12

# CYCLOALKANES, CYCLOALKENES, AND CYCLOALKYNES

Many important hydrocarbons, known as **cycloalkanes,** contain rings of carbon atoms linked together by single bonds. The simple cycloalkanes of formula $(CH_2)_n$ make up a particularly important homologous series in which the chemical properties change in a much more dramatic way with increasing $n$ than do those of the acyclic hydrocarbons $CH_3(CH_2)_{n-1}H$. The cycloalkanes with *small* rings ($n = 3$–6) are of special interest in exhibiting chemical properties intermediate between those of alkanes and alkenes. In this chapter we will show how this behavior can be explained in terms of angle strain and steric hindrance, concepts that have been introduced previously and will be used with increasing frequency as we proceed further.

We also discuss the conformations of cycloalkanes, especially cyclohexane, in detail because of their importance to the chemistry of many kinds of naturally occurring organic compounds. Some attention also will be paid to polycyclic compounds, substances with more than one ring, and to cycloalkenes and cycloalkynes.

## 12-1 NOMENCLATURE AND PHYSICAL PROPERTIES OF CYCLOALKANES

The IUPAC system for naming cycloalkanes and cycloalkenes was presented in some detail in Sections 3-2 and 3-3, and you may wish to review that material before proceeding further. Additional procedures are required for naming

**Table 12-1**
Physical Properties of Alkanes and Cycloalkanes

| Compounds | Bp, °C | Mp, °C | Density, $d_4^{20}$, g ml$^{-1}$ |
|---|---|---|---|
| propane | −42 | −187 | 0.580[a] |
| cyclopropane | −33 | −127 | 0.689[a] |
| butane | −0.5 | −135 | 0.579[b] |
| cyclobutane | 13 | −90 | 0.689[b] |
| pentane | 36 | −130 | 0.626 |
| cyclopentane | 49 | −94 | 0.746 |
| hexane | 69 | −95 | 0.659 |
| cyclohexane | 81 | 7 | 0.778 |
| heptane | 98 | −91 | 0.684 |
| cycloheptane | 119 | −8 | 0.810 |
| octane | 126 | −57 | 0.703 |
| cyclooctane | 151 | 15 | 0.830 |
| nonane | 151 | −54 | 0.718 |
| cyclononane | 178 | 11 | 0.845 |

[a]At −40°. [b]Under pressure.

polycyclic compounds, which have rings with common carbons, and these will be discussed later in this chapter.

The melting and boiling points of cycloalkanes (Table 12-1) are somewhat higher than those of the corresponding alkanes. In contrast to the more rigid cyclic compounds, the general "floppiness" of open-chain hydrocarbons makes them harder to fit into a crystal lattice (hence their lower melting points) and less hospitable toward neighboring molecules of the same type (hence their lower boiling points).

**Exercise 12-1** Write expanded structures showing the C–C bonds for each of the following condensed formulas. Name each substance by the IUPAC system.

**a.** $(CH_2)_{10}$

**b.** $(CH_2)_5CHCH_3$

**c.** $(CH_3)_2C(CH_2)_6CHC_2H_5$

**d.** the position and configurational isomers of trimethylcyclobutane

**e.** $(CH_2)_6CHCH_2C(CH_3)_2CH_2Cl$

**f.** $[(CH_2)_2CH]_2C(CH_3)C_2H_5$

## 12-2 SPECTROSCOPIC PROPERTIES OF CYCLOALKANES

There is considerable similarity in the spectroscopic properties of alkanes and cycloalkanes. We mentioned previously the main features of their infrared

spectra (Section 9-7D), and that their lack of ultraviolet absorption at wavelengths down to 200 nm makes them useful solvents for the determination of ultraviolet spectra of other substances (Section 9-9B).

The proton nmr spectra of alkanes and cycloalkanes are characteristic but difficult to interpret because the chemical shifts between the various kinds of protons are usually small. Although proton spectra of simple cycloalkanes, $(CH_2)_n$, show one sharp line at room temperature, when alkyl substituents are present, *small* differences in chemical shifts between the ring hydrogens occur and, with spin-spin splitting, provide more closely spaced lines than normally can be resolved. The complexity so introduced can be seen by comparing the proton spectra of cyclooctane and methylcyclohexane shown in Figure 12-1. For methyl-substituted cycloalkanes the methyl resonances generally stand out as high-field signals centered on 0.9 ppm, and the area of these signals

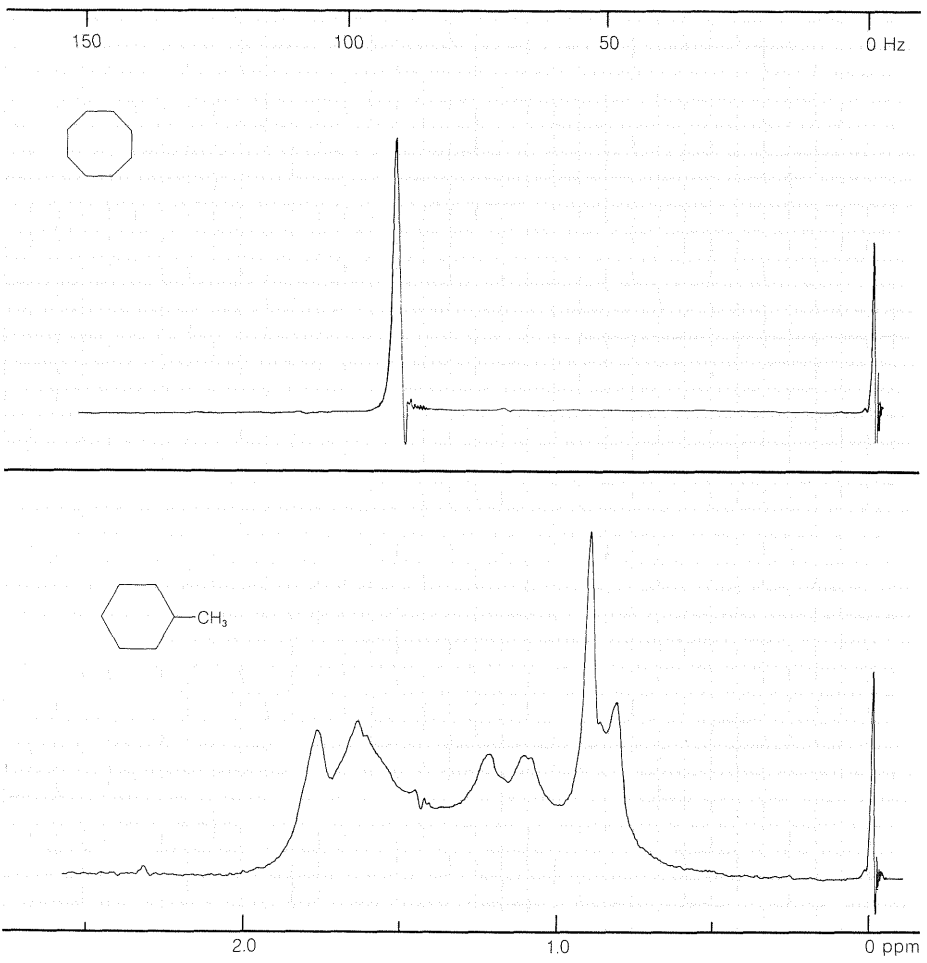



**Figure 12-1** Proton nmr spectra of cyclooctane and methylcyclohexane at 60 MHz with TMS as standard (0 ppm)

relative to the other C–H signals may be useful in indicating how many methyl groups there are (see Section 9-10K, especially Figure 9-46). However, in cyclopropanes the ring protons have abnormally small chemical shifts ($\delta = 0.22$ for cyclopropane), which often overlap with the shifts of methyl groups ($\delta \cong 0.9$ ppm).

Although proton spectra are not very useful for identification purposes, $^{13}C$ nmr spectra are very useful. Chain-branching and ring-substitution normally cause quite large chemical-shift changes, and it is not uncommon to observe $^{13}C$ shifts in cycloalkanes spanning 35 ppm. Some special features of application of $^{13}C$ nmr spectra to conformational analysis of cycloalkanes are described in Section 12-3D.

