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Organic Chemistry

Chapter 3
Molecular Conformations

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Molecular Conformations

Chapter Outline

Objectives

✔ Learn how to draw three-dimensional molecules in two dimensions and how to visualize three-dimensional molecules from two-dimensional representations

✔ Understand the conformational preferences in the structure of acyclic compounds

✔ Be able to name cycloalkanes, substituted cycloalkanes, and bicyclic compounds

✔ Know how ring size affects the stability of cycloalkanes

✔ Visualize the different conformations of cyclohexane

✔ Recognize how one or two substituents affect the conformation of cyclohexane

✔ Know the shapes of cyclopropane, cyclobutane, and cyclopentane

✔ Understand the various types of bicyclic compounds

Full of nimble fiery and delectable shapes.
　　　　　　—Shakespeare

Conformations are the shapes a molecule assumes by rotating about its bonds.

Conformational analysis is the study of the effect of rotation on the properties of a molecule.

The rotational symmetry of a σ bond (a carbon—carbon single bond) allows the atoms or groups of atoms connected by that bond to rotate about it. As a result of this kind of rotation, many molecules assume several different three-dimensional shapes. Chemists call these different shapes **conformations**. Some conformations of a particular molecule are more stable than others are. Knowing this will help you understand how many chemical reactions proceed.

Conformational analysis is the examination of the positions a molecule takes and the energy changes it undergoes as it converts among its different conformations. This chapter covers in detail the conformational analysis of ethane, butane, and cyclohexane. It also gives an overview of other cyclic and polycyclic hydrocarbons.

Because each of the various conformations of a molecule has different properties, the conformation the molecule normally adopts has a profound influence on its physical and chemical properties. Organic chemists use conformational analysis to understand the

behavior of molecules in chemical reactions. Biochemists and molecular biologists also use conformational analysis to study the ways molecules interact with each other in living systems.

3.1 Representing Three-Dimensional Molecules in Two Dimensions

For a reaction to proceed the conformation of the individual molecules must allow them to collide at points where they will react. Conformational analysis visualizes the three-dimensional structures of various conformations. Because two-dimensional illustrations are limiting, invest in a set of molecular models and learn how to use them. Make a model of any molecule you are studying and twist the model back and forth into the molecule's various possible conformations. Continue manipulating the model until you have a thorough understanding of all the possible conformations. Working with a three-dimensional model set will help you learn to visualize molecular structures from a two-dimensional drawing.

Molecular models are an invaluable aid for visualizing the interactions between atoms in a molecule and in seeing how a chemical reaction proceeds. Even the most experienced chemist makes frequent reference to models in order to clarify questions of molecular structure. As you work your way through this text, using a molecular model set will make learning the material much easier.

A molecular model of ethane (CH_3CH_3) is shown in Figure 3.1. The white spheres represent the hydrogen atoms, and the black spheres represent the sp^3 hybridized carbon atoms. The lines connecting the spheres represent the bonds between the atoms. Make a model of ethane to help you visualize this structure in three dimensions.
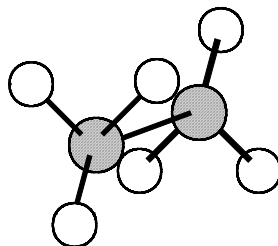
Figure 3.1. A ball-and-stick model of ethane.

To represent the three-dimensional structures of molecules in two-dimensional drawings, chemists have developed two major types of notations. The one they use most frequently is the **wedge-and-dash** representation. In this example, compare the wedge-and-dash representation with the ball-and-stick model.

A wedge-and-dash representation shows a three-dimensional molecule using wedges to show the bonds projecting toward you, dashed wedges to show the bonds projecting away from you, and lines to show the bonds in the plane of the page.

Wedge-and-dash representation   Ball-and-stick model
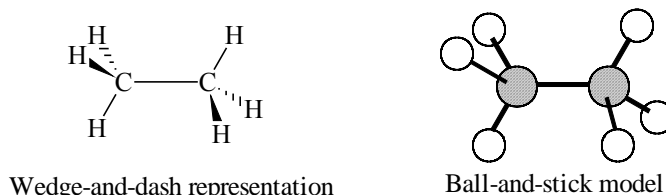
A wedge-and-dash representation shows the side of the carbon—carbon bond being drawn. The wedges (➤) represent bonds that project out of the plane of the paper toward you, the lines are bonds in the plane of the paper, and the dashed wedges (''''') represent bonds receding away from you behind the plane of the paper.

The second type of two-dimensional notation used by chemists to represent structures is the **Newman projection**, which was devised by Professor Melvin S. Newman from Ohio State University. A Newman projection shows the two bonded carbons under consideration with one directly in front of the other.

The Newman projection shows the relationships of groups bonded on adjacent carbon atoms.

Newman projection   Ball-and-stick model
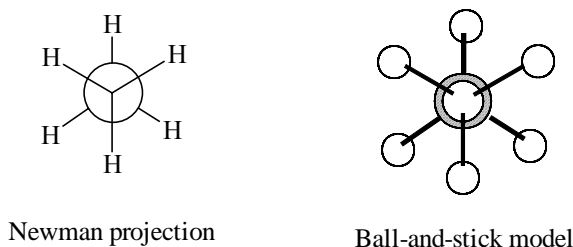
In a Newman projection the point represents the front carbon, the open circle represents the rear carbon, and the bonds connecting the other atoms with the carbons are shown emerging from the point and the circle. Be careful to clearly terminate the bond lines of the rear carbon atom at the perimeter of the circle.

These two structural representations illustrate different aspects of molecular geometry. The wedge-and-dash helps to visualize the molecule in three dimensions. The Newman projection shows the angles between atoms on adjacent carbons.
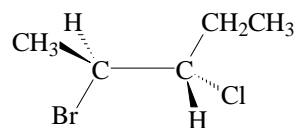

Exercise 3.1

Assign IUPAC names to each of the following structures and draw the other type of two-dimensional representation for each. Be careful to arrange the groups in exactly the same way, so you will be illustrating the same conformation.
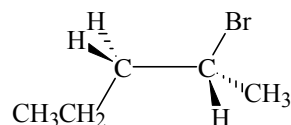
a)
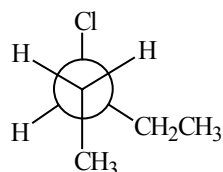
b)

c)

d)
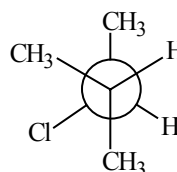
Sample solution

d) The IUPAC name is 2-chloro-3-methylbutane. You were shown the Newman projection so the wedge-and-dash representation is:
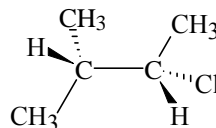
3.2 Dihedral Angles

The σ bond between two carbons permits the two carbons to rotate freely in relation to each other. With your molecular model of ethane, you can twist, or rotate, the carbons around the C—C bond to see the various conformations that ethane forms. Grasp a hydrogen from each CH_3 group, or in some way mark them, so you can remember which hydrogen in each CH_3 group is rotating in relation to the other. Turn your model so that you are looking at the carbons lined up one in front of the other. Then twist the marked hydrogens to match the Newman projections shown below. When the angle between two marked hydrogens is 60°, chemists call this spatial relationship the **gauche** conformation. When the angle is 180°, they call the relationship the **anti** conformation.

In the gauche spatial relationship, two substituents on adjacent carbons are 60° apart in the Newman projection. In the anti spatial relationship they are 180° apart.

Gauche   Anti
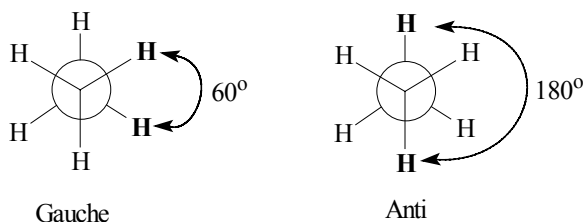
In a staggered conformation, a bond on one carbon appears midway between the bonds on an adjacent carbon in a Newman projection.

In an eclipsed conformation, a bond on one carbon is superimposed over one on the second in a Newman projection.

Dihedral angles are the angles between two bonds on adjacent atoms when you look at a Newman projection.

The definition of torsion is "twisting" of the bonds.

Chemists call a conformation that has only gauche or anti relationships **staggered**. Both of the structures drawn above are staggered. When the angles between adjacent substituents are 0°, the molecule is in an **eclipsed** conformation. Chemists talk of the atoms in ethane having either a gauche, anti, or eclipsed conformation. Keep in mind that ethane has an infinite number of additional conformations that differ from each other by infinitesimal increments of the angles between the two methyl groups.

The angles between the hydrogens on the two methyl groups of ethane are called the **dihedral**, or **torsional**, **angles**. The dihedral angle is the angle formed when one H—C1—C2 plane intersects with one C1—C2—H plane. Each conformation has a characteristic dihedral angle.
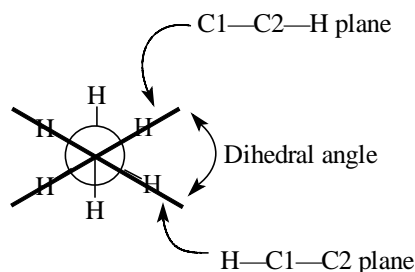
Understanding dihedral angles is an important part of conformational analysis.

Exercise 3.2

Using both a wedge-and-dash representation and a Newman projection, draw the eclipsed conformation of ethane.

Sample solution

The Newman projection of eclipsed ethane looks like this:

Shapes of Alkanes

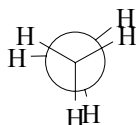The basis for the shapes of alkanes is the ability of a carbon atom to sp^3 hybridize with a tetrahedral geometry and four bonds. Each of these four bonds connects to either a carbon or a hydrogen atom. Also, each bond allows the free rotation of one atom with respect to the other. The following figure illustrates the rotation of one carbon with respect to the other carbon in ethane.
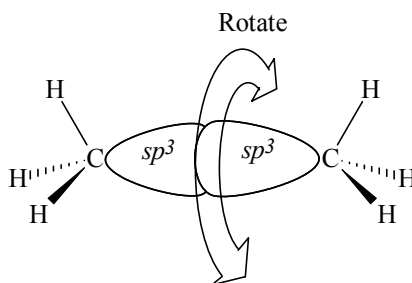
The linear overlap of two sp^3 hybridized orbitals in the carbon—carbon σ bond in ethane allows the free rotation of one carbon with respect to the other.

Rotation about a single bond occurs relatively rapidly. For example, at room temperature, rotation around the C—C bond in ethane occurs millions of times a second. The reason for this rapid rotation, as suggested by molecular orbital theory, is a single bond has internuclear symmetry and therefore, no basis for hindered rotation. That is, a single bond has no preferred orientation of overlap, nor does it change in electron density because of rotation; thus, rotation should occur freely. However, experimental data published in the 1930s demonstrated that, contrary to theory, simple acyclic molecules, such as ethane, do have a small energy barrier of about 3-5 kcal/mole to free rotation about the carbon—carbon bond.

