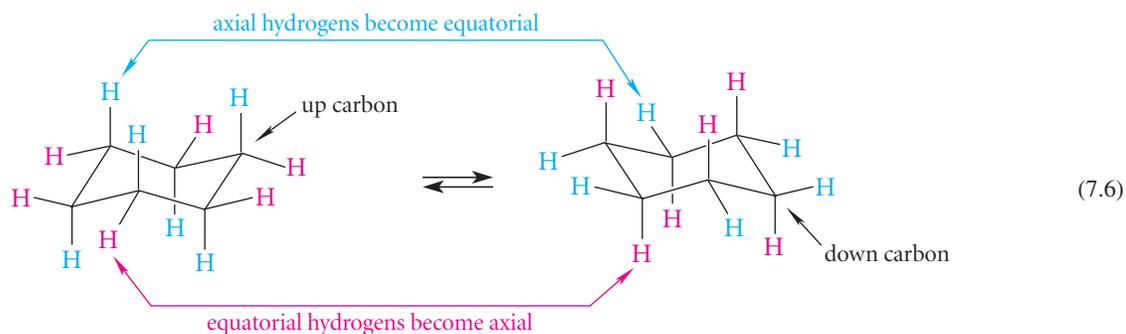
A second useful observation is that if an axial hydrogen is up on one carbon, the two neighboring axial hydrogens are down, and vice versa. The same is true of the equatorial hydrogens.



**Figure 7.2** (a) Up and down equatorial and axial hydrogens. The up-axial hydrogens are on up carbons and the down-axial hydrogens are on down carbons. The opposite is true for equatorial hydrogens. (b) The up- and down-axial hydrogens are equivalent, and the up- and down-equatorial hydrogens are equivalent. This equivalence can be demonstrated by turning the ring “upside down” (green arrow). In doing so, the up carbons trade places with the down carbons, the up-axial hydrogens trade places with the down-axial hydrogens, and the up-equatorial hydrogens trade places with the down-equatorial hydrogens. (The darker colors show explicitly the fate of two hydrogens and the violet color shows the fate of one carbon.)

## B. Interconversion of Chair Conformations

Cycloalkanes, like noncyclic alkanes, undergo internal rotations (Sec. 2.3), but, because the carbon atoms are constrained within a ring, several internal rotations must occur at the same time. When a cyclohexane molecule undergoes internal rotations, *a change in the ring conformation occurs*, as shown in Fig. 7.3 (p. 274). Use a model to follow these changes, shown by the green arrows in Fig. 7.3. Hold carbons 1, 2, and 6—the rightmost carbon and its two neighbors—so that they cannot move, and raise carbon-4 up as far as it will go. The result is a different conformation, called a **boat conformation**. Formation of the boat conformation involves *simultaneous internal rotations* about all carbon–carbon bonds except those to carbon-1. We’ll return to an examination of the boat conformation in Sec. 7.2C. Now hold carbons 3, 4, and 5 of the boat—the leftmost carbon and its two neighbors—so that they cannot move, and lower carbon-1 as far as it will go; the model returns to a chair conformation. In this case, simultaneous internal rotations have occurred about all carbon–carbon bonds except those to carbon-4. Thus, upward movement of the leftmost carbon and downward movement of the rightmost carbon changes one chair conformation into another, completely equivalent, chair conformation. But notice what has happened to the hydrogens: In this process, *the equatorial hydrogens have become axial, and the axial hydrogens have become equatorial*. In addition, up carbons have become down carbons, and vice versa.



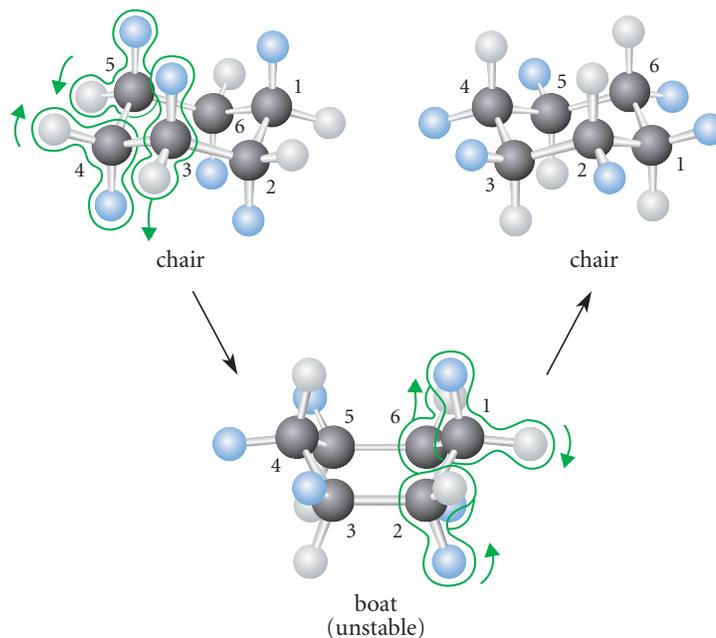
(Confirm these points with your model by using groups of different colors for the axial and equatorial hydrogens.)