## 12-3 CONFORMATIONS OF CYCLOALKANES

The equilibria (relative stabilities) and equilibration (rate of interconversion) of the rotational conformations of ethane and butane were discussed in Section 5-2. If you review this material, it will be clear that forming a ring from a hydrocarbon chain will greatly reduce the number of possible staggered and eclipsed conformations.

We will begin our discussion with cyclohexane because of its special importance, proceed to smaller rings, then give a brief exposition of the conformations of the larger rings.

### 12-3A Cyclohexane Conformations

If the carbons of a cyclohexane ring were placed at the corners of a regular *planar* hexagon, all the C–C–C bond angles would have to be 120°. Because the expected normal C–C–C bond angle should be near the tetrahedral value of 109.5°, the suggested planar configuration of cyclohexane would have *angle strain* at each of the carbons, and would correspond to less stable cyclohexane molecules than those with more normal bond angles. The actual normal value for the C–C–C bond angle of an open-chain $—CH_2—CH_2—CH_2—$ unit appears to be about 112.5°, which is 3° greater than the tetrahedral value. From this we can conclude that the angle strain at each carbon of a planar cyclohexane would be $(120° - 112.5°) = 7.5°$. Angle strain is not the whole story with regard to the instability of the planar form, because in addition to having C–C–C bond angles different from their normal values, the planar structure also has its carbons and hydrogens in the unfavorable *eclipsed* arrangement, as shown in Figure 12-2. How both of these factors can be taken into account is illustrated in Exercises 12-2 and 12-3.

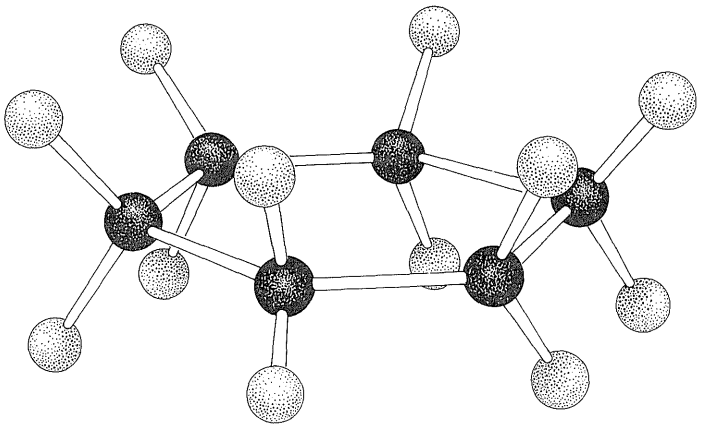


**Figure 12-2** Cyclohexane in the strained planar configuration showing how the hydrogens become eclipsed

**Exercise 12-2** The energy required to distort C–C–C bond angles from their normal values is approximately 17.5 cal (not kcal!) per degree squared per mole. Assuming the normal C–C–C angle to be 112.5°, calculate the angle-strain energy of a mole of planar cyclohexane (Figure 12-2). The actual C–C–C bond angles of cyclohexane are 111.5°; what strain energy corresponds to this angle?

**Exercise 12-3*** Figure 5-8 indicates that the difference in energy between the conformation of butane with eclipsed methyls and the gauche form is about 5 kcal $mole^{-1}$. Use this number to estimate the contribution of eclipsing to the instability of planar cyclohexane. Then calculate the instability of planar cyclohexane by including the angle strain from Exercise 12-2 in your estimate.

If the carbon valence angles are kept near the tetrahedral value, you will find that you can construct ball-and-stick models of the cyclohexane six-carbon ring with two quite different conformations. These are known as the "chair" and "boat" conformations (Figure 12-3). It has not been possible

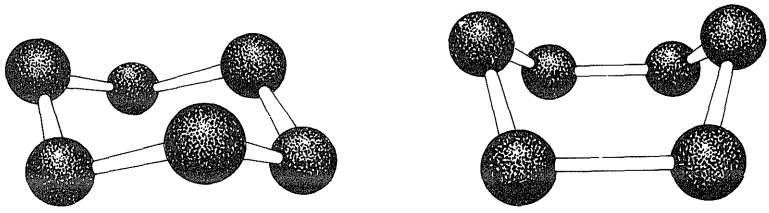


**Figure 12-3** Chair (left) and boat (right) conformations of the six carbons of a cyclohexane ring with normal C–C–C bond angles

to separate cyclohexane at room temperature into pure isomeric forms that correspond to these conformations, and actually the two forms appear to be rapidly interconverted. The chair conformation is considerably more stable and comprises more than 99.9% of the equilibrium mixture at room temperature.[1]

Why is the boat form less stable than the chair form, if both have normal C—C—C bond angles? The answer is that the boat form has unfavorable nonbonded interactions between the hydrogen atoms around the ring. If we make all of the bond angles normal and orient the carbons to give the "extreme boat" conformation of Figure 12-4, a pair of 1,4 hydrogens (the so-called "flagpole" hydrogens) have to be very close together (1.83 A). Hydrogens this close together would be on the rising part of a repulsion potential energy curve, such as Figure 4-6, for hydrogen-hydrogen nonbonded interactions. This *steric hindrance* at an H—H distance of 1.83 A corresponds to a repulsion energy of about 3 kcal mole$^{-1}$. There is still another factor that makes the extreme boat form unfavorable; namely, that the eight hydrogens along the "sides" of the boat are eclipsed, which brings them substantially closer together than they would be in a staggered arrangement (about 2.27 A compared with 2.50 A). This is in striking contrast with the chair form (Figure 12-5), for which adjacent hydrogens are in staggered positions with respect to one another all around the ring. Therefore the chair form is expected to be more stable than the boat form because it has less repulsion between the hydrogens.

You should make and inspect models such as those in Figure 12-3 to see the rather striking difference between the chair and boat conformations that is not obvious from the diagrams. You will find that the chair structure is quite rigid, and rotation does *not* occur around the C–C bonds with interconversion to the boat structure. In contrast, the boat form is quite flexible. Rotation about the C–C bonds permits the ring to twist one way or the other from the extreme boat conformation to considerably more stable, equal-energy conformations, in which the flagpole hydrogens move farther apart and the eight hydrogens along the sides become largely but not completely staggered. These arrangements are called the **twist-boat** (sometimes **skew-boat**) conformations (see Figure 12-6) and are believed to be about 5 kcal mole$^{-1}$ less stable than the chair form.

> It is possible to measure the spectral properties of the twist-boat form by a very elegant technique employed by F. A. L. Anet. Because the equilibrium constant for conversion of chair to boat increases with temperature, a considerable proportion of the molecules exist as the twist-boat form in the vapor at 800°. If such vapor is allowed to impinge on a surface cooled to 20°K, the film condensate contains about 25% of the twist-boat form. At this low temperature, the twist-boat form is converted to the more stable chair form at a very slow rate. Infrared spectra can be taken of the boat-chair mixture at 10°K. If the mixture is allowed to warm to 75°K, the normal equilibrium favoring the chair form is established in a short time.

[1]Pioneering work on the conformations of cyclohexane and its derivatives was carried out by O. Hassel (Norway) and D. H. R. Barton (United Kingdom) for which they shared a Nobel Prize in 1969.