3.3 The Conformations of Ethane

Figure 3.2 is an energy diagram that shows how the internal energy of ethane changes as one of its methyl groups rotates with respect to the other. The plot shows the relative angle on the horizontal axis and the energy change on the vertical axis. Use your model of ethane as you look at this graph. Understanding the energy relationships it diagrams can help you later in understanding many chemical and physical processes.
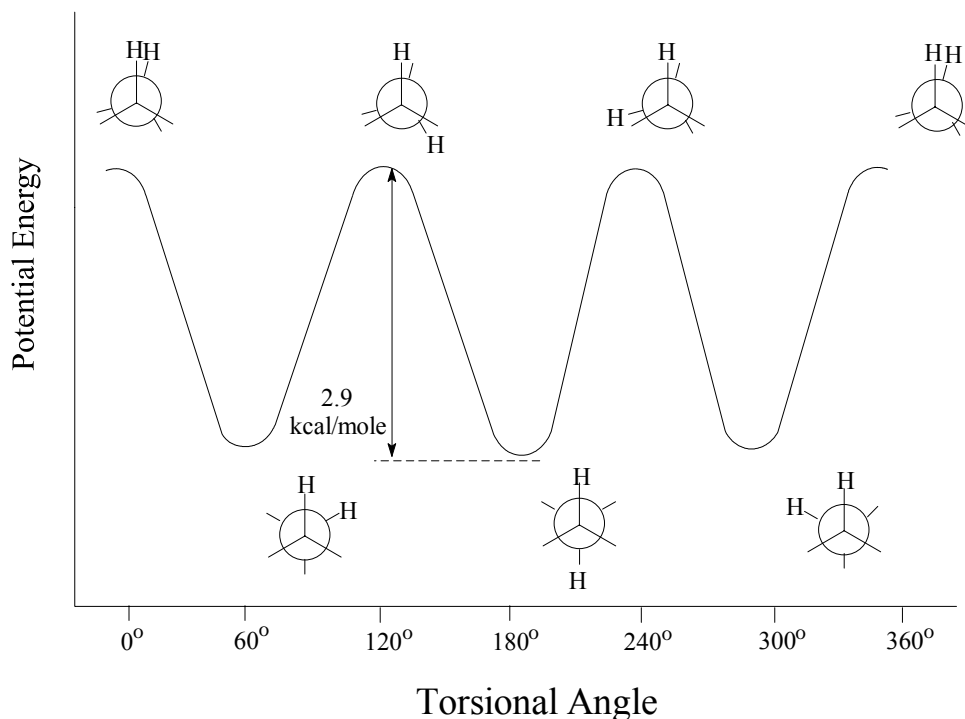
**Figure 3.2**. Energy diagram for rotation in ethane. Only two of the hydrogens are shown for clarity. For ethane, the rotational energy barrier is 2.9 kcal/mole.

    Among the various conformations of ethane, the one with the least energy is the most stable. The graph in Figure 3.2 indicates that the staggered conformations are 2.9 kcal/mole lower in energy than the eclipsed conformations. The three staggered conformations correspond to the energy minima, and the three eclipsed conformations correspond to the energy maxima. Of course, distinguishing between the various eclipsed or staggered conformations is impossible because the hydrogens are all identical.

    A staggered conformation of ethane is more stable than an eclipsed conformation because the staggered conformation maximizes the separation of the electron pairs in the molecular orbitals of the C—H bonds. In the eclipsed conformation, the hydrogens are closer; thus, the repulsions of the electron pairs are greater. Chemists call this increase of energy associated with eclipsed bonds on adjacent atoms **torsional strain**. Figure 3.3 illustrates the change in distance between the C—H bonds in the staggered and eclipsed conformations of ethane.

Torsional strain is the increase in energy due to eclipsing interactions in a molecule.

Staggered C—H bonds   Eclipsed C—H bonds

250 pm   Rotation   220 pm
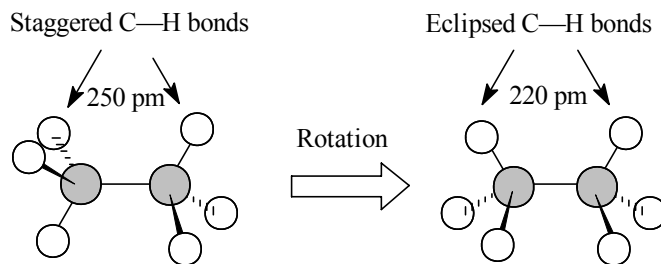
Figure 3.3. The C—H bonds of adjacent carbon atoms of ethane are closer together in the eclipsed conformation (220 pm) than in the staggered conformation (250 pm).

The energy barrier to rotation for different substituents varies with the size of the group on the molecule. Table 3.1 lists the sizes for substituents found in a variety of organic molecules. The larger the group on the molecule the closer that group will be to another group on an adjacent carbon atom. Consequently the barrier to free rotation increases.

Atom or Group	Size (pm)	Atom or Group	Size (pm)
H	120	Cl	180
N	150	Br	195
O	140	I	215
P	190	CH_3	200
S	185	CH_2	200
F	135		

Table 3.1. Selected van der Waals radii, measured in picometers (pm).

**The van der Waals Radius and van der Waals Strain**

Every atom or group of atoms has a measure of size called its **van der Waals radius**. When two groups that are not bonded to each other get within close distance of their van der Waals radii, they begin repelling one another. The electrons surrounding one group repel the electrons surrounding the other group. The van der Waals radii indicate how close two groups can approach each other before these electron-electron repulsions occur. Chemists call such repulsion **van der Waals strain**. Table 3.1 has a list of the van der Waals radii of some selected atoms and groups that are important in organic chemistry.

The van der Waals radius of an atom, or group of atoms, is the distance from the center of the electron cloud surrounding the atom or group to its outer edge.

The van der Waals strain is a repulsion that arises when two groups come close to each other.

3.4 Conformational Analysis of Butane

Make a model of butane and twist it into its different conformations as you read through this section. Consider only the conformations related to the rotation about the C2—C3 bond.

$$CH_3 \text{—} CH_2 \text{—} CH_2 \text{—} CH_3$$

Rotation here
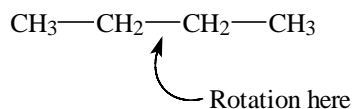
The structure of butane has two distinctly different staggered conformations. In one, the two methyl groups have a gauche conformation. In the other, the two methyl groups have an anti conformation. In the gauche conformation, the torsional angle between the two methyl groups is 60°. For the anti conformation, the two methyl groups have a torsional angle of 180°.
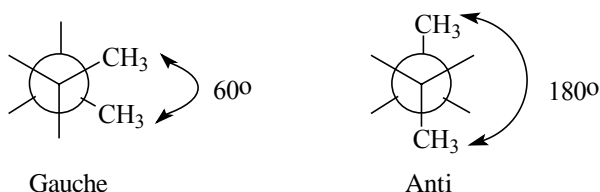

Gauche   Anti

The anti and gauche conformations of butane have an energy difference of 0.8 kcal/mole. The anti conformation is more stable than the gauche conformation because the two methyl groups are farther apart in the anti conformation. Thus, the anti conformation has less van der Waals strain than the gauche conformation. The van der Waals radius of a hydrogen atom is 120 pm, and that of a methyl group is 200 pm—nearly twice as large as a hydrogen. Because the methyl groups of butane are closer in the gauche conformation than they are in the anti, the compound has greater van der Waals strain in the gauche conformation. At 25^oC, about three times as many butane molecules have the anti conformation as the gauche conformation.

Butane has two distinct eclipsed conformations about its C2—C3 bond. In one, the two methyl groups eclipse each other. In the second, each methyl group eclipses with a hydrogen atom. Both conformations have the same number of eclipsed bonds and the same amount of torsional strain. However, the methyl—methyl eclipsed conformation has significantly more van der Waals strain than does the methyl—hydrogen eclipsed conformation. The greater strain arises from the larger methyl groups that take up more space, and thus have more electron repulsion, than the hydrogens.

Eclipsed conformations of butane

Figure 3.4 shows the energy diagram for the different conformations of butane. As with ethane, the staggered conformations of butane are more stable than the eclipsed ones. Notice in the figure, however, that the staggered conformations of butane do not have the same energy level, nor do all the eclipsed conformations have the same energy level. The conformation with the greatest energy is the one with the methyl groups eclipsed; the conformation with the least energy is the one with the methyl groups anti. The energy difference of 6.1 kcal/mole between that maximum and minimum is the energy barrier for rotation about the C2—C3 bond in butane. It is higher than the 2.9 kcal/mole rotational energy of ethane because of the addition of the van der Waals strain to the torsional strain. Although rotation about the C2—C3 bond of butane is still a rapid process, it is much slower than the rotation about the C—C bond in ethane.
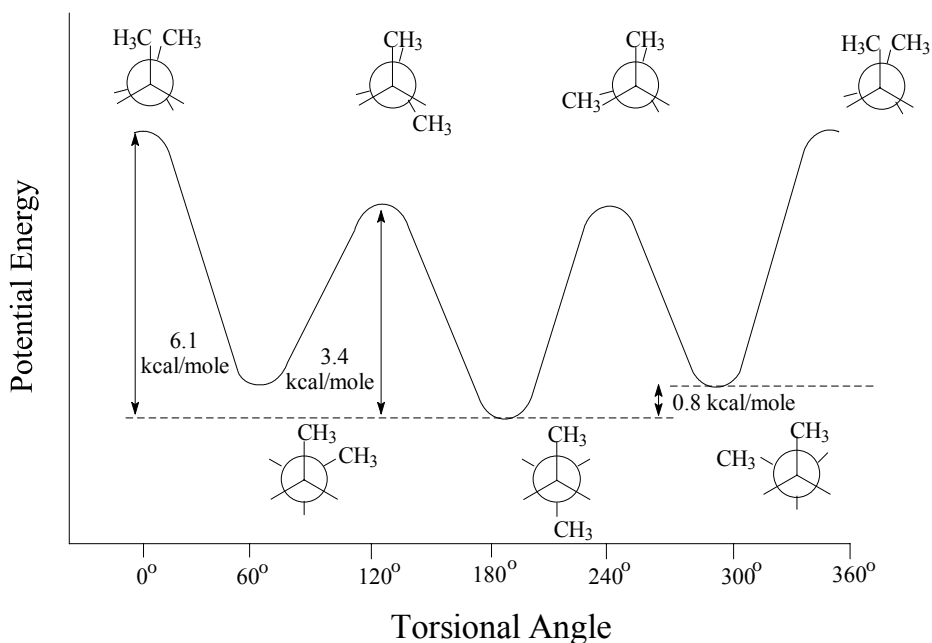
Figure 3.4. Energy diagram for rotation about the C—C bond between the second and third carbons in butane.


Exercise 3.3

a) Sketch an energy diagram for the rotation about the C1—C2 bond in propane. Clearly identify the conformation for each of the energy maxima and minima. Does this diagram look more like that of ethane or butane? Would you expect a higher rotational energy level for propane than for ethane or butane?

b) Repeat this for the C1—C2 bond in 1-iodopropane.

