Table 2.8	Solubilities of Alkyl Halides in Water		
CH_3F **very soluble**	CH_3Cl **soluble**	CH_3Br **slightly soluble**	CH_3I **slightly soluble**
CH_3CH_2F **soluble**	CH_3CH_2Cl **slightly soluble**	CH_3CH_2Br **slightly soluble**	CH_3CH_2I **slightly soluble**
$CH_3CH_2CH_2F$ **slightly soluble**	$CH_3CH_2CH_2Cl$ **slightly soluble**	$CH_3CH_2CH_2Br$ **slightly soluble**	$CH_3CH_2CH_2I$ **slightly soluble**
$CH_3CH_2CH_2CH_2F$ **insoluble**	$CH_3CH_2CH_2CH_2Cl$ **insoluble**	$CH_3CH_2CH_2CH_2Br$ **insoluble**	$CH_3CH_2CH_2CH_2I$ **insoluble**

PROBLEM 24◆

Rank the following groups of compounds in order of decreasing solubility in water:

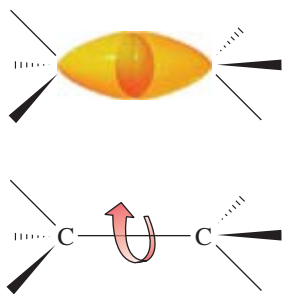a. $CH_3CH_2CH_2OH$ $CH_3CH_2CH_2CH_2Cl$ $CH_3CH_2CH_2CH_2OH$

$HOCH_2CH_2CH_2OH$

b.   CH₃   NH₂   OH

PROBLEM 25◆

In which of the following solvents would cyclohexane have the lowest solubility: pentanol, diethyl ether, ethanol, or hexane?

2.10 Conformations of Alkanes: Rotation About Carbon–Carbon Bonds

▲ **Figure 2.3**
A carbon–carbon bond is formed by the overlap of cylindrically symmetrical sp^3 orbitals. Therefore, rotation about the bond can occur without changing the amount of orbital overlap.
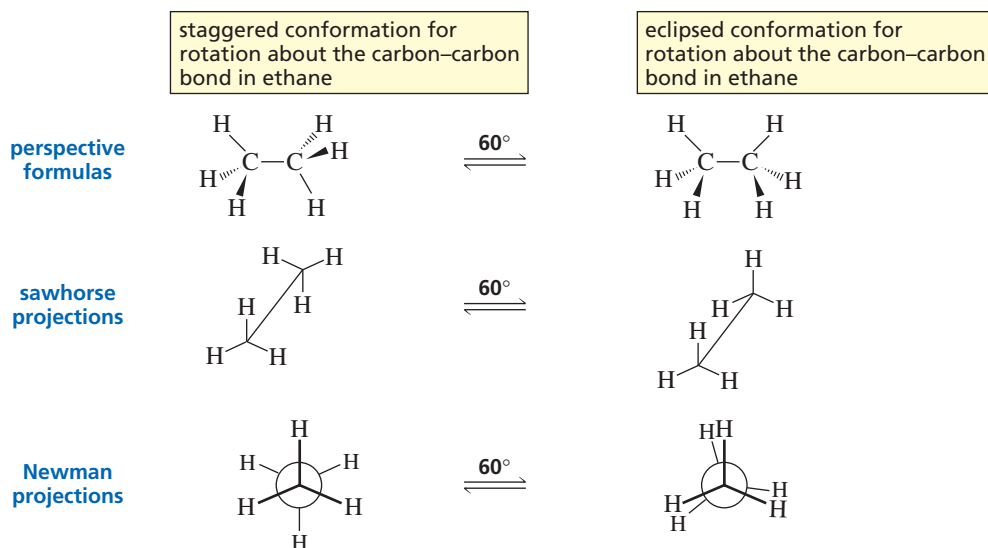
We have seen that a carbon–carbon single bond (a σ bond) is formed when an sp^3 orbital of one carbon overlaps an sp^3 orbital of a second carbon (Section 1.7). Because σ bonds are cylindrically symmetrical (i.e., symmetrical about an imaginary line connecting the centers of the two atoms joined by the σ bond), rotation about a carbon–carbon single bond can occur without any change in the amount of orbital overlap (Figure 2.3). The different spatial arrangements of the atoms that result from rotation about a single bond are called **conformations**. A specific conformation is called a **conformer**.

When rotation occurs about the carbon–carbon bond of ethane, two extreme conformations can result—a *staggered conformation* and an *eclipsed conformation*. An infinite number of conformations between these two extremes are also possible.

Compounds are three dimensional, but we are limited to a two-dimensional sheet of paper when we show their structures. Perspective formulas, sawhorse projections, and Newman projections are methods chemists commonly use to represent on paper the three-dimensional spatial arrangements of the atoms that result from rotation about a σ bond. In a **perspective formula**, solid lines are used for bonds that lie in the plane of the paper, solid wedges for bonds protruding out from the plane of the paper, and hatched wedges for bonds extending behind the paper. In a **sawhorse projection**, you are looking at the carbon–carbon bond from an oblique angle. In a **Newman projection**, you are looking down the length of a particular carbon–carbon bond. The carbon in front is represented by the point at which three bonds intersect, and the carbon in back is represented by a circle. The three lines emanating from each of the carbons represent its other three bonds. In discussing the conformations of alkanes, we

will use Newman projections because they are easy to draw and they do a good job of representing the spatial relationships of the substituents on the two carbon atoms.

Melvin S. Newman (1908–1993) *was born in New York. He received a Ph.D. from Yale University in 1932 and was a professor of chemistry at Ohio State University from 1936 to 1973.*

staggered conformation for rotation about the carbon–carbon bond in ethane

eclipsed conformation for rotation about the carbon–carbon bond in ethane

perspective formulas

sawhorse projections

Newman projections

The electrons in a C—H bond will repel the electrons in another C—H bond if the bonds get too close to each other. The **staggered conformation**, therefore, is the most stable conformation of ethane because the C—H bonds are as far away from each other as possible. The **eclipsed conformation** is the least stable conformation because in no other conformation are the C—H bonds as close to one another. The extra energy of the eclipsed conformation is called *torsional strain*. **Torsional strain** is the name given to the repulsion felt by the bonding electrons of one substituent as they pass close to the bonding electrons of another substituent. The investigation of the various conformations of a compound and their relative stabilities is called **conformational analysis**.

Rotation about a carbon–carbon single bond is not completely free because of the energy difference between the staggered and eclipsed conformers. The eclipsed conformer is higher in energy, so an energy barrier must be overcome when rotation about the carbon–carbon bond occurs (Figure 2.4). However, the barrier in ethane is small