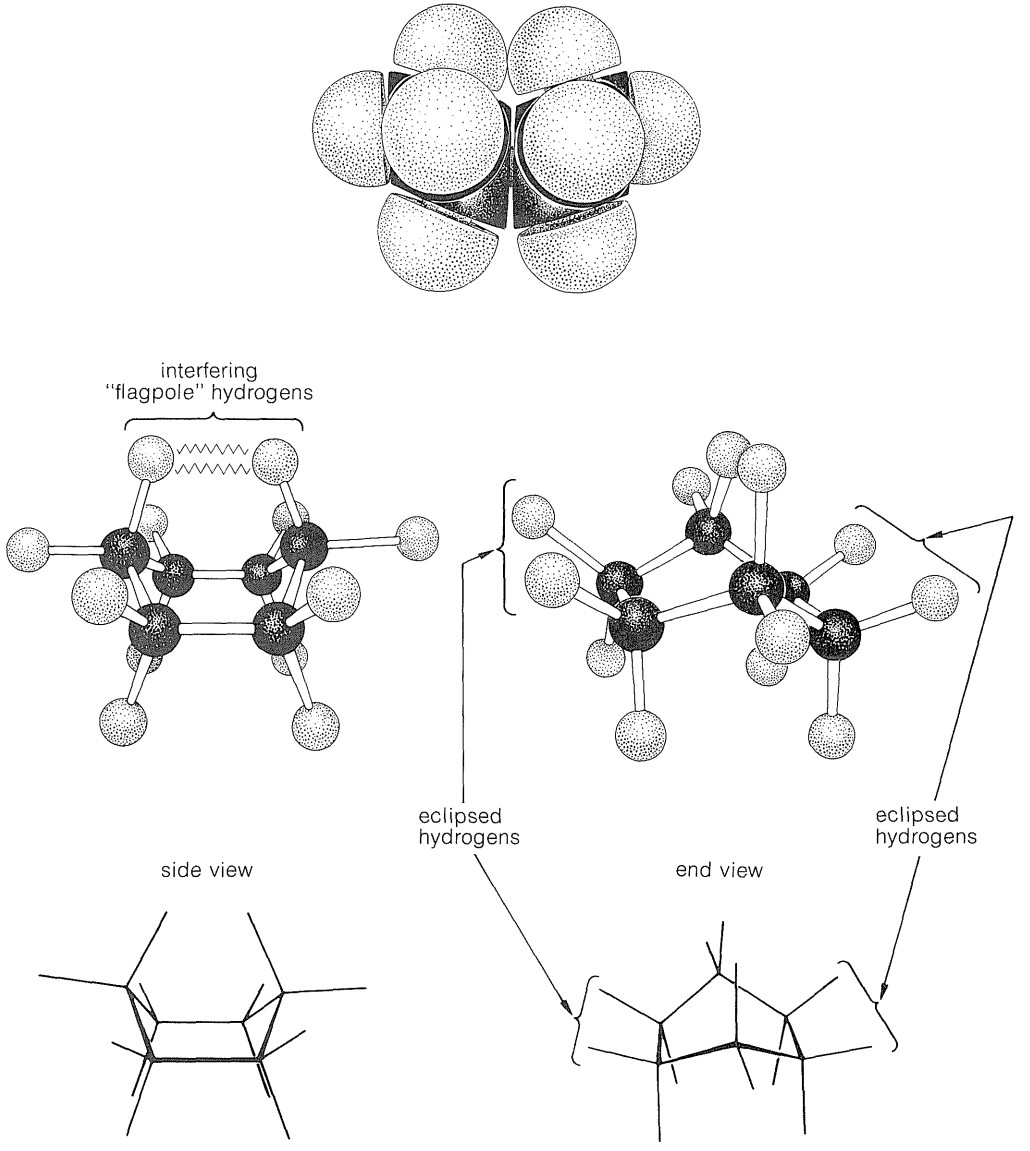



**Figure 12-4** Extreme boat form of cyclohexane showing interfering and eclipsed hydrogens. Top, space-filling model; center, ball-and-stick models; bottom, sawhorse representations

## 12-3B Dreiding Models

The spatial arrangement (stereochemistry) of cyclohexane and other organic compounds are studied conveniently with the aid of *Dreiding models,* which are made with standard bond angles and scaled bond distances. The bonds

have stainless-steel rods that make a snap-fit into stainless-steel sleeves. Rotation is smooth about the bonds and there is sufficient flexibility to accommodate some angle strain. Dreiding models of the conformations of cyclohexane are shown in Figure 12-7. Notice that these models correspond closely to the sawhorse representations in Figures 12-4, 12-5, and 12-6.

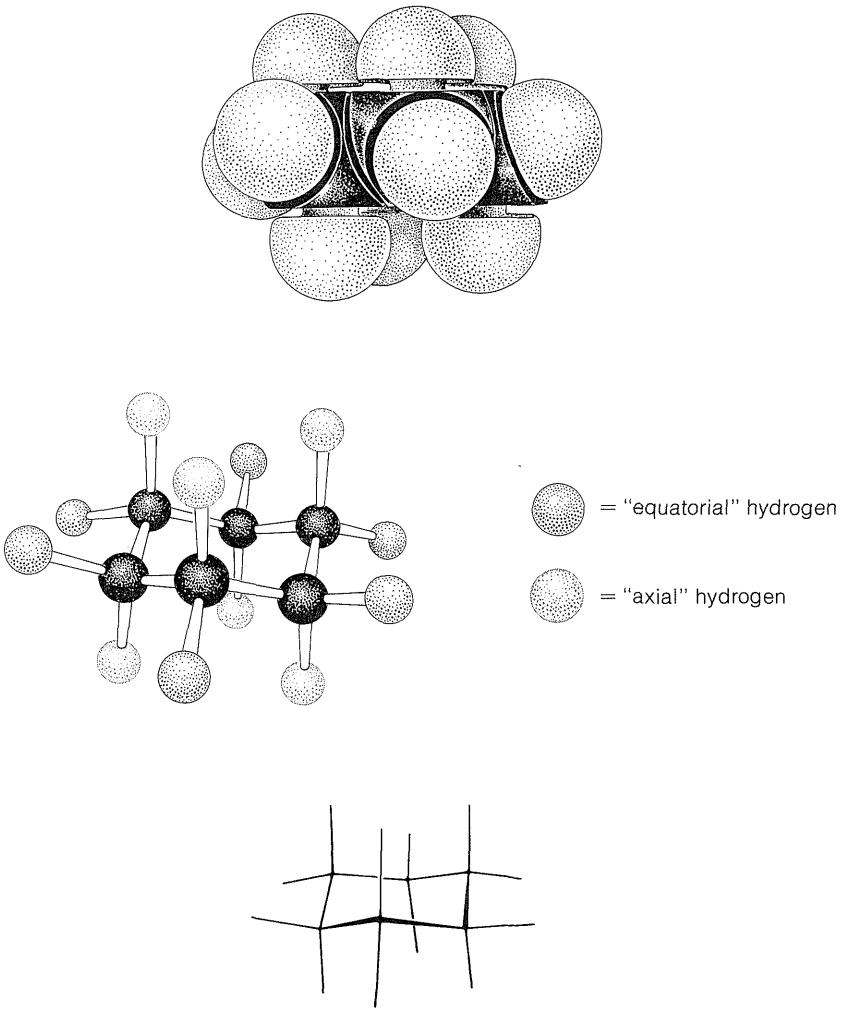



**Figure 12-5** Chair form of cyclohexane showing equatorial and axial hydrogens. Top, space-filling model; center, ball-and-stick model; bottom, sawhorse representation. Notice that all the axial positions are equivalent and all the equatorial positions are equivalent. By this we mean that a substituent on any one of the six axial positions gives the same axial conformation, whereas a substituent on any one of the six equatorial positions gives the same equatorial conformation.