Conformations of Other Alkanes

For longer-chain alkanes, instead of viewing the molecules from the end in Newman projections, look at them from the side. The "carbon skeletons" tend to have a zigzag arrangement with all of the bonds staggered and all of the interactions between the groups anti. This completely anti conformation is the most stable conformation of all unbranched hydrocarbons.
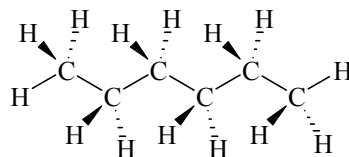
Zigzag structure of hexane

3.5 Angle Strain in Cycloalkanes

In 1885, Adolph von Baeyer declared that the carbon skeletons of the cycloalkanes were planar. He stated that cyclopentane was the most stable of the cycloalkanes and based his belief on his observation that rings containing five or six carbons are the most common and the most stable in naturally occurring materials. From that observation, Baeyer suggested that cyclic stability relates to how closely the C—C—C angles come to 109.5º, the measurement of a tetrahedral angle. The C—C—C angles in cyclopentane come the closest, because the angles in a pentagon are 108º—almost a tetrahedral angle. The next closest are the 120º angles in cyclohexane. In polygons larger than a hexagon, the angles deviate more and more from the ideal tetrahedral angle. Thus, von Baeyer predicted that those cycloalkanes larger than cyclopentane would be increasingly strained and correspondingly less stable. For rings smaller than cyclopentane, he predicted a C—C—C bond angle of 60º for cyclopropane, which is a 49.5º deviation from the tetrahedral value, and of 90º for cyclobutane, a 19.5º deviation from the tetrahedral value. He called this destabilizing strain **angle strain**. That is, when the molecular orbitals of the bonding carbons cannot overlap end to end to form a tetrahedral angle, the bonds "bend," causing strain.

Angle strain is the strain that occurs in a molecule when a bond angle is different from its optimum angle.

Just five years later, in 1890, Herman Sachse pointed out that cyclohexane, the most common naturally occurring cycloalkane and the most stable, could adopt a strain-free conformation, with normal tetrahedral bond angles, if the ring was nonplanar. Using molecular models, he showed that a nonplanar cyclohexane molecule would have two conformations, both without the ring strain that the von Baeyer theory predicted. He called the two isomers the C-form (or movable)

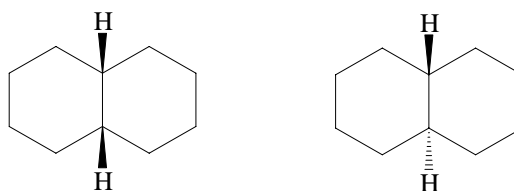and the Z-form (or rigid), because the models looked somewhat like the letters C and Z.

Exercise 3.4

Construct a molecular model of cyclohexane. Identify Sachse's C-form and Z-form. Draw the two forms.

For more on decalin see Section 3.11, page 000.

As is often the case with young upstarts, after only a brief evaluation and a brief attempt to isolate the two structures, Sachse's proposed structures were largely ignored. Support of the planar structures, an inability to isolate Sachse's structures and von Baeyer's stature as a chemist meant Sachse was ignored. In 1918, however, E. Mohr suggested that Sachse might be correct. He pointed out that a nonplanar cyclohexane would have conformational mobility; thus, allowing the two forms to easily interconvert by rotating about their C—C bonds. Because they could interconvert so easily, the two forms could not be readily isolated. Although this was important, what finally confirmed Sachse's proposal was another of Mohr's suggestions: that decalin, a two-ring cycloalkane, existed in two forms that could interconvert only by breaking and reforming bonds. Finally, in 1925, Walter Hückel isolated the two postulated isomers of decalin.

The two forms of decalin

Von Baeyer's theory is useful in that it identifies bond angle strain. Except for cyclopropane, all cycloalkanes are nonplanar. The shape that each molecule adopts is the one that minimizes the angle strain.

Heat of Combustion

The heat of combustion is the energy given off when a substance is burned under controlled conditions.

The most convenient method for determining the amount of angle strain within a molecule, and thereby accessing the molecule's thermodynamic stability, is by measuring its **heat of combustion**. All hydrocarbons burn. As they burn, they give off energy and produce water and carbon dioxide. These products, water and carbon dioxide, are the same for the combustion reaction of every hydrocarbon. The differences in the heats of combustion for a homologous series relate to the relative stabilities of the molecules. The following equation is the general form for the combustion of cycloalkanes:

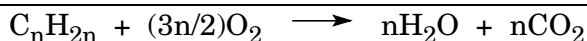---

$$C_nH_{2n} + (3n/2)O_2 \longrightarrow nH_2O + nCO_2$$

Table 3.2 lists the heats of combustion for various cycloalkanes, including the heat of combustion for both the whole molecule and each methylene (—CH$_2$—) group within the molecule. The heat of combustion for an individual methylene group is more important than the heat of combustion for the whole molecule, as the more stable molecules are those that have the lower heats of combustion per group. As you examine this table, note that the angle strain is lowest for cyclohexane, not cyclopentane as von Baeyer predicted. Note also that the angle strain per methylene group for rings of five or more carbons deviates little from approximately 1 kcal/mole.

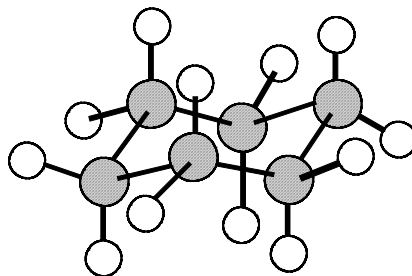| Cycloalkane	Heat of Combustion (kcal/mole)	Number of Methylene Groups	Heat of Combustion Per Methylene Group (kcal/mole)	Angle Strain per Methylene Group (kcal/mole)
Cyclopropane	499.8	3	166.6	9.2
Cyclobutane	655.9	4	164.0	7.6
Cyclopentane	793.5	5	158.7	1.3
Cyclohexane	944.5	6	157.4	0
Cycloheptane	1108.2	7	158.3	0.9
Cyclooctane	1269.1	8	158.6	1.2
Cyclononane	1429.5	9	158.8	1.4
Cyclodecane	1586.0	10	158.6	1.2
Cyclopentadecane	2363.3	15	157.6	0.2
Normal Alkane			157.4	

Table 3.2. Heats of combustion of cycloalkanes.

3.6 Conformations of Cyclohexane

As noted in Section 3.5, there are two basic forms of the cyclohexane ring—initially called the C- and Z-forms. In current terminology, these forms are known as the **boat** and **chair conformations**. This section discusses which of these two structures is the more stable and why.

*The boat is the C-form, and the chair is the Z-form.*

In 1943, Odd Hassel of the University of Oslo established the chair form as the most stable conformation of cyclohexane. Later, Sir Derek Barton used Hassel's results in an analysis of chemical reactivity. For their work, Hassel and Barton shared the Nobel Prize in chemistry in 1969. Figure 3.5 shows a ball-and-stick model of the chair conformation. By using your imagination, you can see a lounge chair in this conformation.

Figure 3.5. A ball-and-stick model of the chair form of cyclohexane.
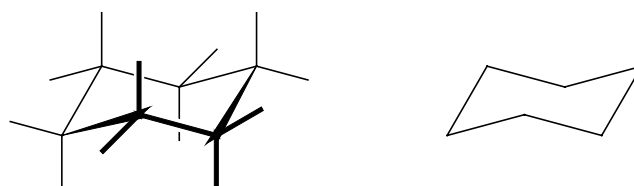
Figure 3.6. Bond line structural formulas for the chair form of cyclohexane. The structure on the left shows the positions of the hydrogens; the structure on the right shows only the C—C bonds.

Using your model of cyclohexane, twist it into the chair conformation. Note that, unlike the drawings, cyclohexane is not a planar hexagon. When cyclohexane is in the chair conformation, any carbon you look at on the ring and the carbon opposite it is a part of the chair—either its back or its footrest. The chair form of cyclohexane is nearly free of angle strain. Because all the bonds are staggered, it is almost free from torsional strain as well. Looking along two of the C—C bonds in a Newman projection makes the staggered arrangement of the bonds in the chair form of cyclohexane more apparent. Compare your molecular model with the following representation:
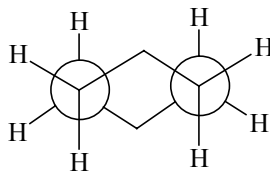

Newman projection of the chair form of cyclohexane

### How to Draw a Chair Conformation of Cyclohexane

Drawing a chair conformation of cyclohexane is not difficult but does require some practice. The rules are quite simple. First, draw the "seat" of the chair. They are two slanted and slightly offset parallel lines.
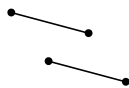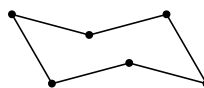

Next, draw two more parallel lines connecting the first lines with the "footrest" and "headrest" carbons.
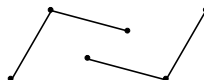
Finally, add two more parallel lines connecting to the footrest and headrest carbons with the two lines of the "sides" of the chair to complete the ring.
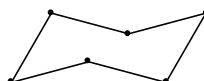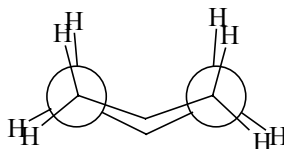
Of course, the chair can also be drawn as follows:

Practice these skills until you have mastered the art of drawing the chair structure. This skill is used throughout the book.

Now twist your model of cyclohexane into the boat form:

Newman projection of the boat form of cyclohexane

The bond angles are close to tetrahedral, so there is little angle strain, but the boat form of cyclohexane does have eclipsed bonds on four of its carbon atoms. This eclipsing produces a significant amount of torsional strain. More importantly, the close contact of the **"flagpole" hydrogens** at either end of the molecule destabilizes the boat conformation. Figure 3.7 shows a ball-and-stick model of the boat conformation.

The "flagpole" hydrogens are the two hydrogens that point upward and slightly toward each other from the two upturned ends of the boat.

Flagpole hydrogens
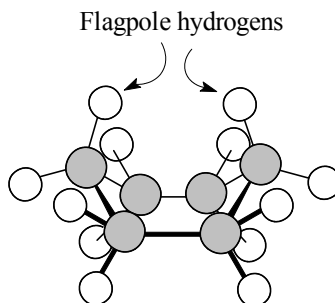
Figure 3.7. A ball-and-stick model of the boat form of cyclohexane with emphasis on the flagpole hydrogens.

Flagpole hydrogens

H   H
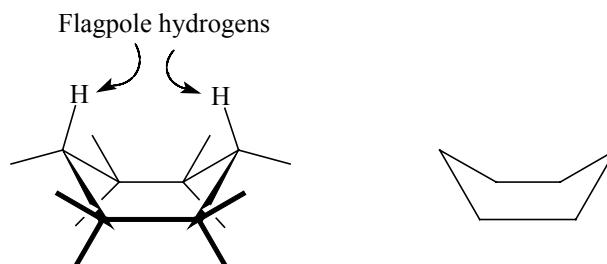
Figure 3.8. Bond-line structural formulas of the boat form of cyclohexane. The structure on the left shows the flagpole hydrogens.

These hydrogens are only about 180 pm apart, a distance that is closer than the sum (240 pm) of the van der Waals radii of two hydrogens. Thus, the van der Waals repulsions between the flagpole hydrogens add to the torsional strain. This torsional strain further increases the energy of the boat form. The boat form is 6.2 kcal/mole (see Figure 3.10) higher in energy than the chair form.

The twist or skew boat is slightly rotated to relieve the flagpole and eclipsing interactions of the boat.