3-D Molecule: Staggered and eclipsed conformations of ethane

2.9 kcal/mol or 12 kJ/mol

eclipsed conformers

staggered conformers
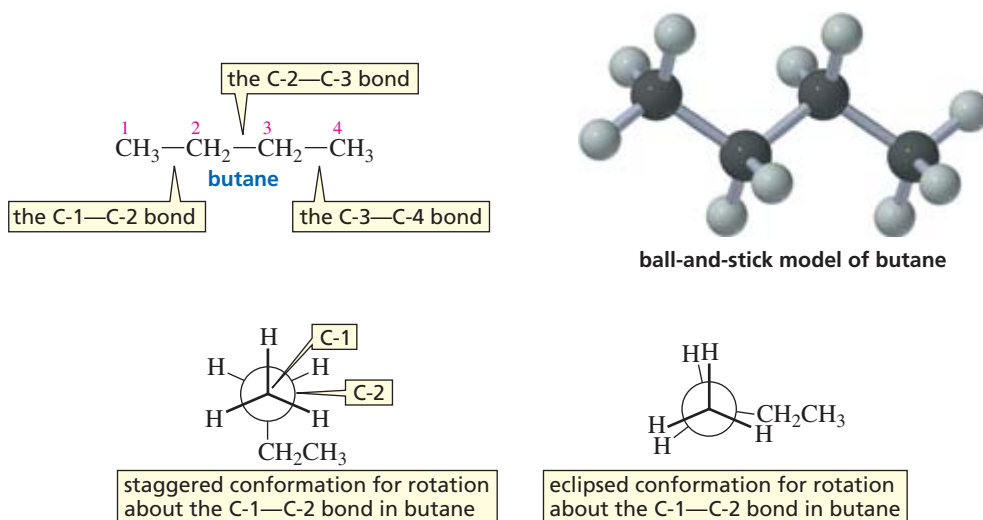
Potential energy

Degrees of rotation
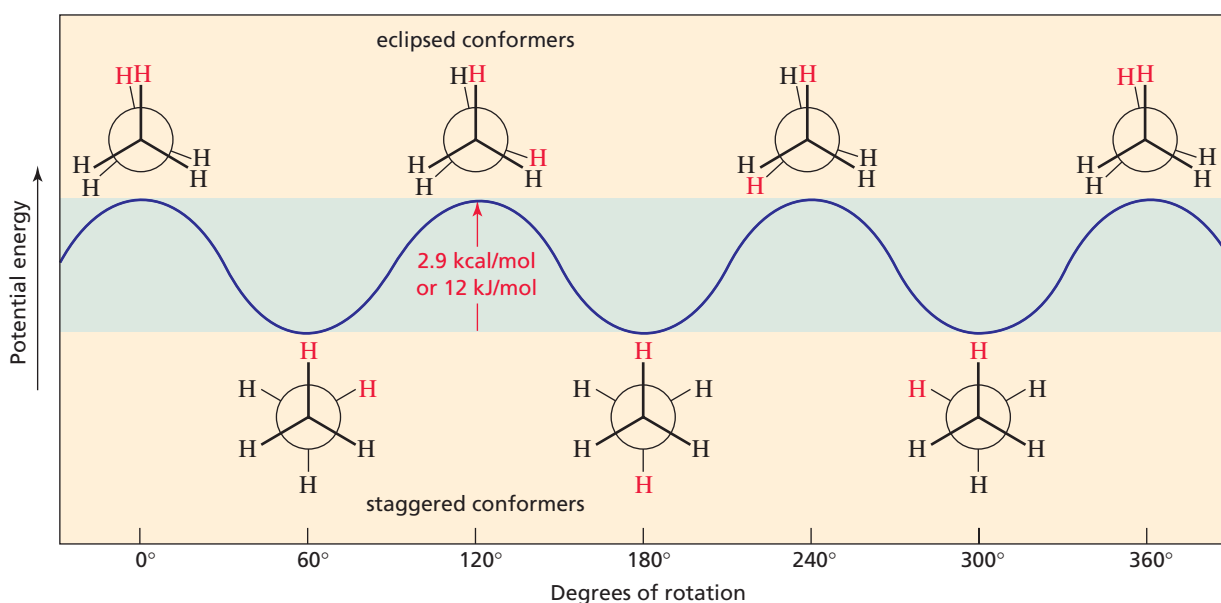
▲ **Figure 2.4**
Potential energy of ethane as a function of the angle of rotation about the carbon–carbon bond.

enough (2.9 kcal/mol or 12 kJ/mol) to allow the conformers to interconvert millions of times per second at room temperature. Because the conformers interconvert, they cannot be separated.

Figure 2.4 shows the potential energies of all the conformers of ethane obtained during one complete 360° rotation. Notice that the **staggered conformers** are at energy minima, whereas the **eclipsed conformers** are at energy maxima.

Butane has three carbon–carbon single bonds, and the molecule can rotate about each of them. In the following figure, staggered and eclipsed conformers are drawn for rotation about the C-1—C-2 bond:

the C-2—C-3 bond

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$$
butane

the C-1—C-2 bond   the C-3—C-4 bond

ball-and-stick model of butane

staggered conformation for rotation about the C-1—C-2 bond in butane

eclipsed conformation for rotation about the C-1—C-2 bond in butane
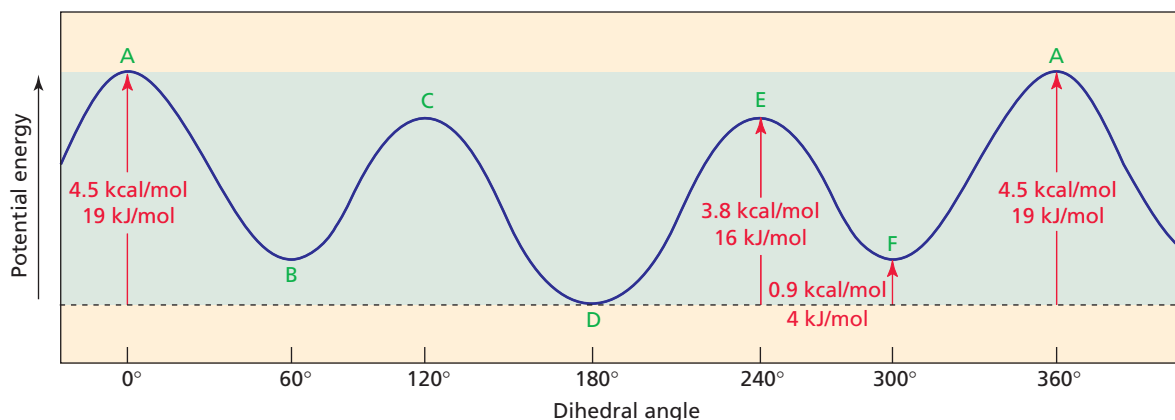
Note that the carbon in the foreground in a Newman projection has the lower number. Although the staggered conformers resulting from rotation about the C-1—C-2 bond in butane all have the same energy, the staggered conformers resulting from rotation about the C-2—C-3 bond do not have the same energy. The staggered conformers for rotation about the C-2—C-3 bond in butane are shown below.

A	B	C	D	E	F	A
	gauche		**anti**		**gauche**	
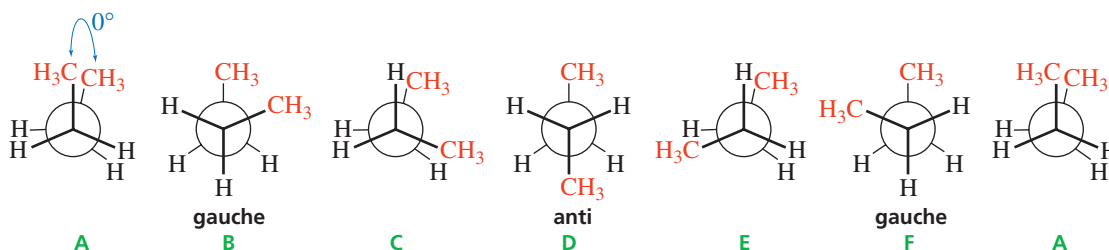
Conformer D, in which the two methyl groups are as far apart as possible, is more stable than the other two staggered conformers (B and F). The most stable of the staggered conformers (D) is called the **anti conformer**, and the other two staggered conformers (B and F) are called **gauche** ("goesh") **conformers**. (*Anti* is Greek for "opposite of"; *gauche* is French for "left.") In the anti conformer, the largest substituents are opposite each other; in a gauche conformer, they are adjacent. The two gauche conformers have the same energy, but each is less stable than the anti conformer.

Anti and gauche conformers do not have the same energy because of steric strain. **Steric strain** is the strain (i.e., the extra energy) put on a molecule when atoms or groups are too close to one another, which results in repulsion between the electron

Potential energy

4.5 kcal/mol
19 kJ/mol

3.8 kcal/mol
16 kJ/mol

4.5 kcal/mol
19 kJ/mol

0.9 kcal/mol
4 kJ/mol

A   C   E   A
B   D   F

0°   60°   120°   180°   240°   300°   360°

Dihedral angle

▲ **Figure 2.5**
Potential energy of butane as a function of the degree of rotation about the C-2—C-3
bond. Green letters refer to the conformers (A–F) shown on page 90.
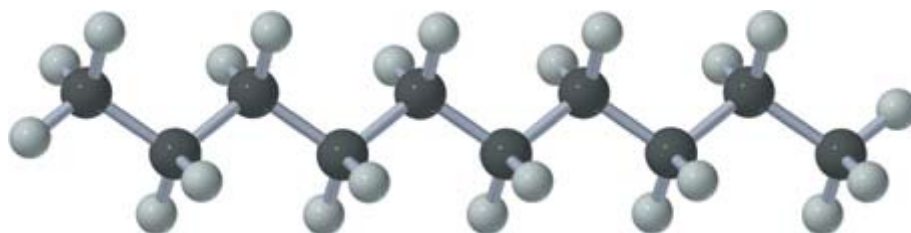
Movie:
Potential energy of butane
conformers

clouds of these atoms or groups. For example, there is more steric strain in a gauche
conformer than in the anti conformer because the two methyl groups are closer togeth-
er in a gauche conformer. This type of steric strain is called a **gauche interaction**.