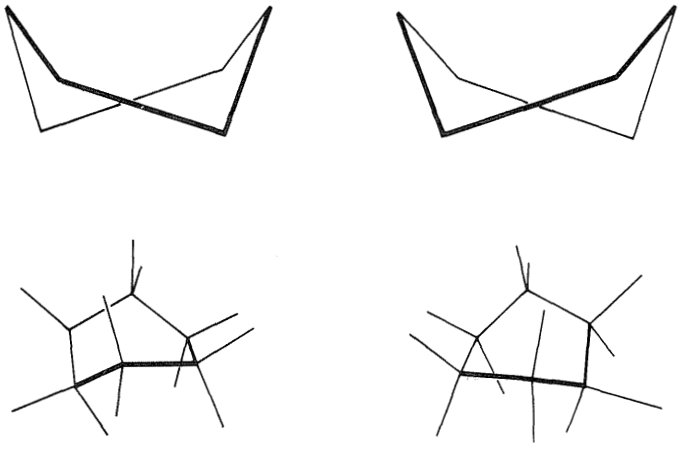


**Figure 12-6** The twist-boat conformations of cyclohexane

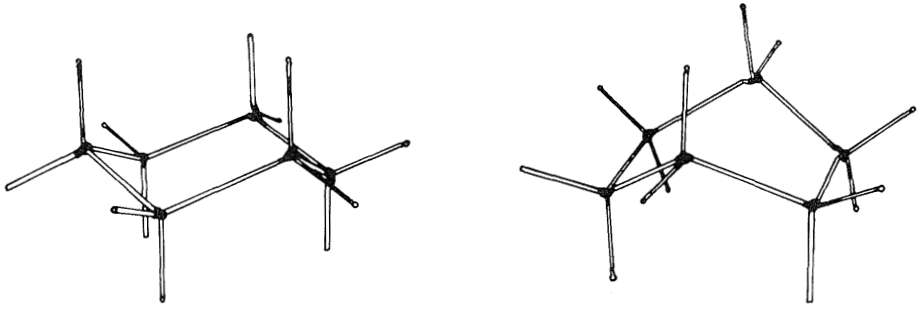
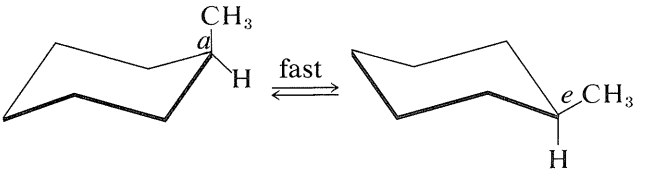


**Figure 12-7** Dreiding models of the cyclohexane conformations

## 12-3C Conformational Equilibria and Equilibration for Cyclohexane Derivatives

Figure 12-5 shows that there are two distinct kinds of hydrogen in the chair form of cyclohexane—six that are close to the "average" plane of the ring (called **equatorial** hydrogens) and three above and three below this average plane (called **axial** hydrogens). This raises interesting questions in connection with substituted cyclohexanes: For example, is the methyl group in methylcyclohexane equatorial or axial? Since only *one* methylcyclohexane is known, the methyl group must be exclusively equatorial (*e*), exclusively axial (*a*), or the two forms must be interconverted so rapidly that they cannot be separated into isomeric forms. It appears that the latter circumstance prevails, with the

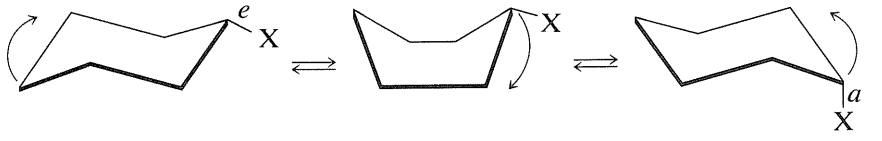
ring changing rapidly from one chair form to another by flipping one end of the chair up and the other end down:




(axial) (equatorial)

Such a change would cause a substituent in an axial position to go to an equatorial position and *vice versa*. This process is called **ring inversion** and its rate often is called the **inversion frequency.** With cyclohexane, inversion is so fast at room temperature that, on the average, the molecules flip about 100,000 times per second, over an energy barrier of about 11 kcal mole$^{-1}$.

You will understand this flipping process if you make a model of a cyclohexane ring carrying a single substituent. By manipulating the model you can discover some of the different ways the process can occur. The simplest route is simply to flip up one corner of the ring to convert the chair into a boat and then flip down the opposite carbon:




Because of the flexibility of the boat conformation, it is possible to transform it to other boat conformations whereby carbons other than the one indicated flip down and complete the interconversion.

At room temperature the conformation of methylcyclohexane with the methyl equatorial is more stable than the one with the methyl axial by 1.7 kcal mole$^{-1}$. The same is true of all monosubstituted cyclohexanes to a greater or lesser degree. Reasons for this can be seen from space-filling models (Figure 12-8), which show that a substituent group has more room when the substituent is equatorial than when it is axial. In the axial position the substituent is considerably closer to the two axial hydrogens on the same side of the ring than to other hydrogens, even hydrogens on adjacent carbons when the substituent is in the equatorial position (Figure 12-8). For example, when the substituent is bromine, which has a C–Br bond length of 1.94 A, the distance from axial bromine to the axial hydrogen at C3 or C5 on the same side of the ring is about 2.7 A. In contrast, the distance from equatorial bromine to any of the hydrogens on the adjacent carbons is about 3.1 A.

There is a very important general aspect of the difference between these two nonbonded H···Br interactions at 2.7 A and 3.1 A. Whenever two nonbonded atoms are brought close together, and before the massive repul-

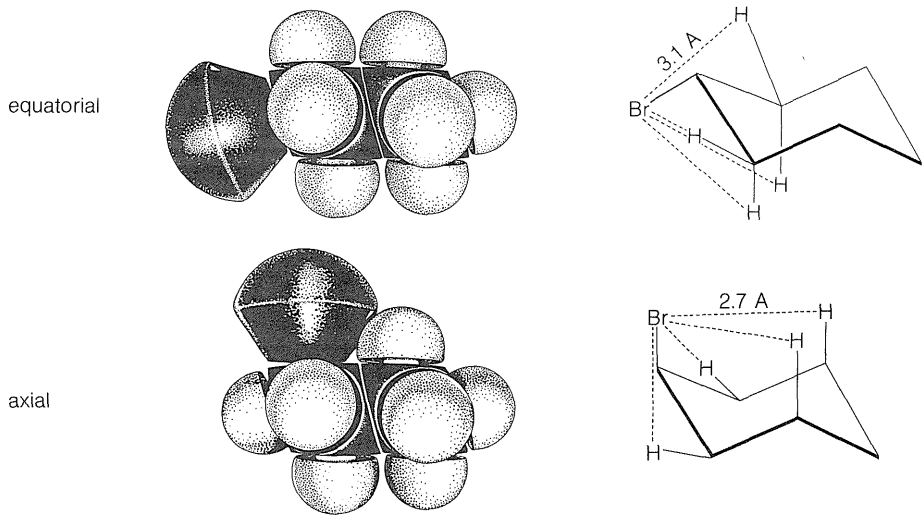



**Figure 12-8** Space-filling models of equatorial and axial chair conformations of cyclohexyl bromide. Significant nonbonded interactions are indicated for the sawhorse formulas by dashed lines; these interactions are more severe in the axial than the equatorial conformation.

sion sets in (which is so evident in Figure 4-6), there is a slight *dip* in the energy curve corresponding to *attraction.*[2] For nonbonded H · · · Br interactions the bottom of the dip comes at about 3.1 A (Figure 12-9), and the resulting attraction between the atoms will provide some stabilization of the equatorial conformation relative to the axial conformation.

Weak attractive forces between nonbonded atoms are called *van der Waals attractive forces, London*[3] *forces,* or *dispersion forces,* and are of great importance in determining the properties of liquids. They also can be expected to play a role in determining conformational equilibria whenever the distances between the atoms in the conformations correspond to the so-called *van der Waals minima.*

Table 12-2 shows the contribution made by various substituents to the free-energy change from the axial to the equatorial orientations of the substituent. Thus, for bromine, the free-energy change, $\Delta G^0$, is $-0.5$ kcal mole$^{-1}$, which means that at 25°, the equilibrium constant, $K$, for the axial $\rightleftharpoons$ equatorial equilibrium is about 2.3 (from $-2.303\ RT \log K = \Delta G^0$; see Section 4-4A).

[2]The vertical scale of Figure 4-6 does not permit seeing the dip in the curve resulting from attractive forces between neon atoms. It is deepest when $r$ is about 3.12 A and amounts to 0.070 kcal mole$^{-1}$.

[3]After F. London, who developed a quantum-mechanical theory of the origin of these forces and also pioneered many quantum calculations of great consequence to chemistry, including bonding in $H_2$, which will be discussed in Section 21-1.