A third conformation of cyclohexane is the **twist**, or **skew**, **boat** (see Figure 3.9). With your model still in the boat conformation, take the flagpole hydrogens and rotate, or twist, them in opposite directions from one another, so that instead of facing each other, they are more to the side. Twisting the flagpole hydrogens increases the distance between them and moves the eclipsed hydrogens farther apart. This relieves some of both the torsional strain and the van der Waals repulsion. The twist boat is 0.6 kcal/mole lower in energy than the boat conformation.
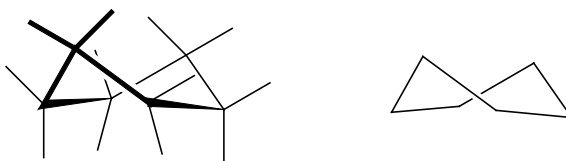
Figure 3.9. The twist boat form of cyclohexane.

At room temperature, ring flip occurs almost constantly. If it were possible to isolate the various conformations existing at a given instant, you would find some of each kind, but most molecules (more than 99%) would be in the chair conformation. This is due to the fact that the chair conformation is more stable than the boat conformation. Because most of the molecules are in the chair conformation most of the time, chemists know that when considering the physical and chemical properties of cyclohexane and its derivatives, they are thinking mostly of the chair conformation. This fact is significant to you, because this book uses cyclohexane derivatives frequently to illustrate reaction pathways.

The chair conformation of cyclohexane has two distinct types of carbon—hydrogen bonds: **axial** and **equatorial**. Six of these bonds are axial and the other six equatorial, with one axial and one equatorial bond on each carbon.

Axial hydrogens point above and below the "plane" of the ring. Equatorial hydrogens are within the "plane" of the ring.
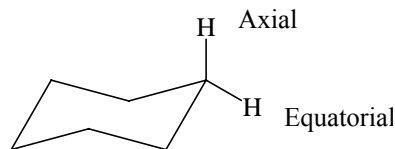

Drawing Substituents on a Chair Cyclohexane

Draw the axial bonds parallel to each other alternately up and down around the ring. That is, if you draw the axial bond to hydrogen on carbon 1 pointing up, draw it pointing down on carbon 2, up on carbon 3, and so on around the ring. Draw the bond up on carbon 1 if the bond angle points up and down if it points down.
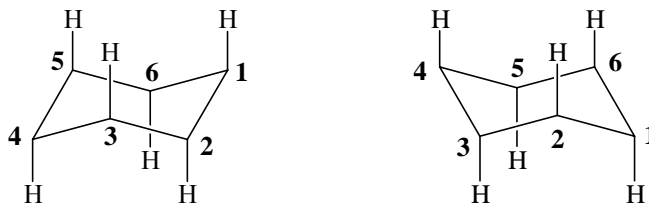

Axial hydrogens on cyclohexane

The equatorial hydrogens lie approximately in the plane formed by the ring of carbons and point out from the equator of the ring. (Keep in mind that the cyclohexane molecule does not lie in a flat plane, so the term equatorial fits rather loosely.) When a vertex of the ring points *down*, the equatorial hydrogen is *up* and away from the ring.
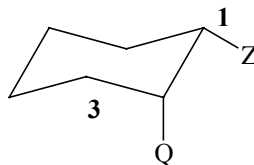

Equatorial hydrogens on cyclohexane
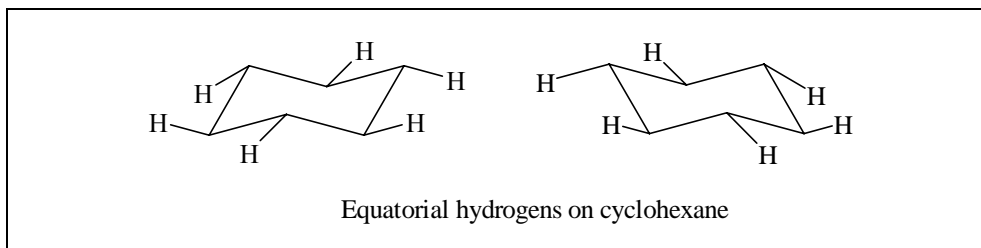
Exercise 3.5

Using the following partial structure of cyclohexane, add a substituent, Z, to C1 to obtain each of the following relationships:
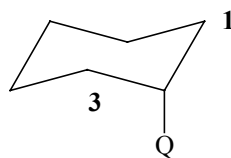
a)   gauche to Q   b)   anti to Q
c)   gauche to C3   d)   anti to C3

Sample Solution

a) Substituent Z is gauche to Q when Z is in the equatorial position. The Z—C—C—Q torsional angle is 60°.

3.7 Conformational Inversion of Cyclohexane

Ring inversion or the chair-boat-chair interconversion is the process where one chair form converts to another chair form of a molecule.

        Through a process called **ring inversion**, or **chair-boat-chair interconversion**, one chair form of cyclohexane converts to another chair form of cyclohexane. That is, the back rotates down to become the footrest and the footrest opposite it on the ring rotates up to become the back. Use your model of cyclohexane to help yourself visualize this. Grasp one of the carbons in the back position in your right hand, call it C1, and grasp the carbon opposite it on the ring, which is in the footrest position and is C4, in your left hand.
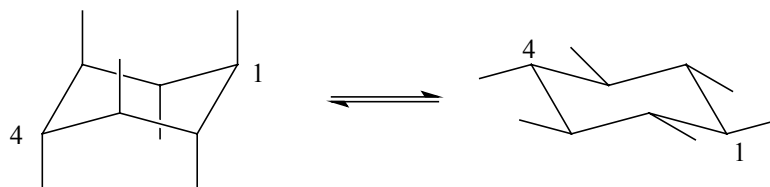
Ring flipping is another term for ring inversion.

Rotate C1, the back, down; then rotate C4, the footrest opposite it, up. In this process of **ring flipping**, the equatorial substituents become axial, and the axial substituents become equatorial. Also, all carbons in the back position move down to the footrest position, and all carbons that were in the footrest position move up to the back position. As you can see, when you rotate one of the C—C bonds in the ring, that rotation affects the relative positions of all the constituent atoms of that molecule.

In the half chair conformation the footrest of the chair forms a plane with the seat of the chair.

The process of ring inversion takes cyclohexane through a conformation called the **half-chair conformation**. The half-chair conformation exists at the point in the inversion process when the footrest carbon, C4, has rotated up to form a plane with carbons C2, C3, C5, and C6.
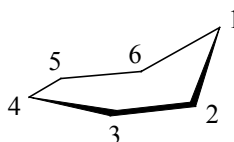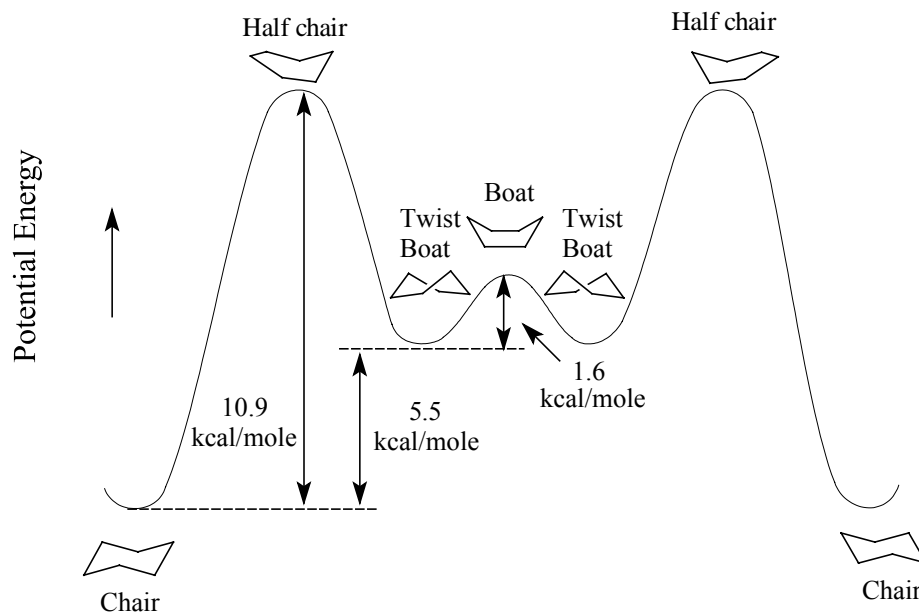

Half-chair conformation of cyclohexane

The position of C1, the back of the chair, is still, at this point, unchanged. This conformation is the transitional state between the chair and the twist boat forms.

At room temperature, this process of inversion goes on constantly. The half-life of a particular chair conformation of cyclohexane is approximately 10^{-5} seconds. That is, every 10^{-5} seconds half of the molecules in a given sample of cyclohexane undergo a ring flip.

The energy diagram in Figure 3.10 illustrates each step of ring flipping from one chair form to the other chair form and shows the variation in energy that accompanies the ring inversion. Use your molecular model of cyclohexane and follow the sequence.

Figure 3.10. The energy diagram for the ring inversion of cyclohexane.

3.8 Conformational Analysis of Monosubstituted Cyclohexanes

The ring inversion, or ring flipping, that occurs in a molecule of cyclohexane takes place between two equivalent conformations. Thus, when a cyclohexane molecule flips between chair forms, the energy level for both forms is the same. However, if there is a substituent on the ring, the number of molecules in each conformation is different because the conformations are no longer equivalent. For example, if a hydrogen of cyclohexane is replaced with a methyl group to form methylcyclohexane, the two chair forms are different. In one the methyl group is equatorial, and in the other, it is axial.

The arrows between the two methylcyclohexanes indicate that the two conformations are not present in equal quantities. The conformation on the right is the more common conformation.

Methylcyclohexane
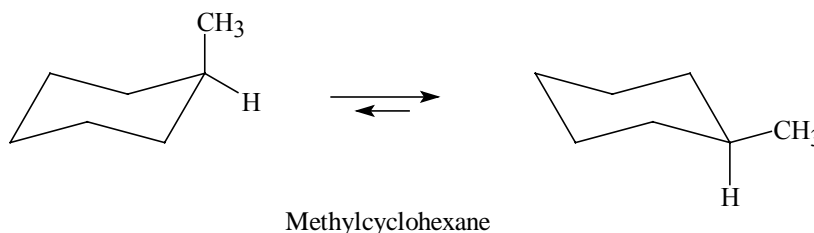
The two chair forms are not present in equal amounts. Experimental evidence shows that at room temperature approximately 95% of the methyl groups are equatorial. This preponderance is due to the

differences in stability of the two conformations. In any equilibrium process, the most stable chemical species is present in greater quantities, and the chair form of methylcyclohexane having the equatorial methyl group is the more stable one.

To help you visualize why 95% of the methyl groups in a room-temperature sample of methylcyclohexane are in the equatorial position, make a model of methylcyclohexane and put the methyl group in an axial position on C1. As you see, an axial methyl group is quite close to the axial hydrogens on C3 and C5. When they are at their closest position, the hydrogens on the methyl group are less than 200 pm away from these axial hydrogens. Figure 3.11 illustrates the structure of methylcyclohexane.
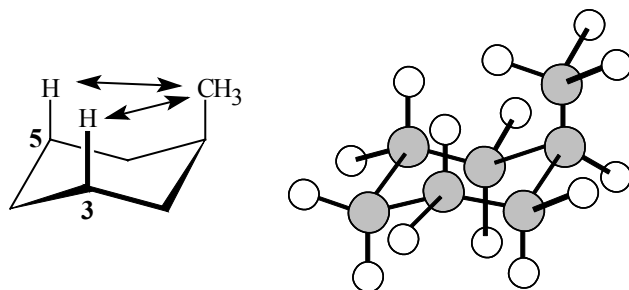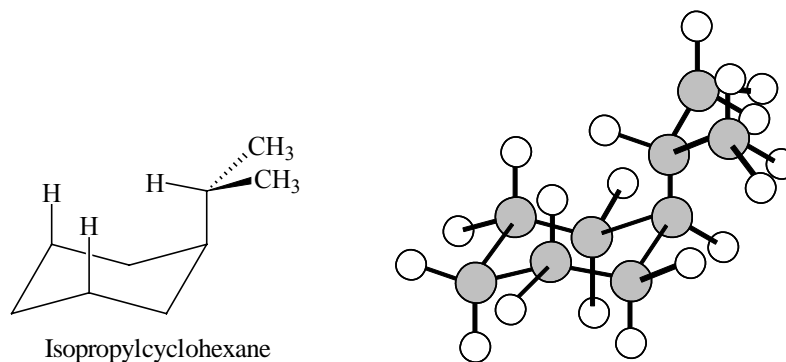

Figure 3.11. Bond-line and ball-and-stick model of methylcyclohexane with the methyl group axial.