The eclipsed conformers resulting from rotation about the C-2—C-3 bond in bu-
tane also have different energies. The eclipsed conformer in which the two methyl
groups are closest to each other (A) is less stable than the eclipsed conformers in
which they are farther apart (C and E). The energies of the conformers obtained from
rotation about the C-2—C-3 bond of butane are shown in Figure 2.5. (The dihedral
angle is the angle between the CH_3—C—C and C—C—CH_3 planes. Therefore,
the conformer in which one methyl group stands directly in front of the other—the
least stable conformer—has a dihedral angle of 0°.) All the eclipsed conformers have
both torsional and steric strain—torsional strain due to bond–bond repulsion and steric
strain due to the closeness of the groups. In general, steric strain in molecules increas-
es as the size of the group increases.

Because there is continuous rotation about all the carbon–carbon single bonds in a
molecule, organic molecules with carbon–carbon single bonds are not static balls and
sticks—they have many interconvertible conformers. The conformers cannot be sepa-
rated, however, because their small energy difference allows them to interconvert
rapidly.

The relative number of molecules in a particular conformation at any one time de-
pends on the stability of the conformation: The more stable the conformation, the
greater is the fraction of molecules that will be in that conformation. Most molecules,
therefore, are in staggered conformations, and more molecules are in an anti confor-
mation than in a gauche conformation. The tendency to assume a staggered conforma-
tion causes carbon chains to orient themselves in a zigzag fashion, as shown by the
ball-and-stick model of decane.

3-D Molecule:
Decane

ball-and-stick model of decane

PROBLEM 26

a. Draw all the staggered and eclipsed conformers that result from rotation about the C-2—C-3 bond of pentane.

b. Draw a potential-energy diagram for rotation of the C-2—C-3 bond of pentane through 360°, starting with the least stable conformer.

PROBLEM 27◆

Using Newman projections, draw the most stable conformer for the following:

a. 3-methylpentane, considering rotation about the C-2—C-3 bond

b. 3-methylhexane, considering rotation about the C-3—C-4 bond

c. 3,3-dimethylhexane, considering rotation about the C-3—C-4 bond

## 2.11 Cycloalkanes: Ring Strain

Early chemists observed that cyclic compounds found in nature generally had five- or six-membered rings. Compounds with three- and four-membered rings were found much less frequently. This observation suggested that compounds with five- and six-membered rings were more stable than compounds with three- or four-membered rings.

In 1885, the German chemist Adolf von Baeyer proposed that the instability of three- and four-membered rings was due to angle strain. We know that, ideally, an sp^3 hybridized carbon has bond angles of 109.5° (Section 1.7). Baeyer suggested that the stability of a cycloalkane could be predicted by determining how close the bond angle of a planar cycloalkane is to the ideal tetrahedral bond angle of 109.5°. The angles in an equilateral triangle are 60°. The bond angles in cyclopropane, therefore, are compressed from the ideal bond angle of 109.5° to 60°, a 49.5° deviation. This deviation of the bond angle from the ideal bond angle causes strain called **angle strain**.

The angle strain in a three-membered ring can be appreciated by looking at the orbitals that overlap to form the σ bonds in cyclopropane (Figure 2.6). Normal σ bonds are formed by the overlap of two sp^3 orbitals that point directly at each other. In cyclopropane, overlapping orbitals cannot point directly at each other. Therefore, the orbital overlap is less effective than in a normal C—C bond. The less effective orbital overlap is what causes angle strain, which in turn causes the C—C bond to be weaker than a normal C—C bond. Because the C—C bonding orbitals in cyclopropane can't point directly at each other, they have shapes that resemble bananas and, consequently, are often called **banana bonds**. In addition to possessing angle strain, three-membered rings have torsional strain because all the adjacent C—H bonds are eclipsed.

The bond angles in planar cyclobutane would have to be compressed from 109.5° to 90°, the bond angle associated with a planar four-membered ring. Planar cyclobutane would then be expected to have less angle strain than cyclopropane because the bond angles in cyclobutane are only 19.5° away from the ideal bond angle.
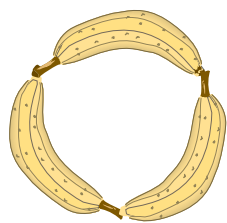
banana bonds

Figure 2.6 ▶
(a) Overlap of sp^3 orbitals in a normal σ bond. (b) Overlap of sp^3 orbitals in cyclopropane.

a.

good overlap
strong bond

b.

poor overlap
weak bond
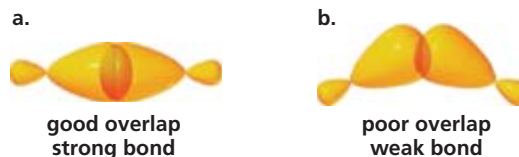
PROBLEM 28◆

The bond angles in a regular polygon with n sides are equal to

$$180° - \frac{360°}{n}$$

a. What are the bond angles in a regular octagon?

b. In a regular nonagon?

HIGHLY STRAINED HYDROCARBONS

Organic chemists have been able to synthesize some highly strained cyclic hydrocarbons, such as bicyclo[1.1.0]butane, cubane, and prismane.[1] Philip Eaton, the first to synthesize cubane, recently also synthesized octanitro- cubane—cubane with an NO_2 group bonded to each of the eight corners. This compound is expected to be the most powerful explosive known.[2]

bicyclo[1.1.0]butane   **cubane**   **prismane**

[1]Bicyclo[1.1.0]butane was synthesized by David Lemal, Fredric Menger, and George Clark at the University of Wisconsin (*Journal of the American Chemical Society*, 1963, *85*, 2529). Cubane was synthesized by Philip Eaton and Thomas Cole, Jr., at the University of Chicago (*Journal of the American Chemical Society*, 1964, *86*, 3157). Prismane was synthesized by Thomas Katz and Nancy Acton at Columbia University (*Journal of the American Chemical Society*, 1973, *95*, 2738).

[2]Mao-Xi Zhang, Philip Eaton, and Richard Gilardi, *Angew. Chem. Int. Ed.*, 2000, *39 (2)*, 401.

Baeyer predicted that cyclopentane would be the most stable of the cycloalkanes because its bond angles (108°) are closest to the ideal tetrahedral bond angle. He predicted that cyclohexane, with bond angles of 120°, would be less stable and that as the number of sides in the cycloalkanes increases, their stability would decrease.

"planar" cyclopentane
bond angles = 108°

"planar" cyclohexane
bond angles = 120°

"planar" cycloheptane
bond angles = 128.6°

cyclopropane

Contrary to what Baeyer predicted, cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of sides increases. The mistake Baeyer made was to assume that all cyclic molecules are planar. Because three points define a plane, the carbons of cyclopropane must lie in a plane. The other cycloalkanes, however, are not planar. Cyclic compounds twist and bend in order to attain a structure that minimizes the three different kinds of strain that can destabilize a cyclic compound:

1. *Angle strain* is the strain induced in a molecule when the bond angles are different from the ideal tetrahedral bond angle of 109.5°.

2. *Torsional strain* is caused by repulsion between the bonding electrons of one substituent and the bonding electrons of a nearby substituent.