The interconversion of two chair forms of cyclohexane is called the **chair interconversion**. The energy barrier for the chair interconversion is about  $45 \text{ kJ mol}^{-1}$  ( $11 \text{ kcal mol}^{-1}$ ). Although this barrier is larger than that for internal rotation in butane, it is small enough that the chair interconversion is very rapid (it occurs about  $10^5$  times per second) at room temperature.

Let's review: Although the axial hydrogens are stereochemically different from the equatorial hydrogens in any one chair conformation, the chair interconversion causes these hydrogens to change positions rapidly. Hence, *averaged over time*, the axial and equatorial hydrogens are equivalent and indistinguishable.

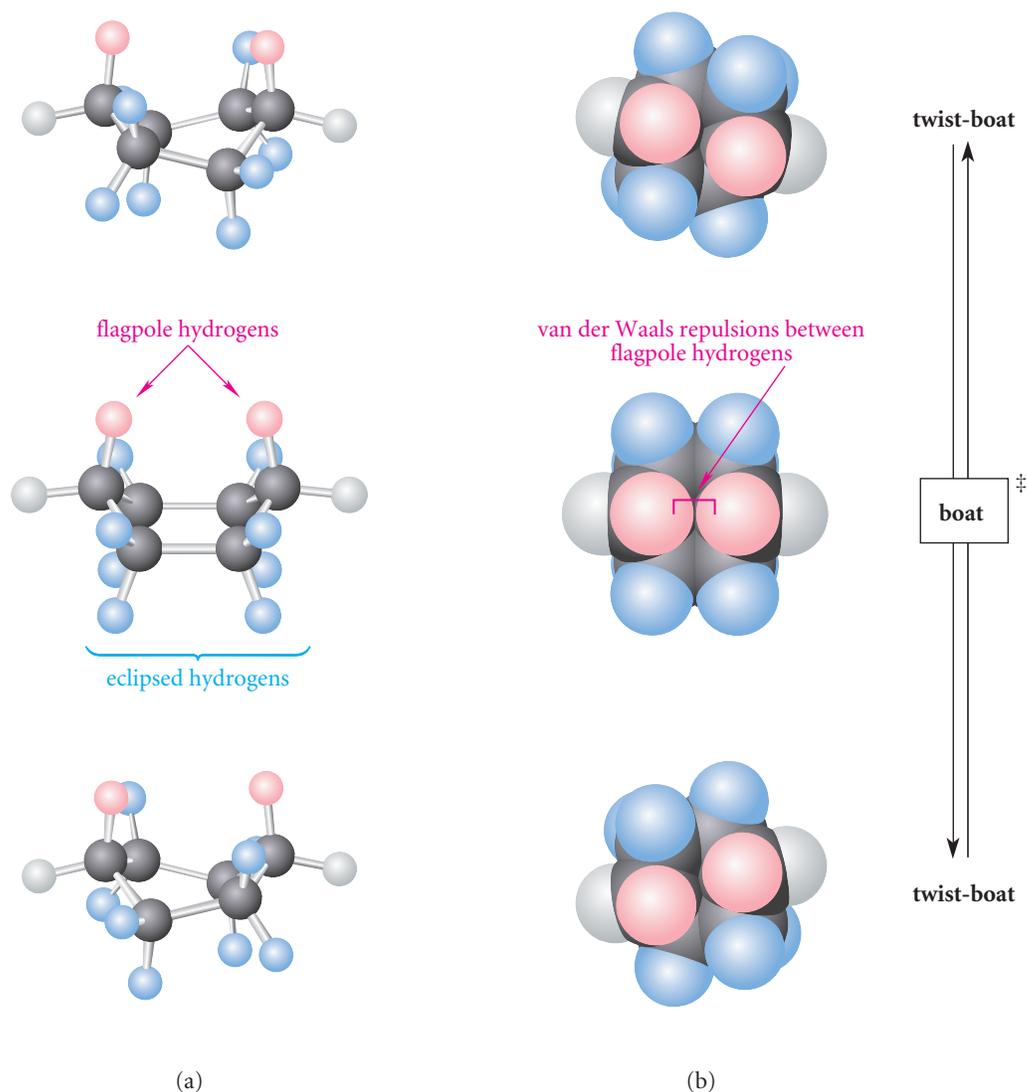
### C. Boat and Twist-Boat Conformations