This distance is less than the sum of the van der Waals radii for two hydrogens (240 pm), so the axial conformation of methylcyclohexane is destabilized by the strain of the van der Waals repulsive forces. The van der Waals repulsive forces arise when the electron clouds surrounding the atoms get close enough to repel one another.

Now rotate the methyl group to the equatorial position. Here all the hydrogens are in the axial positions, and the distance between them is about 400 pm, much greater than the combined van der Waals radii.

The stability of cyclohexanes having other axial substituents depends on the size of the substituent. For example, for fluorocyclohexane, about 40% of the molecules have fluorine in the axial position. When the substituent is an isopropyl group, about 3% of the molecules have the substituent in the axial position. This percentage is so similar to that for the methyl substituent that it might at first seem surprising because the isopropyl group is larger than the methyl group. However, the isopropyl group orients itself so that a hydrogen points toward the axial hydrogens on C3 and C5. This orients the two methyl groups away from the center of the molecule as shown in Figure 3.12.

Figure 3.12. Bond-line and ball-and-stick model of isopropylcyclohexane with the isopropyl group axial.

A *tert*-butyl group is so large that *tert*-butylcyclohexane exists almost entirely with this group in the equatorial position. In fact, the number of molecules with the *tert*-butyl group axial is too small to measure. The reason for so little ring flipping is that with the *tert*-butyl group in the axial position, one of its three methyl groups must point toward the axial hydrogens on C3 and C5. Figure 3.13 shows that the distance between the hydrogens in this methyl group and the axial hydrogens is only 50 pm, creating a large van der Waals strain.
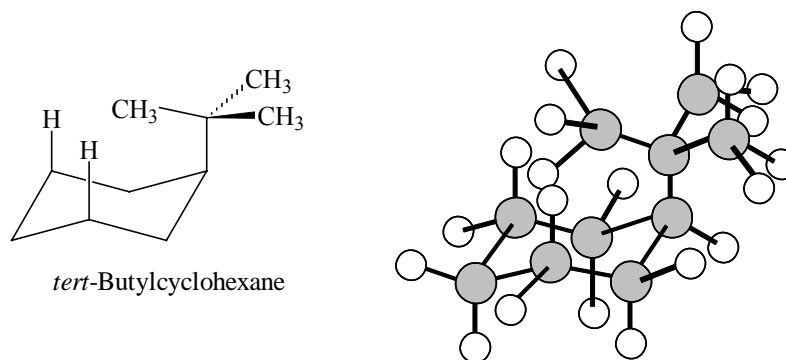

Figure 3.13. Bond-line and ball-and-stick model of *tert*-butylcyclohexane with the *tert*-butyl group axial.

Solved Exercise 3.1

Draw a chair conformation of a cyclohexane ring with a bromine axial on the ring.

Solution: Draw the chair structure. Because the question does not specify the location of the axial substituent, there are six possible drawings. Three have the bromine axial and up, three axial and down. One of each is drawn below.

Br

Axial and up   Br
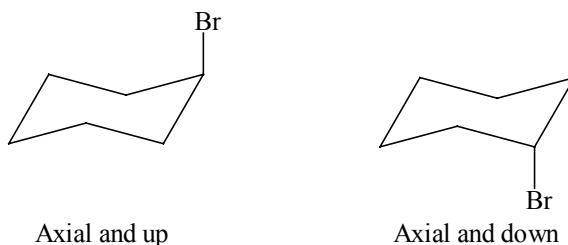
                             Axial and down

Exercise 3.6

Consider the chair conformation of the cyclohexane ring shown below, and answer the following questions. (**Note**: "Up" and "down" are relative to how the structure is drawn.)

5   6   1
4   3   2
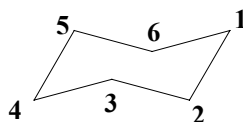
       a) Is a methyl group that is "up" at C5 axial or equatorial?
       b) Is a *tert*-butyl group that is "down" at C1 more or less stable than one that is "down" at C4?
       c) Which is more stable, a methyl group that is "down" at C3 or one that is "down" at C6?
       d) Using the van der Waals radii (Table 3.1, page 000), place an iodine in its most stable position on C2.

Sample solution

a) Placing the substituents on C5 indicates that a methyl that is up must be axial.

CH_3

H
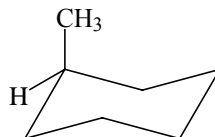
3.9 Naming Stereoisomers

       Many compounds have isomers with identical bond sequences but different geometries. Chemists call these compounds **stereoisomers**. A number of cycloalkanes exist as stereoisomers. Cycloalkanes are less flexible than acyclic alkanes because the ring structure restrains the rotation about the C—C bonds. Because cycloalkanes are geometrically constrained, they have two sides: a

Stereoisomers are isomers that have identical bond sequences but different spatial arrangements of their atoms.

"top" and a "bottom." Thus, one compound of a pair of disubstituted cycloalkane stereoisomers will have the substituents on the same side of the ring, and the other compound will have the substituents on opposite sides of the ring. For example, there are two stereoisomers of the cyclohexane having methyl groups on adjacent carbon atoms. One stereoisomer has the methyl groups on the same side of the ring, and the other has two methyl groups are on opposite sides of the ring.

Methyl groups on the same side   Methyl groups on opposite sides
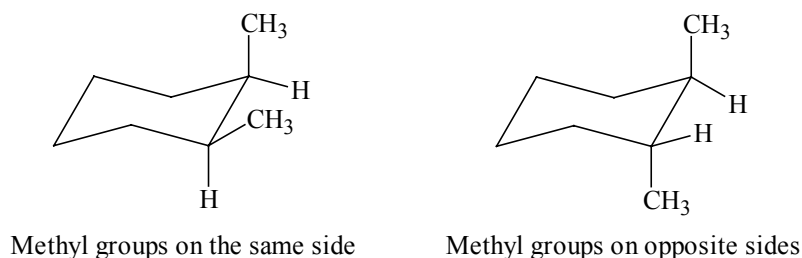
To name stereoisomers, follow these steps:

Step 1 Name the parent compound.
Step 2 Determine the names and positions of the substituents.
Step 3 If the isomer has both substituent groups on the same side of the ring, use the prefix *cis-* before the name of the compound.
Step 4 If the isomer has both substituent groups on opposite sides of the ring, use the prefix *trans-* before the parent name of the compound.

To name the example stereoisomers, follow these steps:

Step 1 The parent name is cyclohexane.
Step 2 Both substituents are methyl groups, and they are on carbons 1 and 2.
Step 3 Both methyl groups are on the same side of the ring in the first compound, so its name is *cis*-1,2-dimethylcyclohexane.
Step 4 The methyl groups are on opposite sides of the ring in the second compound, so its name is *trans*-1,2-dimethylcyclohexane.
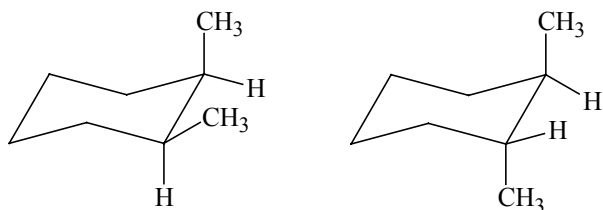
cis-1,2-Dimethylcyclohexane   *trans*-1,2-Dimethylcyclohexane

Groups do not have to be on adjacent carbon atoms to be *cis* or *trans* on a ring, as the following examples demonstrate:
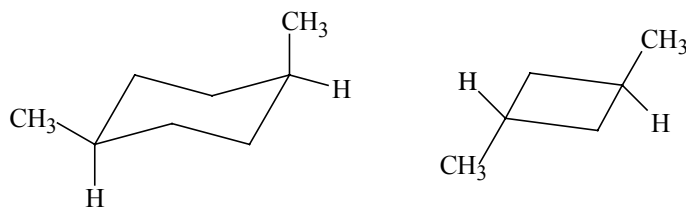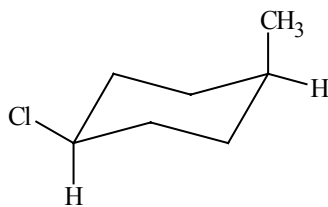

cis-1,4-Dimethylcyclohexane   *trans*-1,3-Dimethylcyclobutane
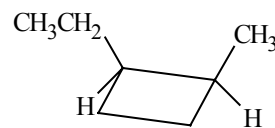
Exercise 3.7
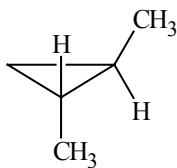
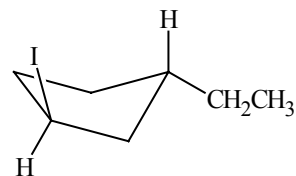Name each of the following using the IUPAC system.

a)

b)
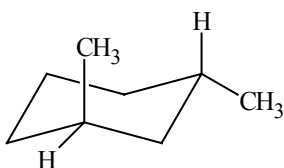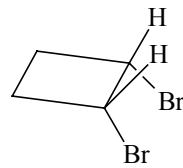

c)

d)

e)

f)

*Sample solution*
      d) *trans*-1-Ethyl-3-iodocyclopentane

3.10 Conformational Analysis of Disubstituted Cyclohexanes

When a cyclohexane ring bears two substituents, the substituents occupy positions that are either on the same side or on opposite sides of the ring. To help yourself visualize this positioning, make molecular models of two cyclohexane rings and four methyl groups. Rotate both cyclohexane rings into the chair conformation. Choose a back carbon on one of the rings and call it C1. Replace the equatorial hydrogen on C1 with one of the methyl groups. Move to C2 and replace the axial hydrogen on that carbon with a methyl substituent. Both substituents are on the same side of the ring—one in the equatorial position and the other in the axial position.
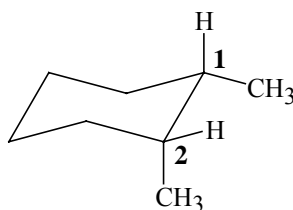
cis-1,2-Dimethylcyclohexane

Because both substituents are on the same side of the ring, they are *cis* to each other. Flip your molecular model of *cis*-1,2-dimethylcyclohexane into the other chair conformation. Note that the methyl group on C1 is now in the axial position, and the methyl group on C2 is in the equatorial position.
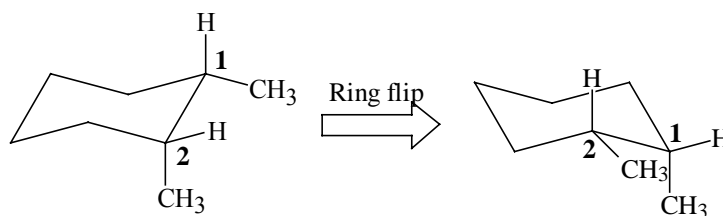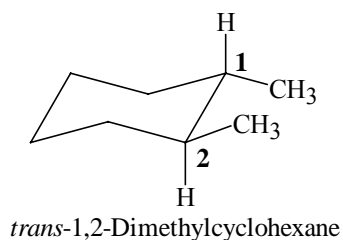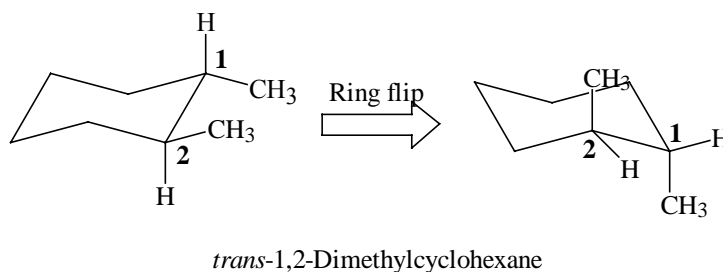

cis-1,2-Dimethylcyclohexane

When two substituents on adjacent carbons in cyclohexane are *cis*, one is always axial and the other is always equatorial in either of the chair

conformations of the molecule. Also, with a *cis* isomer of dimethylcyclohexane, both methyl groups point up from the carbon ring—straight up for the axial methyl and slightly up for the equatorial methyl, (Or, if you turn the model upside down, they both point down from the carbon ring).