3. *Steric strain* is caused by atoms or groups of atoms approaching each other too closely.

cyclobutane

Although planar cyclobutane would have less angle strain than cyclopropane, it could have more torsional strain because it has eight pairs of eclipsed hydrogens, compared with the six pairs of cyclopropane. So cyclobutane is not a planar molecule—it is a bent molecule. One of its methylene groups is bent at an angle of about 25° from the plane defined by the other three carbon atoms. This increases the angle strain, but the increase is more than compensated for by the decreased torsional strain as a result of the adjacent hydrogens not being as eclipsed, as they would be in a planar ring.
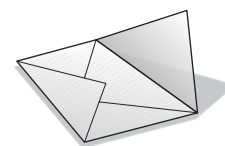
If cyclopentane were planar, as Baeyer had predicted, it would have essentially no angle strain, but its 10 pairs of eclipsed hydrogens would be subject to considerable torsional strain. So cyclopentane puckers, allowing the hydrogens to become nearly staggered. In the process, however, it acquires some angle strain. The puckered form of cyclopentane is called the *envelope conformation* because the shape resembles a squarish envelope with the flap up.
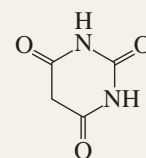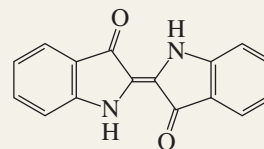
cyclopentane

VON BAEYER AND BARBITURIC ACID

Johann Friedrich Wilhelm Adolf von Baeyer (1835–1917) was born in Germany. He discovered barbituric acid—the first of a group of sedatives known as barbiturates—in 1864 and named it after a woman named Barbara. Who Barbara was is not certain. Some say she was his girlfriend, but because Baeyer discovered barbituric acid in the same year that Prussia defeated Denmark, some believe he named the acid after Saint Barbara, the patron saint of artillerymen. Baeyer was the first to synthesize indigo, the dye used in the manufacture of blue jeans. He was a professor of chemistry at the University of Strasbourg and later at the University of Munich. He received the Nobel Prize in chemistry in 1905 for his work in synthetic organic chemistry.
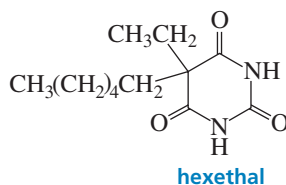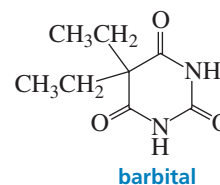
barbituric acid

indigo

3-D Molecules:
Cyclopropane; Cyclobutane;
Cyclopentane

PROBLEM 29◆

The effectiveness of a barbiturate as a sedative is related to its ability to penetrate the non-polar membrane of a cell. Which of the following barbiturates would you expect to be the more effective sedative?

hexethal

barbital

2.12 Conformations of Cyclohexane

The cyclic compounds most commonly found in nature contain six-membered rings because such rings can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation** (Figure 2.7). In the chair conformer of cyclohexane, all the bond angles are 111°, which is very close to the ideal tetrahedral bond angle of 109.5°, and all the adjacent bonds are staggered. The chair conformer is such an important conformer that you should learn how to draw it:

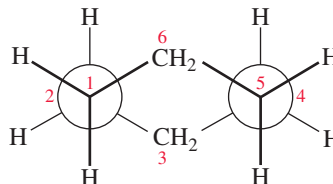1. Draw two parallel lines of the same length, slanted upward. Both lines should start at the same height.

Figure 2.7 ▶
The chair conformer of cyclohexane, a Newman projection of the chair conformer, and a ball-and-stick model showing that all the bonds are staggered.
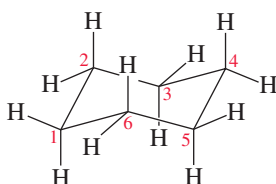
chair conformer of
cyclohexane

Newman projection of
the chair conformer

ball-and-stick model of the
chair conformer of cyclohexane

2. Connect the tops of the lines with a V; the left-hand side of the V should be slightly longer than the right-hand side. Connect the bottoms of the lines with an inverted V; the lines of the V and the inverted V should be parallel. This completes the framework of the six-membered ring.

3. Each carbon has an axial bond and an equatorial bond. The **axial bonds** (red lines) are vertical and alternate above and below the ring. The axial bond on one of the uppermost carbons is up, the next is down, the next is up, and so on.
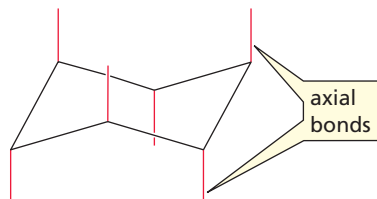
axial bonds

4. The **equatorial bonds** (red lines with blue balls) point outward from the ring. Because the bond angles are greater than 90°, the equatorial bonds are on a slant. If the axial bond points up, the equatorial bond on the same carbon is on a downward slant. If the axial bond points down, the equatorial bond on the same carbon is on an upward slant.
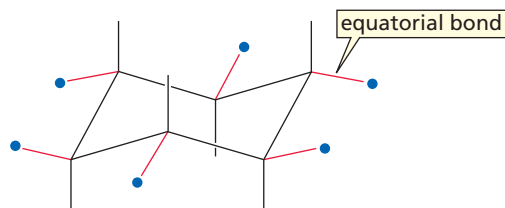
equatorial bond

Notice that each equatorial bond is parallel to two ring bonds (two carbons over) and parallel to the opposite equatorial bond.
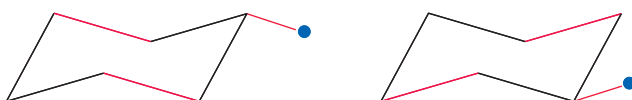
Remember that cyclohexane is viewed on edge. The lower bonds of the ring are in front and the upper bonds of the ring are in back.

▲ = axial bond
● = equatorial bond

3-D Molecule:
Chair cyclohexane
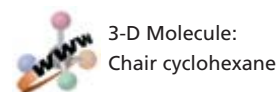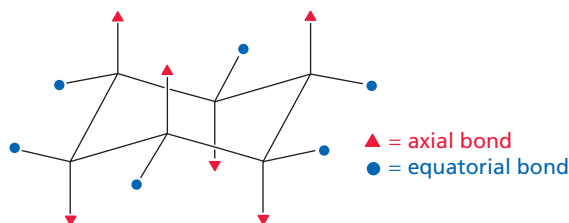
PROBLEM 30

Draw 1,2,3,4,5,6-hexamethylcyclohexane with

a. all the methyl groups in axial positions

b. all the methyl groups in equatorial positions

Table 2.9   Heats of Formation and Total Strain Energies of Cycloalkanes

	Heat of formation		"Strainless" heat of formation		Total strain energy	
	(kcal/mol)	(kJ/mol)	(kcal/mol)	(kJ/mol)	(kcal/mol)	(kJ/mol)
Cylopropane	+12.7	53.1	−14.6	−61.1	27.3	114.2
Cyclobutane	+6.8	28.5	−19.7	−82.4	26.5	110.9
Cyclopentane	−18.4	−77.0	−24.6	−102.9	6.2	25.9
Cyclohexane	−29.5	−123.4	−29.5	−123.4	0	0
Cycloheptane	−28.2	−118.0	−34.4	−143.9	6.2	25.9
Cyclooctane	−29.7	−124.3	−39.4	−164.8	9.7	40.6
Cyclononane	−31.7	−132.6	−44.3	−185.4	12.6	52.7
Cyclodecane	−36.9	−154.4	−49.2	−205.9	12.3	51.5
Cycloundecane	−42.9	−179.5	−54.1	−226.4	11.2	46.9