Figure 7.3 shows a boat conformation of cyclohexane. Let's examine this conformation in more detail. The boat conformation is not a stable conformation of cyclohexane; it contains two sources of



**Figure 7.3** Use of models to show the interconversion of the two chair conformations of cyclohexane. The carbons within the green outlines undergo internal rotation. The green arrows show how the outlined  $\text{CH}_2$  groups move at each step. Notice that the chair interconversion interchanges the positions of the hydrogens: axial hydrogens in one chair conformation become equatorial hydrogens in the other.

instability, both of which are shown in Fig. 7.4. One is that certain hydrogens (shaded in blue) are eclipsed. The second is that the two hydrogens on the “bow” and “stern” of the boat, called *flagpole hydrogens*, experience modest van der Waals repulsion. (The flagpole hydrogens are shaded in pink in Fig. 7.4.) For these reasons, the boat undergoes very slight internal rotations that reduce both the eclipsing interactions and the flagpole van der Waals repulsions. The result is another stable conformation of cyclohexane called a **twist-boat conformation**. To see the conversion of a boat into a twist-boat, view a model of the boat conformation from above the flagpole hydrogens, as shown in Fig. 7.4b. Grasping the model by its flagpole hydrogens, nudge one flagpole hydrogen up and the other down to obtain a twist-boat conformation. As shown in Fig. 7.4, this motion can occur in either of two ways, so that two twist-boats are related to any one boat conformation.



**Figure 7.4** Boat cyclohexane (*center*) and its two related twist-boat conformations (*top* and *bottom*). The flagpole hydrogens are pink, and the hydrogens that are eclipsed in the boat conformation are blue. (a) Ball-and-stick models. Note in the boat conformation the eclipsed relationship among the pairs of blue hydrogens. This eclipsing is reduced in the twist-boat conformation. (b) Space-filling models viewed from above the flagpole hydrogens. Note the van der Waals repulsion between the flagpole hydrogens in the boat conformation. This unfavorable interaction is reduced in the twist-boat conformations because the flagpole hydrogens (*pink*) are farther apart.

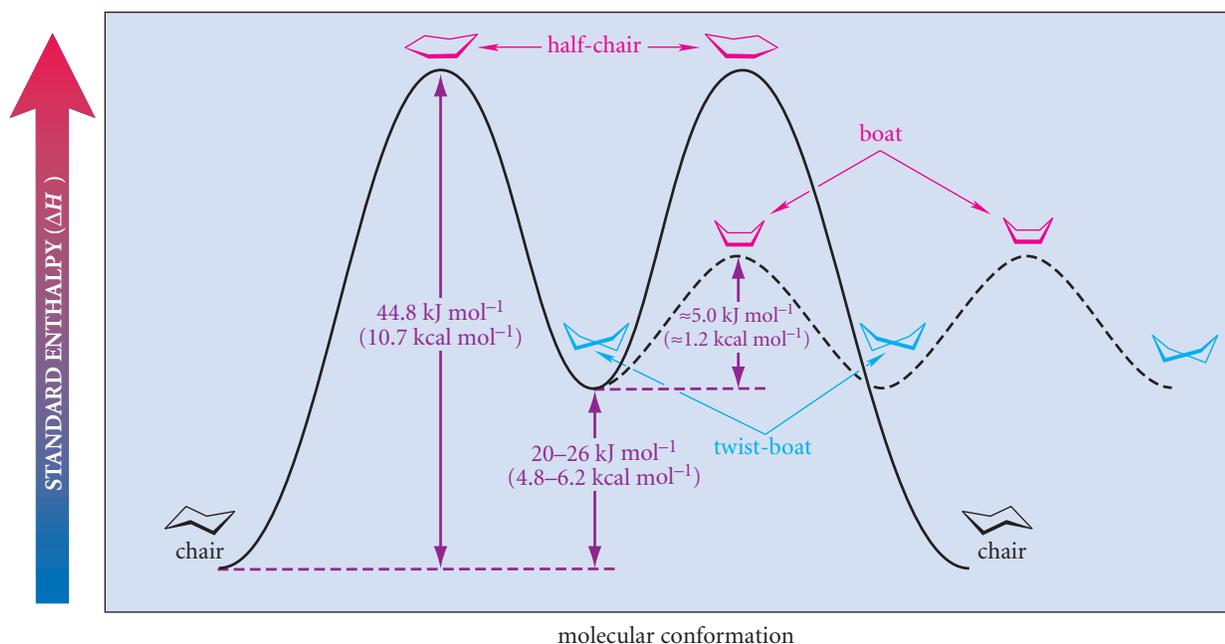


Figure 7.5 Relative enthalpies of cyclohexane conformations.