Now take the other molecular model of cyclohexane. Locate one of the carbons, call it C1, and replace the equatorial hydrogen with a methyl group. Move to C2, and replace the equatorial hydrogen there with another methyl group. Note that both methyl groups are equatorial but on opposite sides of the ring, or in the *trans* conformation.
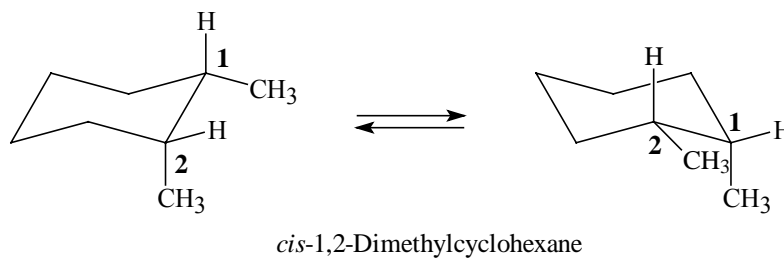

trans-1,2-Dimethylcyclohexane

Flip your model of *trans*-1,2-dimethylcyclohexane into the other chair conformation. Note that both substituents are now in the axial positions.


trans-1,2-Dimethylcyclohexane

With a *trans* isomer of 1,2-dimethylcyclohexane, one methyl group always points up and the other always points down from the carbon ring.

Stereoisomers have different stabilities. To understand the relationship between stereoisomerism and stability, look again at the *cis* and *trans* isomers of 1,2-dimethylcyclohexane in the chair conformations. The two conformations of *cis*-1,2-dimethylcyclohexane are equivalent—no matter which conformation you look at, each has one axial and one equatorial methyl group:

cis-1,2-Dimethylcyclohexane

Recall from Section 3.8 that the methyl group of methylcyclohexane is in the axial position less than 5% of the time because of van der Waals strain. From this you can surmise that *cis*-1,2-dimethylcyclohexane has some torsional strain, but how does it compare with that of the *trans* conformations?

The two conformations of *trans*-1,2-dimethylcyclohexane are not equivalent. In one conformation, both groups are axial; in the other, both are equatorial:

trans-1,2-Dimethylcyclohexane
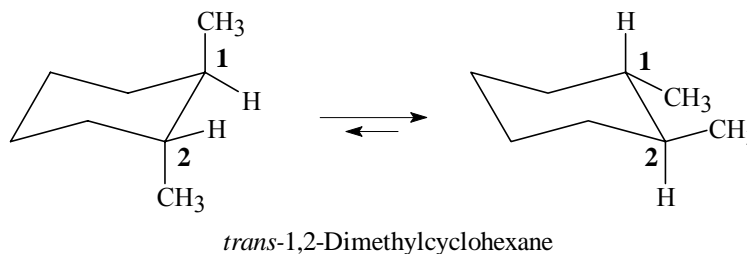
The *trans* conformation with both methyl groups in the axial position constitutes only about 0.4% of the equilibrium mixture. Of the two conformations, the one with the methyl groups in the equatorial positions is definitely more stable. Thus, the *trans* stereoisomer is more stable than the *cis* stereoisomer[1]. The heats of combustion confirm that the *trans* stereoisomer is more stable, as the difference between the *cis* and the *trans* stereoisomers is 1.5 kcal/mole. A general rule is that any substituent on a cyclohexane ring that is equatorial is more stable than one that is axial.

Now look at another constitutional isomer of dimethylcyclohexane: 1,3-dimethylcyclohexane. Both of these isomers have *cis* and *trans* stereoisomers. Make molecular models of the *cis* and *trans* stereoisomers of 1,3-dimethylcyclohexane.

---

[1] Remember that each stereoisomer has two conformations that are in equilibrium. These conformations cannot be separated. Although the diaxial *trans* conformation is much higher in energy than either *cis* conformation, the diaxial *trans* conformation is present only in small quantity. Thus, the *trans* isomer is more stable than the *cis*.
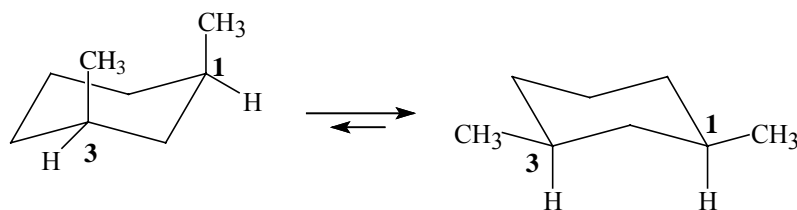
cis-1,3-Dimethylcyclohexane
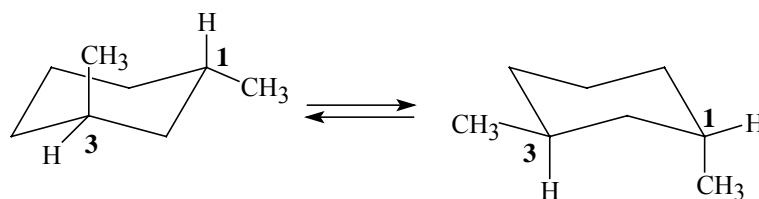
trans-1,3-Dimethylcyclohexane

For ease of comparison, rotate both stereoisomers so that C1 is in the back position of the chair conformation. Remember that for a *cis* stereoisomer of a dimethylcyclohexane both substituents either point up or point down, and for a *trans* stereoisomer, when one points up, the other points down.

Now flip the two stereoisomers between their two chair conformations. The *cis* stereoisomer of 1,3-dimethylcyclohexane has one chair conformation in which both methyl groups are equatorial and another in which both methyl groups are axial. The *trans* stereoisomer has two equivalent chair forms, with one axial and one equatorial methyl group in each. Following the rule that equatorial groups are more stable than axial groups, the *cis* stereoisomer is more stable than the *trans* stereoisomer. Data on the heats of combustion show that the difference is 1.7 kcal/mole.

Solved Exercise 3.2

a) Draw both chair conformations of *cis*-1,4-dimethylcyclohexane. Determine which chair conformation is most stable.

Solution: Notice that one methyl group is axial and the other is equatorial in either of the two conformations. Thus, they have the same energy level. To help visualize this, make a model.

cis-1,4-Dimethylcyclohexane
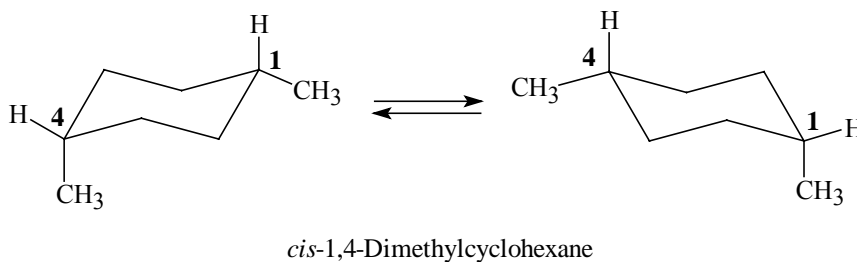
b) Repeat for the chair conformations of *trans*-1,4-dimethylcyclohexane.

Solution: In one conformation of the *trans* isomer, both methyl groups are equatorial, and in the other both methyl groups are axial. The conformation in which the two methyl groups are equatorial is much more stable than the one in which they are both axial.

*trans*-1,4-Dimethylcyclohexane
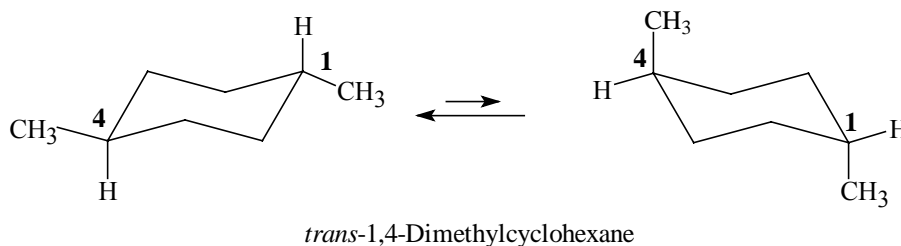
c) Which isomer is more stable?

Solution: The *trans* isomer is more stable because in one conformation, both methyl groups are equatorial. Both *cis* conformations have an axial methyl group and thus are less stable. The difference in energy is about 1.7 kcal/mole.

To determine the more stable stereoisomer for a disubstituted cyclohexane having two different substituents, follow the same rules that you use for a disubstituted cyclohexane having two identical groups. An additional rule is the more stable stereoisomer has the chair conformation with the larger substituent group in the equatorial position. This rule is of the greatest significance for a cyclohexane ring bearing a *tert*-butyl group. A *tert*-butyl group is by far the largest group that is usually attached to a cyclohexane ring. It is so large that it essentially stops any ring flipping at room temperature; that is, it "fixes" the ring in one conformation. This fixing of the ring is especially useful to chemists studying the detailed pathways of organic chemical reactions, as the molecule is unable to flip from one conformation to another.

Solved Exercise 3.3

Draw the two conformations of *cis*-1-ethyl-2-methylcyclohexane. Determine which is more stable.

Solution: Draw the two conformations.

cis-1-Ethyl-2-methylcyclohexane
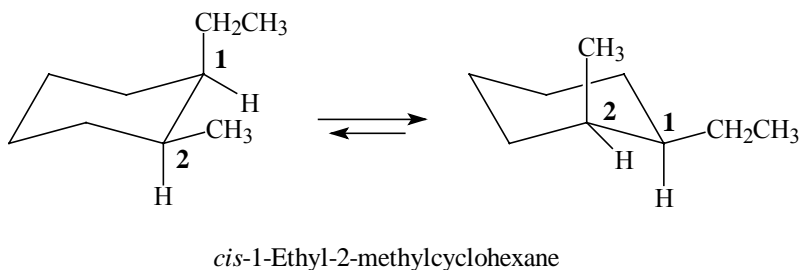
Both of these conformations have one group axial and one group equatorial. Because the ethyl group is slightly larger than the methyl group, the one with the ethyl group equatorial will have a slight preference.