If we assume that cyclohexane is completely free of strain, we can calculate the total strain energy (angle strain + torsional strain + steric strain) of the other cycloalkanes. Taking the *heat of formation* of cyclohexane (Table 2.9) and dividing by 6 for its six CH_2 groups gives us a value of −4.92 kcal/mol (or −20.6 kJ/mol) for a "strainless" CH_2 group ($-29.5/6 = -4.92$). (The **heat of formation** is the heat given off when a compound is formed from its elements under standard conditions.) We can now calculate the heat of formation of a "strainless" cycloalkane by multiplying the number of CH_2 groups in its ring by −4.92 kcal/mol. The total strain in the compound is the difference between its "strainless" heat of formation and its actual heat of formation (Table 2.9). For example, cyclopentane has a "strainless" heat of formation of $(5)(-4.92) = -24.6$ kcal/mol. Because its actual heat of formation is −18.4 kcal/mol, cyclopentane has a total strain energy of 6.2 kcal/mol $[-18.4 - (-24.6) = 6.2]$. (Multiplying by 4.184 converts kcal into kJ.)
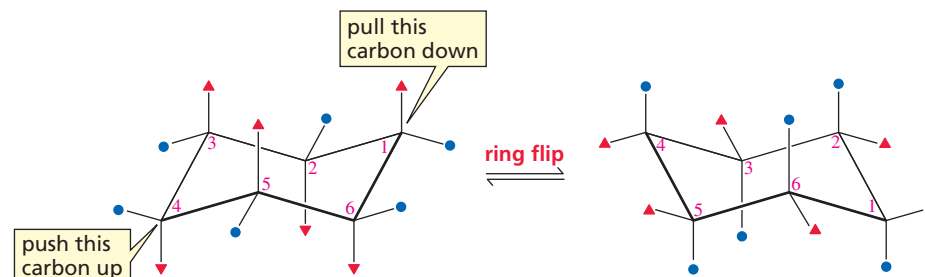
PROBLEM 31◆
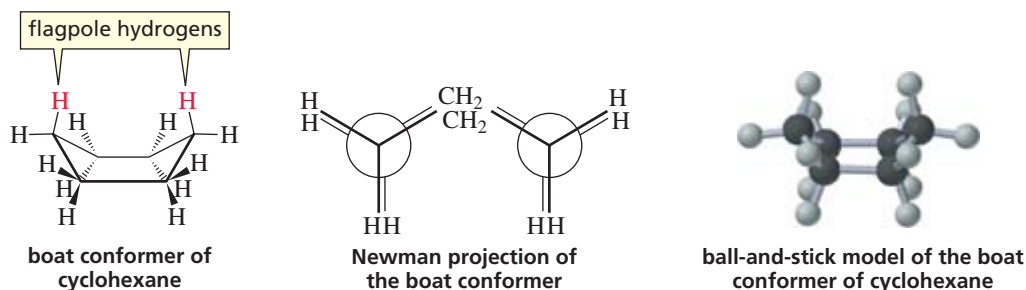
Calculate the total strain energy of cycloheptane.

Cyclohexane rapidly interconverts between two stable chair conformations because of the ease of rotation about its carbon–carbon bonds. This interconversion is known as **ring flip** (Figure 2.8). When the two chair conformers interconvert, bonds that are equatorial in one chair conformer become axial in the other chair conformer and vice versa.

Bonds that are equatorial in one chair conformer are axial in the other chair conformer.
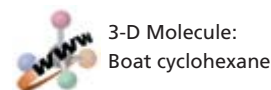
Figure 2.8 ▶
The bonds that are axial in one chair conformer are equatorial in the other chair conformer. The bonds that are equatorial in one chair conformer are axial in the other chair conformer.

flagpole hydrogens

boat conformer of
cyclohexane

Newman projection of
the boat conformer

ball-and-stick model of the boat
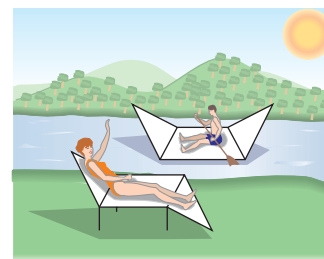conformer of cyclohexane

▲ **Figure 2.9**
The boat conformer of cyclohexane, a Newman projection of the boat conformer, and a
ball-and-stick model showing that some of the bonds are eclipsed.

3-D Molecule:
Boat cyclohexane

Cyclohexane can also exist in a **boat conformation**, shown in Figure 2.9. Like the chair conformer, the boat conformer is free of angle strain. However, the boat conformer is not as stable as the chair conformer because some of the bonds in the boat conformer are eclipsed, giving it torsional strain. The boat conformer is further destabilized by the close proximity of the **flagpole hydrogens** (the hydrogens at the "bow" and "stern" of the boat), which causes steric strain.

The conformations that cyclohexane can assume when interconverting from one chair conformer to the other are shown in Figure 2.10. To convert from the boat conformer to one of the chair conformers, one of the topmost carbons of the boat conformer must be pulled down so that it becomes the bottommost carbon. When the carbon is pulled down just a little, the **twist-boat** (or **skew-boat**) **conformer** is obtained. The twist-boat conformer is more stable than the boat conformer because there is less eclipsing and, consequently, less torsional strain and the flagpole hydrogens have moved away from each other, thus relieving some of the steric strain. When the carbon is pulled down to the point where it is in the same plane as the sides of the boat, the very unstable **half-chair conformer** is obtained. Pulling the carbon down farther produces the *chair conformer.* The graph in Figure 2.10 shows the energy of a cyclohexane molecule as it interconverts from one chair conformer to the other; the energy barrier for interconversion is 12.1 kcal/mol (50.6 kJ/mol). From this value, it can be calculated that cyclohexane undergoes 10^5 ring flips per second at room temperature. In other words, the two chair conformers are in rapid equilibrium.

Because the chair conformers are the most stable of the conformers, at any instant more molecules of cyclohexane are in chair conformations than in any other conformation. It has been calculated that, for every thousand molecules of cyclohexane in

Build a model of cyclohexane, and convert it from one chair conformer to the other. To do this, pull the topmost carbon down and push the bottommost carbon up.
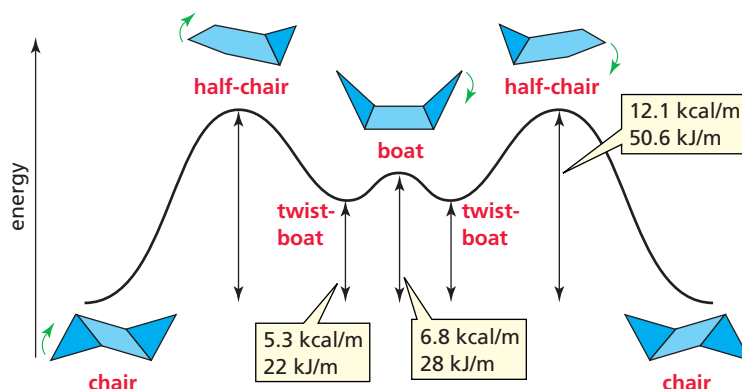
◄ **Figure 2.10**
The conformers of cyclohexane—and their relative energies—as one chair conformer interconverts to the other chair conformer.

half-chair

boat

half-chair

12.1 kcal/m
50.6 kJ/m

twist-
boat

twist-
boat

energy

5.3 kcal/m
22 kJ/m

6.8 kcal/m
28 kJ/m

chair
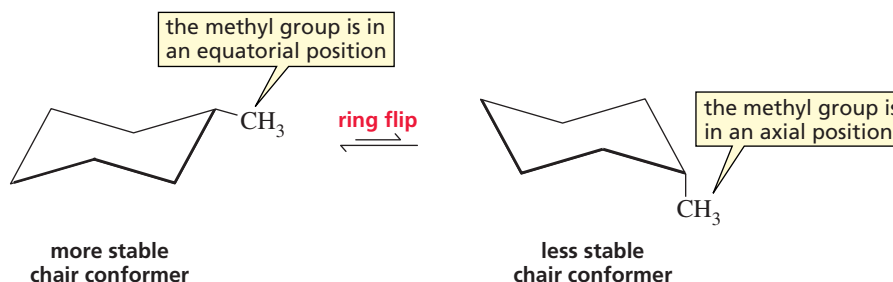
chair

a chair conformation, no more than two molecules are in the next most stable conformation—the twist-boat.

<div style="background:#2e8b57"></div>

2.13 Conformations of Monosubstituted Cyclohexanes

Unlike cyclohexane, which has two equivalent chair conformers, the two chair conformers of a monosubstituted cyclohexane such as methylcyclohexane are not equivalent. The methyl substituent is in an equatorial position in one conformer and in an axial position in the other (Figure 2.11), because substituents that are equatorial in one chair conformer are axial in the other (Figure 2.8).
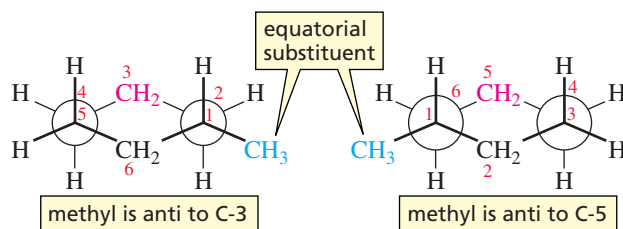
Figure 2.11 ▶
A substituent is in an equatorial position in one chair conformer and in an axial position in the other. The conformer with the substituent in the equatorial position is more stable.

the methyl group is in an equatorial position

ring flip

the methyl group is in an axial position

more stable chair conformer

less stable chair conformer

The chair conformer with the methyl substituent in an equatorial position is the more stable conformer because a substituent has more room and, therefore, fewer steric interactions when it is in an equatorial position. This can be best understood by examining Figure 2.12, which shows that when the methyl group is in an equatorial position, it is anti to the C-3 and C-5 carbons. Therefore, the substituent extends into space, away from the rest of the molecule.