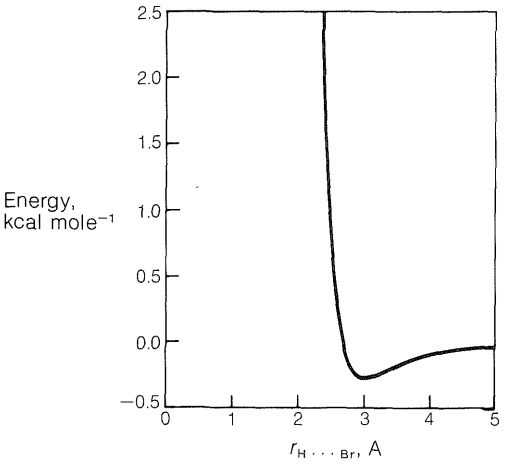



**Figure 12-9** Calculated curve for the energy of nonbonded H · · · Br interactions (the vertical scale is only 1/40 of that of Figure 4-6). Other nonbonded pairs of atoms have similar curves, but with different positions and depths of the minima. The minima usually are considerably deeper with atoms of higher atomic number. The ratios of the attractive forces at the lowest point for He···He, Ne···Ne, Ar···Ar, Kr···Kr, and Xe···Xe are 1:4:14:21:28.

From many studies it is known that the interconversion of conformations with the substituent in the equatorial and the axial positions occurs about 100,000 times per second, which corresponds to a transition-state energy (activation energy) of about 11 kcal mole$^{-1}$ above the ground-state energy. The rate decreases as the temperature is lowered. If one cools chlorocyclohexane to its melting point (−44°), the substance crystallizes to give the pure equatorial isomer. The crystals then can be cooled to −150° and dissolved at this temperature in a suitable solvent. At −150° it would take about 130 days for half of the equatorial form to be converted to the axial form. However, when the solution is warmed to −60° the equatorial conformation is converted to the equilibrium mixture in a few tenths of a second.

---

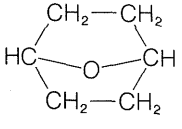
**Exercise 12-4** Using the sawhorse convention, draw the possible conformations of chlorocyclohexane with the ring carbons in the planar, in the chair, and in the extreme boat forms. Arrange these in order of expected stability. Show your reasoning.

**Exercise 12-5** Draw the preferred conformation of each of the following:

**a.** isopropylcyclohexane

**b.** cyclohexylcyclohexane

**c.**

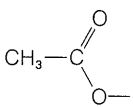
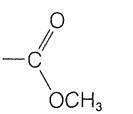


**Exercise 12-6*** **a.** It commonly is stated that the bulkier the substituent, the more favorable will be the conformation in which it occupies an equatorial position. However, it will be seen from Table 12-2 that the $-\Delta G^0$ values for the halogens (F, Cl, Br, and I) are not very large and all are about the same, although there is no question that iodine is a much bulkier substituent than fluorine. Use the following data to account qualitatively for the smallness and the commonality of the $-\Delta G^0$ factors for halogens. In the following table, $r_{C-X}$ is the normal carbon–halogen bond distance, $r_e$ is the distance calculated from the halogen to the nearest hydrogens when equatorial, $r_a$ is the same distance when the halogen is axial, and $r_0$ is the distance corresponding to the minimum on a nonbonded halogen–hydrogen interaction curve, such as shown in Figure 12-9.

| Halogen | $r_{C-X}$, A | $r_e$, A | $r_a$, A | $r_0$, A |
|---|---|---|---|---|
| F | 1.38 | 2.7 | 2.5 | 2.6 |
| Cl | 1.77 | 3.0 | 2.6 | 3.0 |
| Br | 1.94 | 3.1 | 2.7 | 3.1 |
| I | 2.13 | 3.2 | 2.8 | 3.4 |

**b.** How stable would you expect the diaxial conformation of *cis*-1,3-diiodocyclohexane to be relative to the diequatorial conformation? Give your reasoning.

**Table 12-2**
A Selection of $\Delta G^0$ Values for the Change from *Axial* to *Equatorial* Orientation of Substituents for Monosubstituted Cyclohexanes[a]

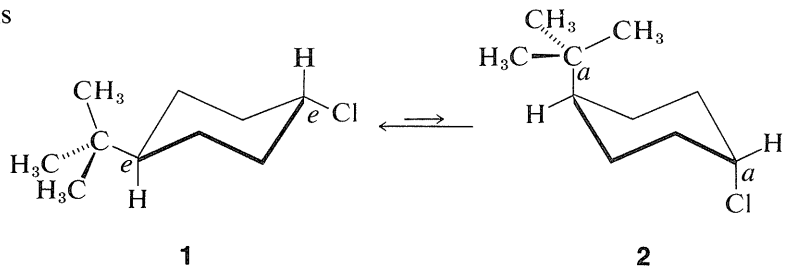
| Substituent | $-\Delta G^0$, kcal mole$^{-1}$ | Substituent | $-\Delta G^0$, kcal mole$^{-1}$ |
|---|---|---|---|
| $CH_3$— | 1.7 | $O_2N$— | 1.1 |
| $C_2H_5$— | 1.8 | N≡C— | 0.2 |
| $(CH_3)_2CH$— | 2.2 | $CH_3O$— | 0.5 |
| $(CH_3)_3C$— | ≥5.0 |  | 0.7 |
| F | 0.3 | | |
| Cl | 0.5 |  | 1.3 |
| Br | 0.5 | | |
| I | 0.5 | $C_6H_5$— | 3.0 |

[a]Values from F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.* **91,** 344 (1969) and J. A. Hirsch in "Topics in Stereochemistry," Vol I, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, 1967.

## 12-3D Cis-Trans Isomerism and Conformational Equilibria for Cyclohexane Derivatives

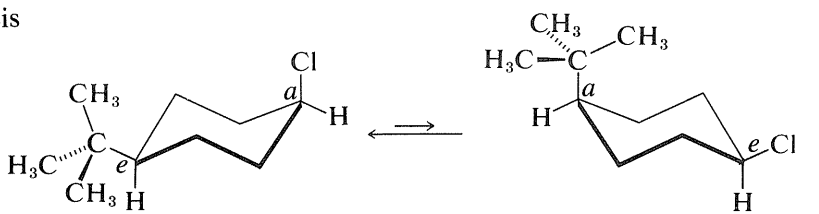
The cis-trans isomerism of cyclohexane derivatives (Section 5-1A) is complicated by conformational isomerism. For example, 4-*tert*-butylcyclohexyl chloride theoretically could exist in four stereoisomeric chair forms, **1**, **2**, **3**, and **4**.

trans




**1** **2**

cis




**3** **4**

Conformations **1** and **2** have the substituents trans to one another, but in **1** they both are equatorial, whereas in **2** they both are axial. Conformations **3** and **4** have the substituents in the cis relationship, with the *tert*-butyl and chlorine equatorial and axial, respectively, in **3**, and the reverse in **4**. A *tert*-butyl group is large and bulky compared to chlorine and considerable steric hindrance results when *tert*-butyl is axial (Figure 12-10). For this reason, **1** and **3** with *tert*-butyl equatorial are much more favorable than **2** and **4**. The properties of a substituent located in an axial or an equatorial position on a cyclohexane ring can be studied by synthesizing the *cis*- or *trans*-4-*tert*-butyl derivative analogous to **3** or **1**. The *tert*-butyl is characterized as a "**holding group**" because its own tendency to be in the equatorial position holds a smaller substituent group axial or equatorial, depending on whether it is cis or trans. However, when there are two large substituents in the *cis*-1,4 arrangement on a cyclohexane ring, neither of which will go easily into an axial position, then it appears that the twist-boat conformation (Section 12-3A) is most favorable (Figure 12-11).