Exercise 3.8

Write the structural formula for the more stable conformation of each of the following compounds. [**Hint**: See Table 3.1 (page 000) for selected van der Waals radii.]

> a) *trans*-1-Fluoro-3-methylcyclohexane
> b) *cis*-1-Iodo-4-methylcyclohexane
> c) *cis*-1-*tert*-Butyl-4-methylcyclohexane
> d) *cis*-1,3,5-Trimethylcyclohexane

Sample Solution

a) The *trans* stereoisomer of a 1,3-disubstituted cyclohexane has one substituent axial and one equatorial. Because the van der Waals radius of fluorine is much smaller than that of a methyl group, in the most stable conformation, the fluorine is axial, and the methyl group is equatorial.
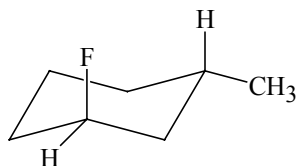
[Special Topic]

Computer Modeling

Computational chemistry is a new discipline in the field of chemistry. It began in a small way in the 1950s, but with the development of inexpensive and powerful computers in the 1980s, computational chemists have made significant contributions to chemical knowledge. Like other specialists in chemistry, computational chemists seek to understand chemical reactions, molecular structure, and chemical processes. Instead of using glassware and electronic instrumentation, their tools are computers and software.

Computational chemists predict the stability of chemical compounds, characterize their structures, and estimate the energy differences between their different energy states. In addition, they try to use these predictions to explain reaction pathways at the atomic level. In the long term, as chemists in the laboratory experimentally verify the results predicted by chemists on the computer, the computer models are refined and ultimately computer predictions can eliminate many time-consuming experiments.

The basis for the software tools of computational chemistry is empirical information. In the laboratory, chemists measure the properties of a number of molecules. They measure such things as the geometry of the molecules, their energy, charges or partial charges, and chemical reactivity. After they construct a database of these data, they analyze it to determine the mathematical relationships of the data. They then use these mathematical relationships to predict the values of those properties on new molecules. Next, they measure the properties of these new molecules in the laboratory, which either verifies the computational method or allows them to correct it. Because no one computational method yields accurate predictions in all cases, a number of computational methods have been developed. Understanding how the databases are constructed and the reliability of each computational method, chemists can choose the most appropriate method for a specific investigation understanding the limits of that method.

A typical molecular modeling program includes facilities for building and displaying two-dimensional representations of molecules. A well-defined structure is needed to calculate the properties of a molecule. This well-defined structure is a minimum energy conformation. The software has geometry optimizers to locate the nearest energy minimum to the structure the chemist drew. The local minimum is the lowest energy conformation nearest to the structure that was drawn. If, for example, the structure entered for cyclohexane looks more like a boat, the local minimum is a twist boat structure. Once a minimized structure is on the display, the bond or dihedral angles, bond lengths, and distances between different parts of a

molecule can be measured. Various chemical properties—such as molecular orbitals, acidities, and chemical reactivity—can also be explored.

⌨Exercise 3.9

Construct a model of *cis*-1,3-dimethylcyclohexane with both methyl groups axial. Minimize this structure. Using the computer fill in the first column of the following table. Make a model with both methyl groups equatorial. Minimize this structure. Fill in the second column of the table below.

Measurement	*cis*-1,3-Dimethylcyclohexane	
	Axial methyl groups	Equatorial methyl groups
The CH_3—C1—H bond angle.		
The CH_3—C1—C2 bond angle.		
The distance between the two CH_3s.		

Are your results reasonable in light of the discussion of conformational preferences in Section 3.10? Why or why not?

3.11 Conformations of Other Cycloalkanes

Conformational analysis of rings smaller than cyclohexane is considerably simpler than conformational analysis of rings larger than cyclohexane. This is because the smaller rings have much less conformational mobility and thus fewer possible conformations.

The smallest possible ring size for a cycloalkane is a ring containing three carbons—cyclopropane. If you can make a molecular model of cyclopropane without breaking your models, do so. The three atoms in cyclopropane define a plane that has no possibility of conformational isomers. Because the C—C—C bond angle is 60º, well away from the ideal tetrahedral angle, the angle strain is large.
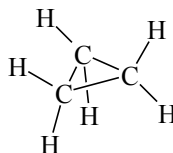
Cyclopropane

The data in Table 3.2 shows enormous bond angle strain that leads to a high heat of combustion. As a result of its high angle strain, cyclopropane is much less stable and, therefore, more reactive than the other cycloalkanes. With cyclopropane, the angle strain is of much greater importance than the torsional strain because all the hydrogens are eclipsed.

To achieve the maximum possible stability, the carbons in the cyclopropane ring overlap their bonding orbitals outside their internuclear axes. Unlike most carbon—carbon σ bonds, which are formed by overlap along the internuclear axis, the bonds in cyclopropane are formed by overlap at an angle that is slightly more than 20º outside the internuclear axis. See Figure 3.14. Chemists call these bonds "bent" bonds or sometimes "banana" bonds. Because the orbitals involved in forming the bent C—C bonds overlap outside the internuclear axes, the bonds are weaker than normal σ bonds.
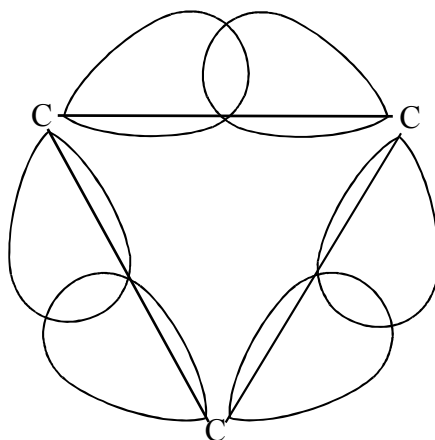
Figure 3.14. The orbitals that form the C—C bonds of cyclopropane do not lie along the internuclear axis. Chemists sometimes refer to these bonds as "bent," or "banana," bonds.

Cyclobutane has bent bonds similar to those in cyclopropane, but with considerably less bend. Again, make a model. Instead of overlapping 20º outside the internuclear axes, as in cyclopropane, cyclobutane's orbitals overlap about 7º outside the internuclear axes. In addition, cyclobutane adopts a folded conformation that relieves the
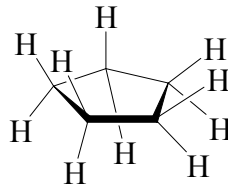
torsional strain of the eclipsed hydrogens. In this conformation, one of the carbon atoms bends out of the plane of the other three by about 20º.
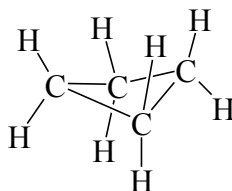
Folded conformation of cyclobutane.

Although this relieves the torsional strain, it does so at the expense of reducing the C—C—C bond angle from 90º to 88º for a planar cyclobutane.

Now make a model of cyclopentane. The amount of bond angle strain in the planar conformation of cyclopentane is small, because the C—C—C bond angle for a regular pentagon is 108º—very close to the tetrahedral angle. However, the amount of torsional strain is substantial, because all the hydrogens around the ring are eclipsed.

Planar cyclopentane showing eclipsed hydrogens.

The shape of the envelope conformation of cyclopentane is like the chair conformation without the footrest.

A nonplanar conformation in which one atom moves out of the plane of the other four relieves some, but not all, of this torsional strain. Chemists call this conformation the **envelope form** of cyclopentane.

Envelope form of cyclopentane
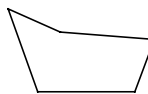
With pseudorotation the conformational changes involve all of the atoms in the ring one at a time.

Each of the carbon atoms in cyclopentane moves out of the plane of the ring for a very short period of time in turn. This movement, known as **pseudorotation**, relieves the eclipsing of the hydrogen atoms at least part of the time. Equilibrium between the various conformations of cyclopentane occurs at rates comparable to the rates of rotation around the carbon—carbon bond of ethane.

Exercise 3.10

Which is more stable, *cis-* or *trans*-1,2-dimethylcyclopropane? Explain your answer.

3.12 Naming Polycyclic Ring Systems

Polycyclic compounds are compounds with two or more rings. Generally, these rings share one or more common atoms.

Cyclic compounds that contain more than one ring are **polycyclic compounds**. The simplest polycyclic compounds contain rings that share either one or two carbons. Molecules made up of two rings with only one common atom are **spirocyclic**. Spiro[2.2]pentane is an example of a spirocyclic compound.

Spiro[2.2]pentane

Spirocyclic molecules have two or more rings. Each pair of rings shares one common atom.

It gets the name pentane because it has a total of five carbon atoms in the two rings. The numbers between the square brackets ([ ]) do not indicate positions of substituents but rather the lengths of the carbon chains connected to the common atom.

To add to your nomenclature skills from Chapter 2, here is how to name a spiro compound. Make a molecular model of the following compound to visualize each step:

Step 1 Determine the parent name of the compound by counting the total number of carbons in the polycyclic ring. This compound has eight, so it is an octane.
Step 2 Identify the carbon that is shared by both rings. It is marked with an asterisk (*) in the example.
Step 3 Determine the numbers that belong in the brackets by counting from, but not including, the shared carbon around the larger ring and then around the smaller ring.
Step 4 Use the prefix *spiro–* to indicate that it is a spirocyclic compound. Thus, the name of this compound is spiro[4.3]octane.
Step 5 Count around the smaller ring and then the larger ring. Begin with a carbon adjacent to the shared carbon.
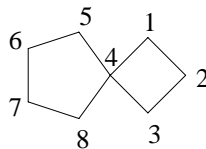
Step 6 Number the carbons first, then add any substituents. The following compound is 2,6,7-trimethylspiro[4.3]octane.
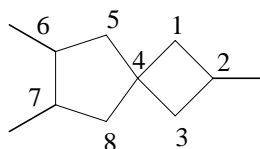

2,6,7-Trimethylspiro[4.3]octane

Bicyclic molecules are two rings sharing two atoms. These rings may be fused, sharing two adjacent atoms, or bridged, sharing atoms not adjacent to each other.

When two rings share two atoms, the compound is a **bicyclic compound**. The two types of bicyclic compounds are fused and bridged. A **fused bicyclic compound** has two rings joined by adjacent carbons. Make a model of bicyclo[3.2.0]heptane to help visualize a fused bicyclic compound.
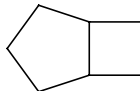
Bicyclo[3.2.0]heptane

In a **bridged bicyclic compound**, the shared carbons of the two rings are not adjacent carbons. Bicyclo[2.2.2]octane is an example of this type of compound.
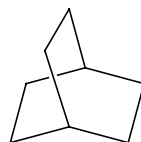
Bicyclo[2.2.2]octane

Here is how to name a bicyclic compound. Make a molecular model of the following compound to visualize each step:
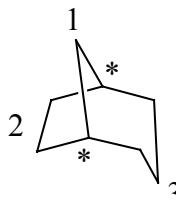
Bridgehead carbons are those carbons shared by both rings in the molecule.

Bridges are the segments of rings between the bridgehead carbons.

Step 1 Determine the parent name of the compound by counting the total number of carbons in the polycyclic ring. This compound has eight, so it is an octane.