In contrast, when the methyl group is in an axial position, it is gauche to the C-3 and C-5 carbons (Figure 2.13). As a result, there are unfavorable steric interactions between the axial methyl group and both the axial substituent on C-3 and the axial substituent on C-5 (in this case, hydrogens). In other words, the three axial bonds on the same side of the ring are parallel to each other, so any axial substituent will be relatively close to the axial substituents on the other two carbons. Because the interacting substituents are on 1,3-positions relative to each other, these unfavorable steric interactions are called **1,3-diaxial interactions**. If you take a few minutes to build models, you will see that a substituent has more room if it is in an equatorial position than if it is in an axial position.

equatorial substituent

methyl is anti to C-3

methyl is anti to C-5

axial substituent
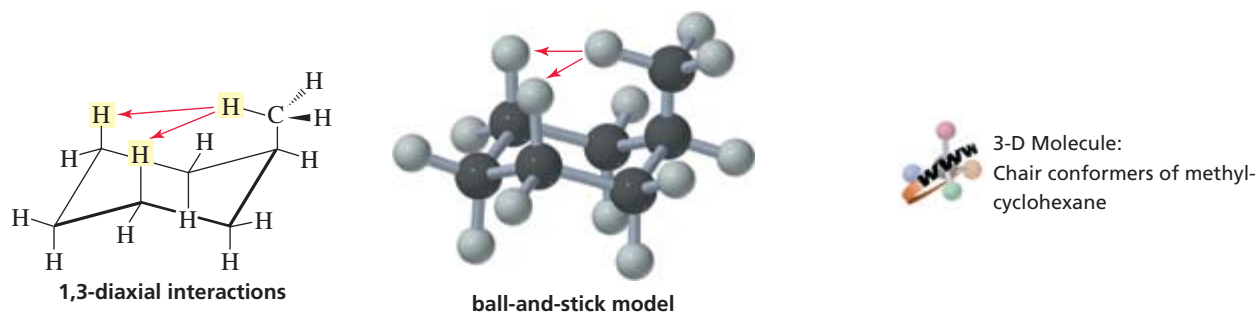
methyl is gauche to C-3

methyl is gauche to C-5

▲ **Figure 2.12**
An equatorial substituent on the C-1 carbon is anti to the C-3 and C-5 carbons.
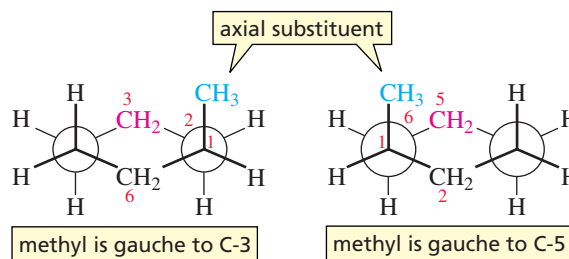
▲ **Figure 2.13**
An axial substituent on the C-1 carbon is gauche to the C-3 and C-5 carbons.

1,3-diaxial interactions

ball-and-stick model

3-D Molecule:
Chair conformers of methyl-
cyclohexane

The gauche conformer of butane and the axial-substituted conformer of methylcyclohexane are compared in Figure 2.14. Notice that the gauche interaction is the same in both—an interaction between a methyl group and a hydrogen bonded to a carbon gauche to the methyl group. Butane has one such gauche interaction and methylcyclohexane has two.
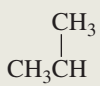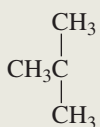

gauche butane

axial
methylcyclohexane
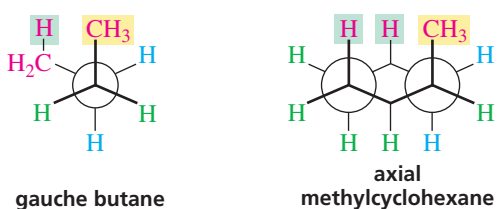
◀ Figure 2.14
The steric strain of gauche butane is the same as the steric strain between an axial methyl group and one of its axial hydrogens. Butane has one gauche interaction between a methyl group and a hydrogen; methylcyclohexane has two.

In Section 2.10, we saw that the gauche interaction between the methyl groups of butane caused the gauche conformer to be 0.9 kcal/mol (3.8 kJ/mol) less stable than the anti conformer. Because there are two such gauche interactions in the chair conformer of methylcyclohexane when the methyl group is in an axial position, this chair conformer is 1.8 kcal/mol (7.5 kJ/mol) less stable than the chair conformer with the methyl group in the equatorial position.

Because of the difference in stability of the two chair conformers, at any one time more monosubstituted cyclohexane molecules will be in the chair conformer with the substituent in the equatorial position than in the chair conformer with the substituent in the axial position. The relative amounts of the two chair conformers depend on the substituent (Table 2.10). The substituent with the greater bulk in the area of the 1,3-diaxial hydrogens will have a greater preference for the equatorial position because it will have stronger 1,3-diaxial interactions. For example, the equilibrium constant

Table 2.10   Equilibrium Constants for Several Monosubstituted Cyclohexanes at 25 °C

Substituent	Axial $\overset{K_{eq}}{\rightleftharpoons}$ Equatorial	Substituent	Axial $\overset{K_{eq}}{\rightleftharpoons}$ Equatorial
		CN	1.4
H	1	F	1.5
CH_3	18		
CH_3CH_2	21	Cl	2.4
$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle \,}{CH}}$	35	Br	2.2
		I	2.2
$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}$	4800	HO	5.4

The larger the substituent on a cyclohexane ring, the more the equatorial-substituted conformer will be favored.

(K_{eq}) for the conformers of methylcyclohexane indicates that 95% of methylcyclohexane molecules have the methyl group in the equatorial position at 25 °C:

$$K_{eq} = \frac{[\text{equatorial conformer}]}{[\text{axial conformer}]} = \frac{18}{1}$$

$$\% \text{ of equatorial conformer} = \frac{[\text{equatorial conformer}]}{[\text{equatorial conformer}] + [\text{axial conformer}]} \times 100$$

$$\% \text{ of equatorial conformer} = \frac{18}{18 + 1} \times 100 = 95\%$$

In the case of *tert*-butylcyclohexane, where the 1,3-diaxial interactions are even more destabilizing because a *tert*-butyl group is larger than a methyl group, more than 99.9% of the molecules have the *tert*-butyl group in the equatorial position.

PROBLEM 32◆

The chair conformer of fluorocyclohexane is 0.25 kcal/mol (1.0 kJ/mol) more stable when the fluoro substituent is in the equatorial position than when it is in the axial position. How much more stable is the anti conformer of 1-fluoropropane compared with a gauche conformer?

PROBLEM 33◆

From the data in Table 2.10, calculate the percentage of molecules of cyclohexanol that have the OH group in the equatorial position.

PROBLEM 34

Bromine is a larger atom than chlorine, but the equilibrium constants in Table 2.10 indicate that a chloro substituent has a greater preference for the equatorial position. Suggest an explanation for this fact.