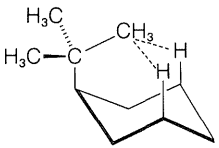



**Figure 12-10** 1,3-Interactions in a cyclohexane ring with an axial *tert*-butyl group

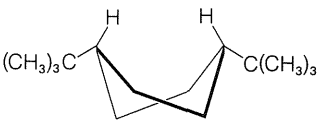


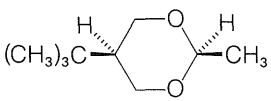

**Figure 12-11** Twist-boat conformation of *cis*-1,4-di-*tert*-butylcyclohexane

**Exercise 12-7** Assuming the effects of substituents in the 1- and 4-positions of cyclohexane on the free energies of equatorial-axial equilibria can be assessed by simple addition of the $\Delta G^0$ values of Table 12-2, calculate the relative free energies of **1**, **2**, **3**, and **4**. Use these values to calculate equilibrium constants for **1** $\rightleftharpoons$ **2**, **3** $\rightleftharpoons$ **4**, and **1** $\rightleftharpoons$ **3** at 25°.[4]

**Exercise 12-8** Explain why simple additivity of $\Delta G^0$ values as proposed in Exercise 12-7 to predict axial-equatorial equilibria for cis and trans 1,4-disubstituted cyclohexanes would be expected to give poor results with 1,2- and 1,3-disubstituted cyclohexanes.

**Exercise 12-9** Draw the possible chair conformations of *trans*- and *cis*-1,3-dimethylcyclohexane. Is the cis or the trans isomer likely to be the more stable? Explain.

**Exercise 12-10** With *cis*-2-methyl-5-*tert*-butyl-1,3-dioxacyclohexane,[5] the conformation with *tert*-butyl axial is more favored than the conformation with *tert*-butyl equatorial.




*cis*-2-methyl-5-*tert*-butyl-1,3-dioxacyclohexane

Explain why this should be so and predict what should be the favored conformation for *trans*-2-methyl-4-*tert*-butyl-1,3-dioxacyclohexane.

[4]It is important to notice that, in some cases, simple additivity of $\Delta G^0$ values can give quite erroneous results when the groups involved are polar. Thus *trans*-1,4-dichlorocyclohexane appears to be more stable in the diaxial conformation than in the diequatorial conformation.

[5]The *oxa* prefix to the name of a hydrocarbon means that a carbon in the chain has been replaced by oxygen (see Section 15-11A).

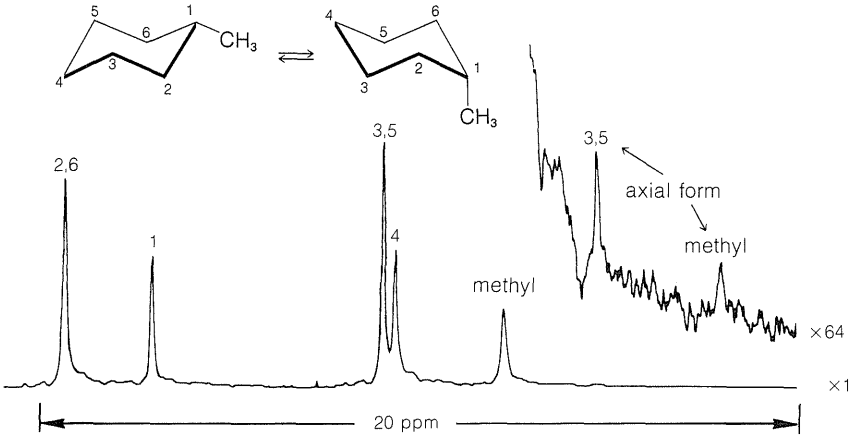
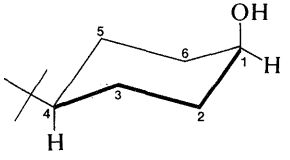
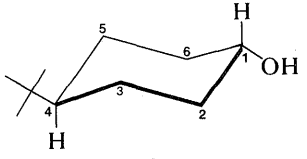



**Figure 12-12** Proton-decoupled, 63.1 MHz, $^{13}C$ spectrum of methylcyclohexane at −110°. The upper right curve was taken with the signal sensitivity control turned up by a factor of 64. (Courtesy of Dr. F. A. L. Anet.)

Use of $^{13}C$ nmr spectroscopy to determine whether a substituent is in an axial or equatorial position is well illustrated with *cis*- and *trans*-4-*tert*-butylcyclohexanols, **5** and **6**:



**5**



**6**

In this case, the *tert*-butyl group acts as a "holding group" so that in the cis isomer the OH is axial and in the trans isomer it is equatorial. The $^{13}C$ resonance of C1 of the axial isomer, **5**, is 5.4 ppm upfield of C1 in **6**, and the resonances of C3 and C5 are 4.7 ppm upfield of those of the corresponding carbons of **6**. Similar large upfield shifts of the ring carbons C1, C3, and C5 also are produced by axial methyl groups. In addition, the $^{13}C$ resonance of an axial methyl carbon is shifted upfield 5–7 ppm compared to the resonance of an equatorial methyl. These effects are clearly evident in the $^{13}C$ spectrum of methylcyclohexane at −110°, shown in Figure 12-12. At −110° the equatorial form is 99% of the mixture and is interconverted only very slowly with the 1% of axial form. Despite the strong $^{13}C$ nmr signals from the equatorial form, the chemical shifts of C3, C5, and $CH_3$ carbons of the axial form are sufficiently different that they can be seen upfield of the methyl resonance of the equatorial form.

---

**Exercise 12-11** With reference to Figure 12-12, sketch the proton-decoupled $^{13}C$ spectrum you would expect for methylcyclohexane at 25°. Give your reasoning. (Review Section 9-10C.)

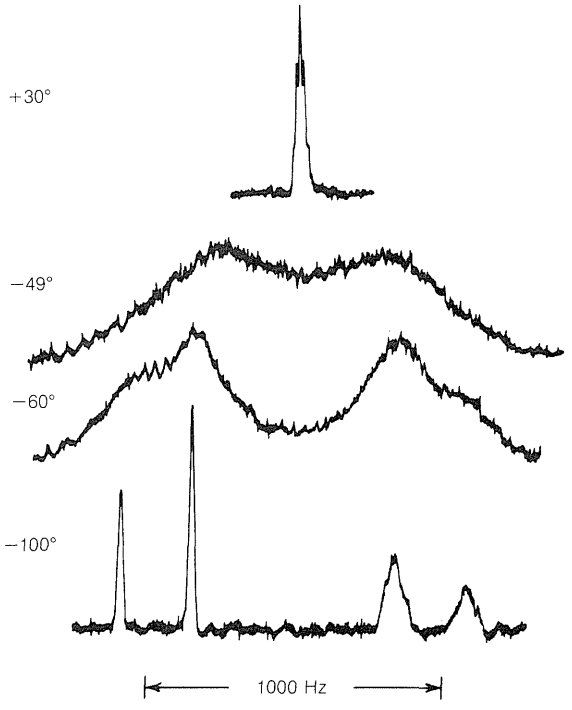


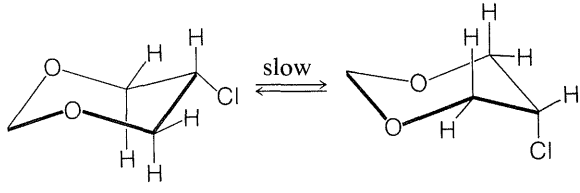

**Figure 12-13** Changes in the $^{19}F$ nmr spectrum of 1,1-difluorocyclohexane with temperature at 56.4 MHz (see Exercise 12-12). Generally, H—C—C—F spin-spin splittings are on the order of 5–15 Hz and change with rotational angles in much the same way as for H—C—C—H couplings.

**Exercise 12-12*** The $^{19}F$ nmr spectrum of 1,1-difluorocyclohexane at several temperatures and 56.4 MHz is shown in Figure 12-13.

**a.** Explain why this spectrum changes so drastically with temperature and account for the appearance of four groups of lines observed at −100°. (Review Sections 9-10C and 9-10I.)

**b.** Sketch the $^{19}F$ spectrum you would expect for 1,1-difluoro-4-*tert*-butylcyclohexane at 25°. Give your reasoning.