Step 2 Identify the **bridgehead carbons**. They are marked by asterisks (*) above.

Step 3 Determine what numbers belong in the brackets.

   a. Count the number of carbons in each **bridge** between the bridgehead atoms.

   b. Arrange the numbers in decreasing order with periods between each number. For this compound, the longest bridge contains three carbons, the next longest two, and the shortest only one.

Step 4 Use the prefix *bicyclo–* to indicate that it is a compound containing two rings. Thus, the name of this example is bicyclo[3.2.1]octane.

Step 5 To number the carbons in a bicyclic compound, start with one bridgehead carbon and count around the longest bridge. Continue to the next longest bridge and finally to the smallest bridge.
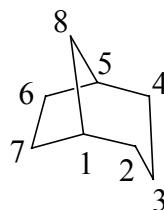
Bicyclo[3.2.1]octane

Step 6 After numbering the carbons, *then* add any substituents. This is true even for compounds with functional groups that would otherwise have high-priority numbering. For example, if there is a double bond between C6 and C7 in the previous compound, call it bicyclo[3.2.1]-6-octene.
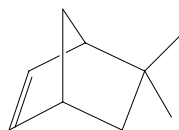
Bicyclo[3.2.1]-6-octene

Compounds with equal length bridges are numbered so that the highest priority substituent is given the lowest number. For example, the following compound is 5,5-dimethylbicyclo[2.2.1]-2-heptene.
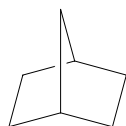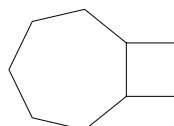

5,5-Dimethylbicyclo[2.2.1]-2-heptene

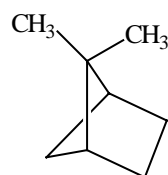
Exercise 3.11

Name each of the following compounds.

a)

b)

c)

d)

CH₃   CH₃
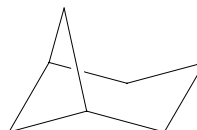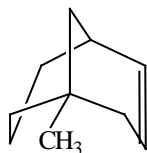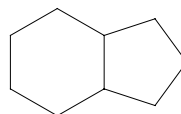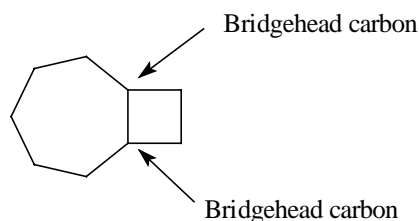

e)
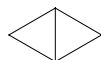
f)

g)

h)

Sample Solution

b) To name this compound, use the steps for naming a bicyclic compound.

   Step 1 Determine the name of the parent compound by counting all the carbons. There are nine, so the parent name is nonane.

   Step 2 Identify the bridgehead carbons.

Bridgehead carbon

Bridgehead carbon

   Step 3 Determine the numbers that go in the brackets by counting the number of carbons in each bridge and arranging them in decreasing order. The longest chain has five carbons, the next longest has two, and the shortest none. Thus, the numbers are [5.2.0].
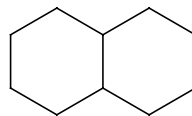
5   0   2
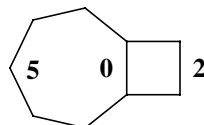
   Step 4 Use the prefix *bicyclo–*.
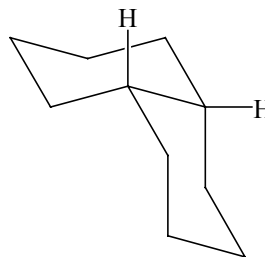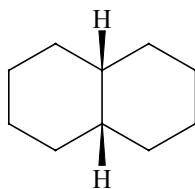   The name of the compound is bicyclo[5.2.0]nonane.

3.13 Stereochemistry of Polycyclic Ring Systems

The rings in a bicyclic compound can be joined in more than one way, forming stereoisomers. For example, the bicyclic compound decalin has two stereoisomers.
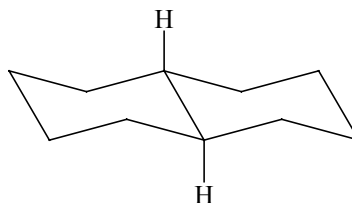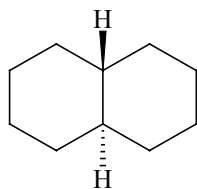
Decalin
(Bicyclo[4.4.0]decane)

Make models of *cis-* and *trans*-decalin (bicyclo[4.4.0]decane).

cis-Decalin

trans-Decalin

　　　　The stereochemistry of *cis-* and *trans*-decalin is essentially the same as that of *cis-* and *trans*-1,2-dimethylcyclohexane (Section 3.9) if you visualize one of the rings in decalin as a cyclohexane and the other ring as two substituents on the first ring. That is, you must temporarily ignore the other atoms of the second ring.
　　　　The two rings of *cis*-decalin undergo ring flips, just like *cis*-1,2-dimethylcyclohexane. However, in *trans*-decalin, the two rings cannot flip between alternate chair conformations; they must always stay with the carbons equatorial to each other. To understand this, first remember that an equatorial substituent of a *trans* stereoisomer becomes axial after a ring flip, and vice versa. Try doing a ring flip with your *trans*-decalin—be careful, don't break your models! Now detach a C—C bond in one of the rings, and do a ring flip on the other ring. Both C—C bonds from the ring junction are axial, and the distance between the two positions is much too great for bonding to occur between them.

Exercise 3.12

a) Using your molecular model set, construct a model of bicyclo-[3.1.0]hexane. Is the ring junction *cis* or *trans*? Can the other ring junction exist? (Don't break your models!)

b) What is the smallest value of *n* to make a bicyclo[*n*.1.0]alkane with that *trans* ring junction? What is the smallest value of *n* for a bicyclo[*n*.*n*.0] alkane with a *trans* ring junction?

Cyclohexene and other small cycloalkenes always have a *cis* double bond. Make a model of *trans*-cyclohexene to better understand why. The bond angles around the C=C double bond are such that with only four other carbons in the ring it is difficult to form a ring from one side of the double bond C1 to the other side of the double bond C2. To do so introduces a great amount of strain on the π bond—any rotation of the bond reduces the efficiency of the overlap of the *p* orbitals, thus, producing a weaker bond. The smallest *trans*-cycloalkene stable enough to be isolated is *trans*-cyclooctene. However, it does have a strain energy of about 10 kcal/mole, when compared to *cis*-cyclooctene.

Bredt's rule states that a bridged bicyclic molecule with small rings cannot have a double bond involving one of the bridgehead carbons.

According to **Bredt's Rule**, a bicyclic compound with a double bond to a bridgehead carbon that is a part of a small ring is unstable. Bicyclo[2.2.1]-1(2)-heptene, an example of a compound that incorporates a *trans*-cyclohexene ring and illustrates Bredt's Rule, is so unstable that no one has ever isolated it. (Note the -1(2)- portion of the name. This states that the double bond is between C1 and C2.)
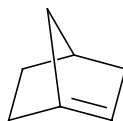
Bicyclo[2.2.1]-1(2)-heptene

Attempt to make a model of it, but note the impossibility of connecting the bridge consisting of only one carbon to the double bond. Also, the sp^2 hybridized carbon at the bridgehead cannot be planar in this structure.

[SIDEBAR]

Higher Polycyclic Structures

Chemists have long been fascinated with imagining, synthesizing, and studying molecules whose structures have some

particularly attractive symmetry, or reminds the chemist of some familiar or not so familiar object, or simply intrigues the chemist. Sometimes there is a rational justification for making such a molecule; at other times, perhaps, it is synthesized for the same reason people climb mountains—because it is there.

Consider the structure of pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane:
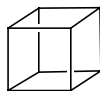
Pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane

Because its enchanting symmetry had intrigued chemists for years, there was great excitement when, in 1964, Philip Eaton's research group at the University of Chicago successfully synthesized it. This eight-carbon structure deserves its descriptive euonym (a name well suited to the person, place, or thing) cubane.

Chemists often give euonyms to the molecules they synthesize. They do so because euonyms are much easier to say than IUPAC names—even chemists like doing things the easy way. Compare saying "cubane" with saying "pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane". The name cubane also allows you to visualize the shape of the molecule much more readily than does the IUPAC name.

A wide variety of euonyms represent not only geometrical shapes, but other things as well like musical instruments, persons, mechanical devices, animals, and many other items. Some names have obvious origins; others don't.

Another euonym that brings to mind the structure it names is basketene:
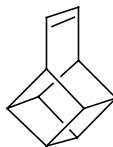
Basketene

The research group of Satoru Masamune at the University of Alberta first synthesized this molecule in 1966. It received its name from its obvious similarity to a basket. Not to mention that basketene is far easier to say than pentacyclo[. . .]decene. For practice, you might try filling in the numbers for the IUPAC name. Beware: it isn't easy.

Here's an example bound to become a favorite of animal lovers. The structure of tetracyclo[4.4.0.0^{2,9}.0^{5,8}]-3-decene is often drawn as follows:
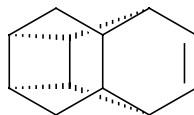
Tetracyclo[4.4.0.0^{2,9}.0^{5,8}]-3-decene

To help yourself visualize the molecule, make a model. The basis for its descriptive euonym becomes much more apparent if you rotate the structure by 90º.
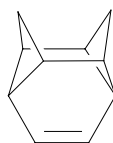
After redrawing it, and taking a little artistic license, it becomes the smiling face of a cat.
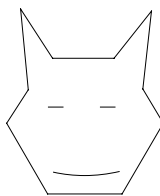
Thus, this molecule was given the name *felicene (felis* is Latin for cat) in the research group of Andrew Gilbert at England's University of Reading in 1976.

Key Ideas from Chapter 3

❏   Wedge-and-dash representations and Newman projections are both ways of visualizing three-dimensional molecules in two dimensions.

❏   As atoms or groups of atoms that are connected by carbon—carbon single bonds rotate relative to each other, different conformations result. Conformations differ only in the spatial arrangement of the atoms.

❏   There are an infinite number of conformations for any carbon—carbon single bond, but this book covers only the two extremes:

the staggered and eclipsed forms. In the staggered form, the torsional angle between attached groups is at 60º. In the eclipsed form, it is at 0º.

❏   A staggered conformation of ethane or butane has a lower rotational energy than the eclipsed conformation.

❏   Except for cyclopropane, all cycloalkanes have nonplanar rings. The nonplanar conformations relieve the torsional strain that would result from eclipsed substituents and the angle strain that would be present in the planar form.

❏   The most stable form of cyclohexane is the chair conformation. In this form, the molecule has both axial and equatorial substituents. Cyclohexane undergoes a chair-boat-chair ring flip in which the axial substituents become equatorial, and vice versa.

❏   Cyclohexanes with axial substituents are less stable than those with the same substituents equatorial, because of unfavorable interactions among axial substituents.

❏   Spirocyclic compounds are those in which two rings share a common atom.

❏   Bicyclic compounds contain two rings that share two or more common atoms. If the common atoms are adjacent (there is a bond between the bridgehead carbons), the compound is a fused bicyclic compound. If the common atoms are not adjacent (there is no bond between the bridgehead carbons), the compound is a bridged bicyclic compound.

❏   Small cyclic alkenes are stable only when they contain a *cis* double bond. A *trans*-cycloalkene is unstable unless the ring has eight or more carbons.