2.14 Conformations of Disubstituted Cyclohexanes

If there are two substituents on a cyclohexane ring, both substituents have to be taken into account when determining which of the two chair conformers is the more stable. Let's start by looking at 1,4-dimethylcyclohexane. First of all, note that there are two different dimethylcyclohexanes. One has both methyl substituents on the *same side* of the cyclohexane ring; it is called the **cis isomer** (*cis* is Latin for "on this side"). The other has the two methyl substituents on *opposite sides* of the ring; it is called the **trans isomer** (*trans* is Latin for "across"). *cis*-1,4-Dimethylcyclohexane and *trans*-1,4-dimethylcyclohexane are called **geometric isomers** or **cis–trans isomers**: They have the same atoms, and the atoms are linked in the same order, but they differ in the spatial arrangement of the atoms.
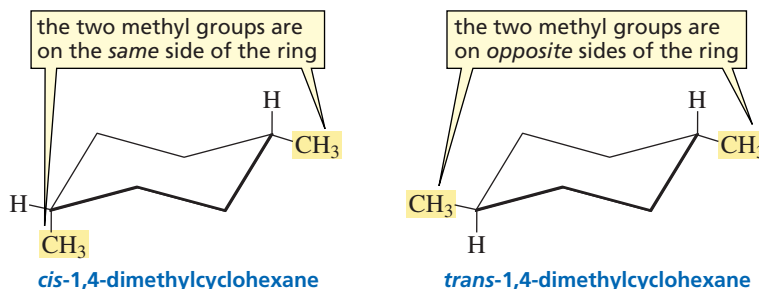
**The cis isomer has its substituents on the same side of the ring.**

The trans isomer has its substituents on opposite sides of the ring.

the two methyl groups are on the *same* side of the ring

the two methyl groups are on *opposite* sides of the ring

cis-**1,4-dimethylcyclohexane**

trans-**1,4-dimethylcyclohexane**

First we will determine which of the two chair conformers of *cis*-1,4-dimethylcyclohexane is more stable. One chair conformer has one methyl group in an equatorial
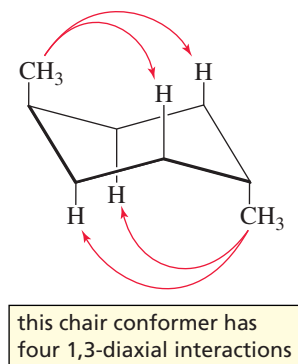
position and one methyl group in an axial position. The other chair conformer also has one methyl group in an equatorial position and one methyl group in an axial position. Therefore, both chair conformers are equally stable.

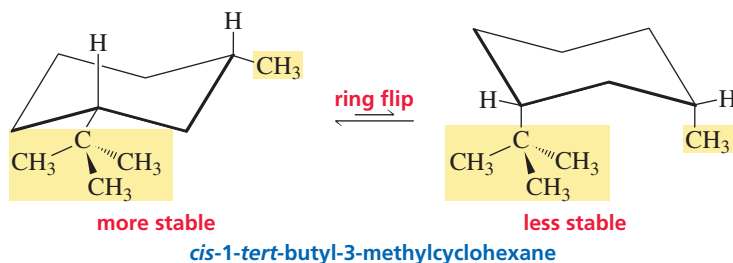***cis*-1,4-dimethylcyclohexane**
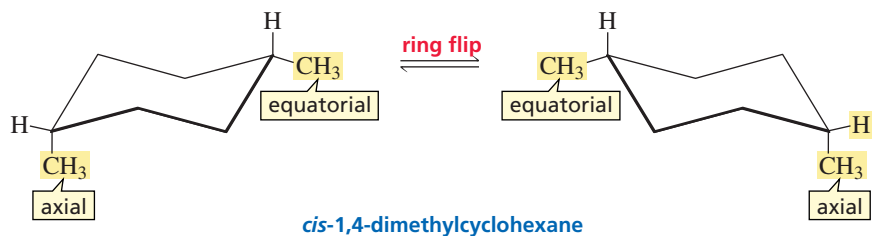
In contrast, the two chair conformers of *trans*-1,4-dimethylcyclohexane have different stabilities because one has both methyl substituents in equatorial positions and the other has both methyl groups in axial positions.

***trans*-1,4-dimethylcyclohexane**
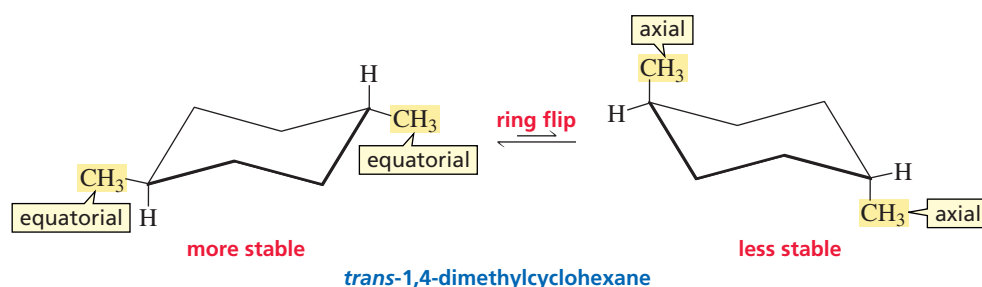
The chair conformer with both substituents in axial positions has four 1,3-diaxial interactions, causing it to be about $4 \times 0.9 \, \text{kcal/mol} = 3.6 \, \text{kcal mol} \, (15.1 \, \text{kJ/mol})$ less stable than the chair conformer with both methyl groups in equatorial positions. We can, therefore, predict that *trans*-1,4-dimethylcyclohexane will exist almost entirely in the more stable diequatorial conformation.

this chair conformer has
four 1,3-diaxial interactions

Now let's look at the geometric isomers of 1-*tert*-butyl-3-methylcyclohexane. Both substituents of the cis isomer are in equatorial positions in one conformer and in axial positions in the other conformer. The conformer with both substituents in equatorial positions is more stable.
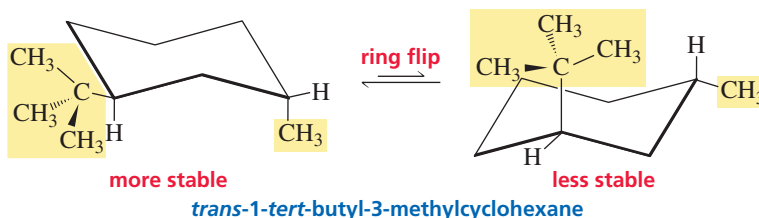

***cis*-1-*tert*-butyl-3-methylcyclohexane**

Both conformers of the trans isomer have one substituent in an equatorial position and the other in an axial position. Because the *tert*-butyl group is larger than the methyl group, the 1,3-diaxial interactions will be stronger when the *tert*-butyl group is in the axial position. Therefore, the conformer with the *tert*-butyl group in the equatorial position is more stable.

3-D Molecule:
trans-1-*tert*-butyl-3-methyl-
cyclohexane

more stable   **less stable**

trans-**1-*tert*-butyl-3-methylcyclohexane**

PROBLEM 35◆

Which will have a higher percentage of the diequatorial-substituted conformer, compared with the diaxial-substituted conformer: *trans*-1,4-dimethylcyclohexane or *cis*-1-*tert*-butyl-3-methylcyclohexane?


PROBLEM-SOLVING STRATEGY

Is the conformer of 1,2-dimethylcyclohexane with one methyl group in an equatorial position and the other in an axial position the cis isomer or the trans isomer?
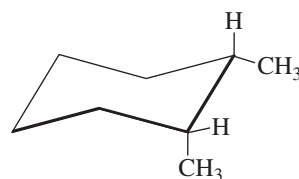
Is this the cis isomer or the trans isomer?

To solve this kind of problem you need to determine whether the two substituents are on the same side of the ring (cis) or on opposite sides of the ring (trans). If the bonds bearing the substituents are both pointing upward or both pointing downward, the compound is the cis isomer; if one bond is pointing upward and the other downward, the compound is the trans isomer. Because the conformer in question has both methyl groups attached to downward-pointing bonds, it is the cis isomer.

**the cis isomer**   **the trans isomer**
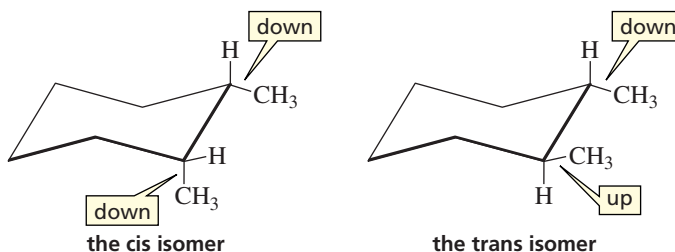
The isomer that is the most misleading when it is drawn in two dimensions is a *trans*-1,2-disubstituted isomer. At first glance, the methyl groups of *trans*-1,2-dimethylcyclohexane appear to be oriented in the same direction, so you might think that the compound is the cis isomer. Closer inspection shows, however, that one bond is pointed upward and the other downward, so we know that it is the trans isomer. (If you build a model of the compound, it is easier to see that it is the trans isomer.)