The enthalpy relationships among the conformations of cyclohexane are shown in Fig. 7.5. You can see from this figure that the twist-boat conformation is an intermediate in the chair interconversion. Although the twist-boat conformation is at an energy minimum, it is less stable than the chair conformation by about  $23 \text{ kJ mol}^{-1}$  ( $5.5 \text{ kcal mol}^{-1}$ ) in standard enthalpy. The standard free-energy difference ( $15.9 \text{ kJ mol}^{-1}$ ,  $3.8 \text{ kcal mol}^{-1}$ ) is also considerable. As Study Problem 7.1 illustrates, a sample of cyclohexane has very little twist-boat conformation present at equilibrium. The boat conformation itself can be thought of as the transition state for the interconversion of two twist-boat conformations.

### Study Problem 7.1

Given that the twist-boat form is  $15.9 \text{ kJ mol}^{-1}$  ( $3.8 \text{ kcal mol}^{-1}$ ) higher in standard free energy than the chair form of cyclohexane, calculate the percentages of each form present in a sample of cyclohexane.

**Solution** What we are interested in is the equilibrium ratio of the two forms of cyclohexane—that is, the equilibrium constant for the equilibrium



This equilibrium constant can be expressed as follows:

$$K_{\text{eq}} = \frac{[\text{T}]}{[\text{C}]}$$

The equilibrium constant is related to standard free energy by Eq. 3.30 (p. 106):

$$\Delta G^\circ = -2.3RT \log K_{\text{eq}}$$

or its rearranged form, Eq. 3.31b,

$$K_{\text{eq}} = 10^{-\Delta G^\circ/2.3RT}$$

Applying this equation with energies in kilojoules per mole and  $R = 8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$  and  $T = 298 \text{ K}$ ,

$$K_{\text{eq}} = \frac{[\text{T}]}{[\text{C}]} = 10^{-\Delta G^\circ/2.3RT} = 10^{-15.9/5.71} = 10^{-2.79} = 1.62 \times 10^{-3}$$

Therefore,  $[\text{T}] = (1.62 \times 10^{-3})[\text{C}]$ . Thus, in one mole of cyclohexane, we have

$$1 = [\text{C}] + [\text{T}] = [\text{C}] + (1.62 \times 10^{-3})[\text{C}] = 1.00162[\text{C}]$$

Solving for  $[\text{C}]$ ,

$$[\text{C}] = 0.998$$

and, by difference,

$$[\text{T}] = 1.000 - [\text{C}] = 0.002$$

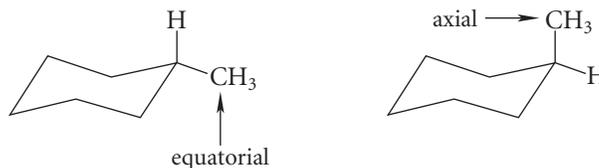
Hence, cyclohexane contains 99.8% chair form and 0.2% twist-boat form at 25 °C.

### PROBLEM

- 7.1 Make a model of chair cyclohexane corresponding to the leftmost model in Fig. 7.3. Raise carbon-4 so that carbons 2–6 lie in a common plane. This is the *half-chair* conformation of cyclohexane, and it is the transition state for the interconversion of the chair and twist-boat conformations. (Notice the position of this conformation on the energy diagram of Fig. 7.5.) Give two reasons why this conformation is less stable than the chair or twist-boat conformation.

## 7.3 MONOSUBSTITUTED CYCLOHEXANES. CONFORMATIONAL ANALYSIS

A substituent group in a substituted cyclohexane, such as the methyl group in methyl cyclohexane, can be in either an equatorial or an axial position.



These two compounds are not identical, yet they have the same connectivity, so they are stereoisomers. Because they are not enantiomers, they must be diastereomers. Like cyclohexane itself, substituted cyclohexanes such as methylcyclohexane also undergo the chair interconversion. As Fig. 7.6 (p. 278) shows, axial methylcyclohexane and equatorial methylcyclohexane are interconverted by this process. Note in this interconversion that a down methyl remains down and an up methyl remains up. (Demonstrate this to yourself with models!) Because this process is rapid at room temperature, methylcyclohexane is a mixture of two *conformational diastereomers* (Sec. 6.10A). Because diastereomers have different energies, one form is more stable than the other.

Equatorial methylcyclohexane is more stable than axial methylcyclohexane. In fact, it is usually the case that *the equatorial conformation of a substituted cyclohexane is more stable than the axial conformation*. Why should this be so?

Examination of a space-filling model of axial methylcyclohexane (Fig. 7.7, p. 278) shows that van der Waals repulsions occur between one of the methyl hydrogens and the two axial hydrogens on the same face of the ring. Such unfavorable interactions between axial groups are called **1,3-diaxial interactions**. These van der Waals repulsions destabilize the axial conformation relative to the equatorial conformation, in which such van der Waals repulsions are absent.