**Exercise 12-13*** Proton nmr spectra often are used to determine whether a substituent is axial or equatorial. Explain what differences one might expect to see in the *splitting* of the nmr signal from the $\diagdown$CHCl— proton of each of the following two $\diagup$ conformations at a temperature low enough so interconversion is very slow. (Review Sections 9-10H and 9-10J.)



## 12-3E Cyclopentane

The five $—CH_2—$ groups of cyclopentane theoretically could form a regular planar pentagon (internal angles of 108°) with only a little bending of the normal C–C–C bond angles. Actually, cyclopentane molecules are *not* flat. The planar structure has completely eclipsed hydrogens, which make it less stable by about 10 kcal $mole^{-1}$ than if there were no eclipsed hydrogens. The result is that each molecule assumes a puckered conformation that is the best compromise between distortion of bond angles and eclipsing of hydrogens. The best compromise conformations have the ring twisted with one or two of the $—CH_2—$ groups bent substantially out of a plane passed through the other carbons (Figure 12-14). The flexibility of the ring is such that these deformations move rapidly around the ring.

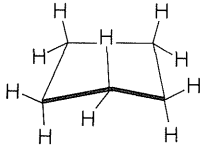
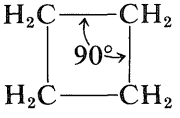


**Figure 12-14** Nonplanar conformation of cyclopentane. Notice that the forward carbon is out of the plane of the other four.

## 12-3F Cyclobutane

Formation of a four-membered ring of carbon atoms can be achieved only with substantial distortion of the normal valence angles of carbon, regardless of whether the ring is planar or nonplanar. In cyclobutane, for example, if the valence bonds are assumed to lie along straight lines drawn between the carbon nuclei, each C–C–C bond angle will be 19.5° smaller than the 109.5° tetrahedral value:




cyclobutane

Of course, the angle distortion will be still greater if the ring is nonplanar. Nonetheless, the energy of eclipsing the hydrogens in cyclobutane is sufficient to cause the ring to be nonplanar. Substituents are located most favorably in what might be called the "quasi-equatorial" positions (Figure 12-15).

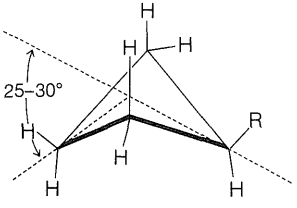
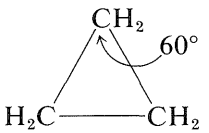



**Figure 12-15** Nonplanar cyclobutane conformation with a substituent R in the less hindered, quasi-equatorial position. The dihedral angle between the two halves of the bent ring usually is 25° to 30°, that is, a 25° to 30° deviation from planarity.

**Exercise 12-14** Given the favored nonplanar conformation of cyclobutane (Figure 12-15), predict whether *cis*-1,2-dibromocyclobutane will be more, or less, stable than the corresponding trans isomer. Do the same for the *cis*- and *trans*-1,3-dibromocyclobutanes. Give your reasoning.

### 12-3G Cyclopropane

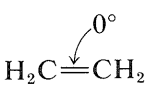
The three carbon atoms of the cyclopropane ring lie in a plane. Therefore the angle strain is expected to be considerable because each C–C–C valence angle must be deformed 49.5° from the tetrahedral value. It is likely that some relief from the strain associated with the eclipsing of the hydrogens of cyclopropane is achieved by distortion of the H–C–H and H–C–C bond angles:




cyclopropane

### 12-3H "Cycloethane" (Ethene)

If one is willing to consider a carbon–carbon double bond as a two-membered ring, then ethene, $C_2H_4$, is the simplest possible cycloalkane ("cycloethane"). As such, $C_2H_4$ has C–C–C valence angles of 0° and therefore an angle strain of 109.5° at each $CH_2$ group compared to the tetrahedral value:




**Exercise 12-15** Write structural formulas for all of the possible cis-trans isomers of the following compounds and designate the configuration of each by name (see Section 5-1):

**a.** 1,3-dichlorocyclopentane
**b.** 1,1,3-trimethylcyclohexane
**c.** 1,2,3-trimethylcyclopropane
**d.** (3-methylcyclobutyl)-3-methylcyclobutane

## 12-4 STRAIN IN CYCLOALKANE RINGS

### 12-4A The Baeyer Theory

Many of the properties of cyclopropane and its derivatives are similar to the properties of alkenes. In 1890, the famous German organic chemist, A. Baeyer, suggested that cyclopropane and cyclobutane derivatives are different from

cyclopentane and cyclohexane, because their C—C—C angles cannot have the tetrahedral value of 109.5°. At the same time, Baeyer hypothesized that the difficulties encountered in synthesizing cycloalkane rings from C7 upward was the result of the angle strain that would be expected if the large rings were regular planar polygons (see Table 12-3). Baeyer also believed that cyclohexane had a planar structure like that shown in Figure 12-2, which would mean that the bond angles would have to deviate 10.5° from the tetrahedral value. However, in 1895, the then unknown chemist H. Sachse suggested that cyclohexane exists in the strain-free chair and boat forms discussed in Section 12-3. This suggestion was not accepted at the time because it led to the prediction of several possible isomers for compounds such as chlorocyclohexane (cf. Exercise 12-4). The idea that such isomers might act as a single substance, as the result of rapid equilibration, seemed like a needless complication, and it was not until 1918 that E. Mohr proposed a definitive way to distinguish between the Baeyer and Sachse cyclohexanes. As will be discussed in Section

**Table 12-3**
Strain and Heats of Combustion of Cycloalkanes

| Cycloalkane, $(CH_2)_n$ | $n$ | Angle strain at each $CH_2$, deg[a] | Heat of combustion,[b] $\Delta H^0$, kcal mole$^{-1}$ | Heat of combustion per $CH_2$, $\Delta H^0/n$, kcal | Total strain,[c] kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| ethene | 2 | 109.5 | 337.2 | 168.6 | 22.4 |
| cyclopropane | 3 | 49.5 | 499.9 | 166.6 | 27.7 |
| cyclobutane | 4 | 19.5 | 655.9 | 164.0 | 26.3 |
| cyclopentane | 5 | 1.5 | 793.4 | 158.7 | 6.4 |
| cyclohexane | 6 | (10.5)[d] | 944.8 | 157.5 | 0.4 |
| cycloheptane | 7 | (19.1)[d] | 1108.1 | 158.4 | 6.3 |
| cyclooctane | 8 | (25.5)[d] | 1268.9 | 158.6 | 9.7 |
| cyclononane | 9 | (30.5)[d] | 1429.5 | 158.8 | 12.9 |
| cyclodecane | 10 | (34.5)[d] | 1586.1 | 158.6 | 12.1 |
| cyclopentadecane | 15 | (46.5)[d] | 2362.5 | 157.5 | 1.5 |
| open-chain alkane | | | | 157.4 | |

[a]Angle strain calculated as the difference between the internal angle of a regular polygon and the tetrahedral angle of 109.5°. The actual strain values are somewhat different because the observed $CH_2$—$CH_2$—$CH_2$ angles are about 112.5° in linear hydrocarbons (Section 12-3A).

[b] For gaseous hydrocarbons to give liquid water at 25°. Data from S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71,** 261 (1952); J. Coops, H. Van Kamp, W. A. Lambgreats, B. J. Visser, and H. Dekker, *Rec. Trav. Chim.* **79,** 1226 (1960); and D. R. Shull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds,* John Wiley and Sons, Inc., New York, 1969.

[c]Calculated by subtracting ($n \times 157.4$) from the observed heat of combustion. [d]Assuming planar rings.

12-9, the result, now known as the Sachse–Mohr theory, was complete confirmation of the idea of nonplanar large rings.

Because cyclopentane and cyclobutane (Sections 12-3E and 12-3F) also have nonplanar carbon rings, it is clear that the Baeyer postulate of planar rings is not correct. Nonetheless, the idea of angle strain in small rings is important. There is much evidence to show that such strain produces thermodynamic instability and usually, but not always, enhanced chemical reactivity.