Now continue on to Problem 36.

PROBLEM 36◆

Determine whether each of the following compounds is a cis isomer or a trans isomer:

a.

d.

b.

e.

c.

f.
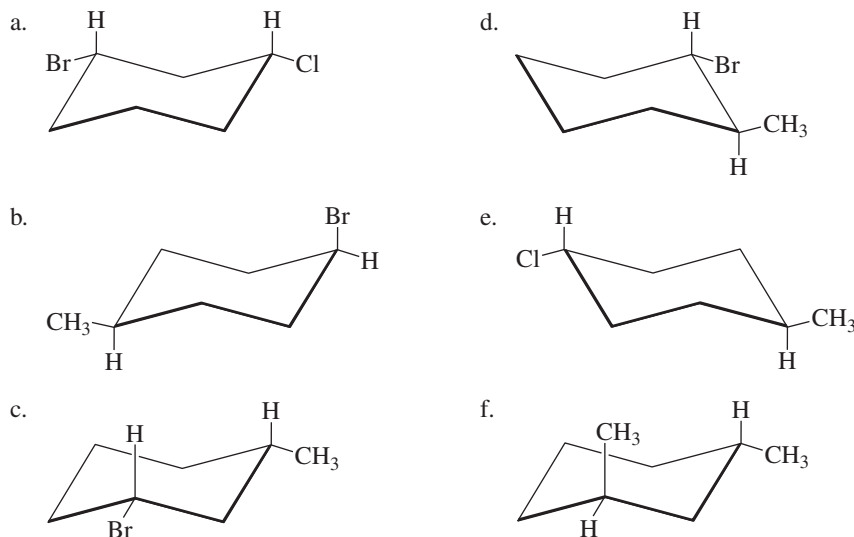
PROBLEM 37   SOLVED

a. Draw the more stable chair conformer of *cis*-1-ethyl-2-methylcyclohexane.

b. Draw the more stable conformer of *trans*-1-ethyl-2-methylcyclohexane.

c. Which is more stable, *cis*-1-ethyl-2-methylcyclohexane or *trans*-1-ethyl-2-methyl-cyclohexane?

SOLUTION TO 37a   If the two substituents of a 1,2-disubstituted cyclohexane are to be on the same side of the ring, one must be in an equatorial position and the other must be in an axial position. The more stable chair conformer is the one in which the larger of the two substituents (the ethyl group) is in the equatorial position.

PROBLEM 38◆

For each of the following disubstituted cyclohexanes, indicate whether the substituents in the two chair conformers would be both equatorial in one chair conformer and both axial in the other *or* one equatorial and one axial in each of the chair conformers:

a. *cis*-1,2-   c. *cis*-1,3-   e. *cis*-1,4-
b. *trans*-1,2-   d. *trans*-1,3-   f. *trans*-1,4-

PROBLEM 39◆

a. Calculate the energy difference between the two chair conformers of *trans*-1,4-dimethylcyclohexane.

b. What is the energy difference between the two chair conformers of *cis*-1,4-dimethyl-cyclohexane?

2.15   Conformations of Fused Rings

When two cyclohexane rings are fused together, the second ring can be considered to be a pair of substituents bonded to the first ring. As with any disubstituted cyclo-hexane, the two substituents can be either cis or trans. If the cyclohexane rings are drawn in their chair conformations, the trans isomer (with one substituent bond point-ing upward and the other downward) will have both substituents in the equatorial

position. The cis isomer will have one substituent in the equatorial position and one substituent in the axial position. **Trans-fused** cyclohexane rings, therefore, are more stable than **cis-fused** cyclohexane rings.

trans-decalin
trans-fused rings
more stable

cis-decalin
cis-fused rings
less stable
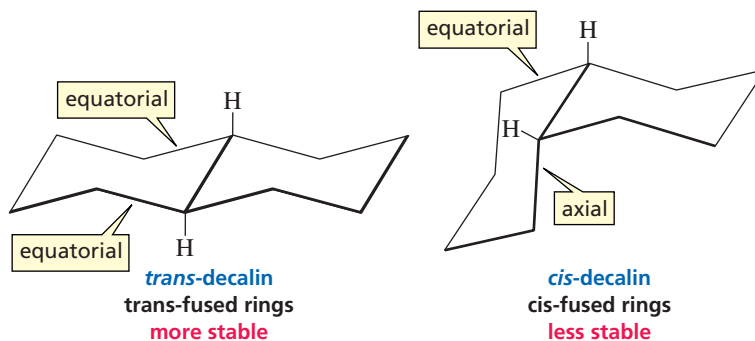
Summary

Alkanes are **hydrocarbons** that contain only single bonds. Their general molecular formula is C_nH_{2n+2}. **Constitutional isomers** have the same molecular formula, but their atoms are linked differently. Alkanes are named by determining the number of carbons in their **parent hydrocarbon**—the longest continuous chain. **Substituents** are listed in alphabetical order, with a number to designate their position on the chain. When there is only a **substituent**, the substituent gets the lowest possible number; when there is only a **functional group suffix**, the functional group suffix gets the lowest possible number; when there is both a functional group suffix and a substituent, the functional group suffix gets the lowest possible number. The **functional group** is the center of reactivity in a molecule.

Alkyl halides and ethers are named as substituted alkanes. Alcohols and amines are named using a functional group suffix. **Systematic names** can contain numbers; **common names** never do. A compound can have more than one name, but a name must specify only one compound. Whether alkyl halides or alcohols are **primary**, **secondary**, or **tertiary** depends on whether the X (halogen) or OH group is bonded to a primary, secondary, or tertiary carbon. A **primary carbon** is bonded to one carbon, a **secondary carbon** is bonded to two carbons, and a **tertiary carbon** is bonded to three carbons. Whether amines are **primary**, **secondary**, or **tertiary** depends on the number of alkyl groups bonded to the nitrogen. Compounds with four alkyl groups bonded to nitrogen are called **quaternary ammonium salts**.

The oxygen of an alcohol has the same geometry it has in water; the nitrogen of an amine has the same geometry it has in ammonia. The greater the attractive forces between molecules—**van der Waals forces**, **dipole–dipole interactions, hydrogen bonds**—the higher is the **boiling point** of the compound. A **hydrogen bond** is an interaction between a hydrogen bonded to an O, N, or F and the lone pair of an O, N, or F in another molecule. The boiling point increases with increasing molecular weight of the **homolog**. Branch-

ing lowers the boiling point. **Polarizability** indicates the ease with which an electron cloud can be distorted: Larger atoms are more polarizable.

Polar compounds dissolve in **polar solvents**, and **nonpolar compounds** dissolve in **nonpolar solvents**. The interaction between a solvent and a molecule or an ion dissolved in that solvent is called **solvation**. The oxygen of an alcohol or an ether can drag about three or four carbons into solution in water.

Rotation about a C—C bond results in two extreme **conformations** that rapidly interconvert: **staggered** and **eclipsed**. A **staggered conformer** is more stable than an **eclipsed conformer** because of **torsional strain**—repulsion between pairs of bonding electrons. There can be two different staggered conformers: The **anti conformer** is more stable than the **gauche conformer** because of **steric strain**—repulsion between the electron clouds of atoms or groups. The steric strain in a gauche conformer is called a **gauche interaction**.

Five- and six-membered rings are more stable than three- and four-membered rings because of **angle strain** that results when bond angles deviate from the ideal bond angle of 109.5°. In a process called **ring flip**, cyclohexane rapidly interconverts between two stable chair conformations. **Bonds** that are **axial** in one chair conformer are **equatorial** in the other and vice versa. The chair conformer with a substituent in the equatorial position is more stable, because there is more room in an equatorial position. A substituent in an axial position experiences unfavorable **1,3-diaxial interactions**. In the case of disubstituted cyclohexanes, the more stable conformer will have its larger substituent in the equatorial position. A **cis isomer** has its two substituents on the same side of the ring; **a trans isomer** has its substituents on opposite sides of the ring. Cis and trans isomers are called **geometric isomers** or **cis–trans isomers**. Cyclohexane rings are more stable if they are **trans fused** than **cis fused**.