## 12-4B Heats of Combustion of Cycloalkanes. Strain Energies

The strain in ring compounds can be evaluated quantitatively by comparing the heats of combustion per $CH_2$ group, as in Table 12-3. The data indicate that cyclohexane is virtually strain-free, because the heat of combustion per $CH_2$ is the same as for alkanes (157.4 kcal mole$^{-1}$). The increase for the smaller rings clearly reflects increasing angle strain and, to some extent, unfavorable interactions between nonbonded atoms. For rings from $C_7$ to $C_{12}$ there appears to be a residual strain for each additional $CH_2$ of 1 to 1.5 kcal mole$^{-1}$. These rings can be puckered into flexible conformations with normal C—C—C angles, but as will be shown in Section 12-6, from $C_7$ to $C_{13}$ such arrangements all have pairs of partially eclipsed or interfering hydrogens. The larger cycloalkanes such as cyclopentadecane appear to be essentially strain-free.

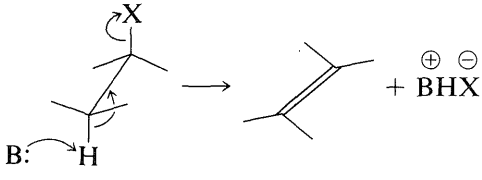
We expect that the total strain in cycloalkanes of the type $(CH_2)_n$ should decrease rapidly in the order $n = 2 > n = 3 > n = 4$. However, the data of Table 12-3 show that the order actually is $3 \cong 4 > 2$. This difference in order often is disguised by dividing the heats of combustion by the numbers of $CH_2$ groups and showing that the heats of combustion per $CH_2$ are at least in the order expected from bond-angle strain. This stratagem does not really solve the problem.

> It is important to recognize that when we evaluate strain from the heats of combustion per $CH_2$ group, we are assuming that the C–H bonds have the *same* strength, independent of $n$. However, the bond-dissociation energies of each of the C–H bonds of ethene and cyclopropane are greater than of the C2–H bonds of propane (Table 4-6). Any amount that these bonds are *stronger* than normal will make the strain energies judged from heats of combustion appear to be *less*. If we take the C–H bonds to be on the average 2 kcal mole$^{-1}$ stronger in cyclobutane, 6 kcal mole$^{-1}$ stronger in cyclopropane, and 13 kcal mole$^{-1}$ stronger in ethene, we can correct the carbon–carbon strain energies accordingly. For cyclobutane the corrected strain then is $8 \times 2$ (for the eight C–H bonds) + 26.3 (total strain from Table 12-3) = 42.3 kcal mole$^{-1}$. The corresponding figures for cyclopropane are $6 \times 6 + 27.6 = 63.6$ kcal, and for ethene, $4 \times 13 + 22.4 = 74.4$ kcal. The results support the intuitive expectations by giving larger differences in the right direction for the strain energies of cyclobutane, cyclopropane, and ethene. Whether this analysis is quantitatively correct or not, it does give some indication of why *strain energy* is not a very precise concept—unless we can reliably estimate the *net* effects of strain.

## 12-5 CHEMICAL PROPERTIES

Strain in small-ring cycloalkanes has a profound influence on their heats of combustion (Table 12-3). We reasonably expect that other chemical properties also will be affected. Indeed, like alkenes, cyclopropane and cyclobutane undergo C–C bond cleavage reactions that are not observed for cyclopentane and cyclohexane, or for saturated, open-chain hydrocarbons. A summary of these reactions is presented in Table 12-4. It will be seen that the reactions result in cleavage of a C–C bond to give an open-chain compound with normal bond angles. Relief of angle strain is an important contributing factor to the driving force for these reactions. Therefore, ethene is highly reactive, whereas cyclopropane and cyclobutane are somewhat less reactive. The C–C bonds of the larger, relatively strain-free cycloalkanes are inert, so these substances resemble the alkanes in their chemical behavior. Substitution reactions, such as chlorination of cyclopentane and higher cycloalkanes, generally are less complex than those of the corresponding alkanes because there are fewer possible isomeric substitution products. Thus cyclohexane gives only one monochloro product, whereas hexane gives three isomeric monochloro hexanes.

Conformation has a major influence on the chemical reactivity of cycloalkanes. To understand its effect in any one reaction, we first need to know what the conformation is of the transition state, and this requires a knowledge of the reaction mechanism. Next, we have to decide what amount of energy is required for the reactants to achieve transition-state conformations. For example, consider the E2 elimination discussed in Section 8-8D. The preferred transition state requires the leaving groups to be antarafacial and coplanar:




For cyclohexane derivatives to react in this way, the transition-state conformation must have both leaving groups *axial:*

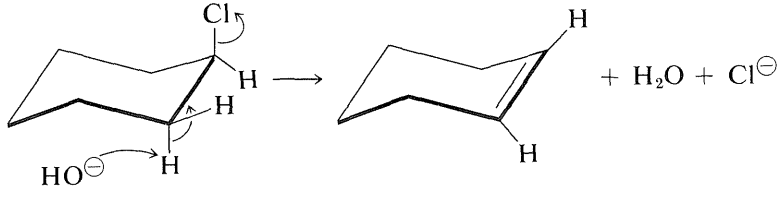


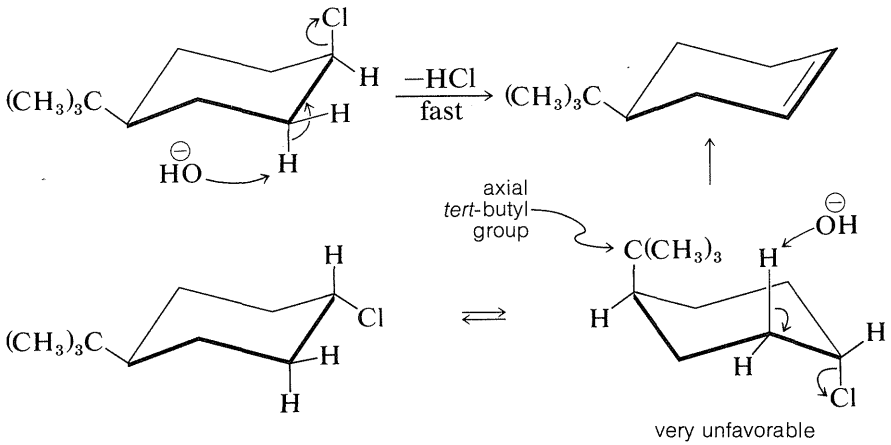
**Table 12-4**
Ring-Cleavage Reactions of Cycloalkanes

| Reaction | "Cycloethane" $n = 2$ | Cyclopropane $n = 3$ | Cyclobutane $n = 4$ | Cyclopentane $n = 5$ | Cyclohexane $n = 6$ |
|---|---|---|---|---|---|
| $(CH_2)_n + Br_2 \longrightarrow \begin{matrix} CH_2Br \\ \vert \\ (CH_2)_{n-2} \\ \vert \\ CH_2Br \end{matrix}$ | very readily[a] | slowly[b] | inert | inert | inert |
| $(CH_2)_n + H_2SO_4 \longrightarrow \begin{matrix} CH_3 \\ \vert \\ (CH_2)_{n-2} \\ \vert \\ CH_2OSO_3H \end{matrix}$ | readily | readily | ? | inert | inert |
| $(CH_2)_n + KMnO_4 \longrightarrow \begin{matrix} CH_2OH \\ \vert \\ (CH_2)_{n-2} \\ \vert \\ CH_2OH \end{matrix}$ | readily | inert | inert | inert | inert |
| $(CH_2)_n + H_2 \longrightarrow \begin{matrix} CH_3 \\ \vert \\ (CH_2)_{n-2} \\ \vert \\ CH_3 \end{matrix}$ | readily | readily at 120° | readily at 200° | inert | inert |

[a]By either polar or radical mechanisms.

[b]Reactions by polar mechanisms are very slow with bromine alone, but apparently are accelerated by electrophilic agents, which activate bromine by facilitating formation of $Br^{\oplus}$ by complexing with $Br^{\ominus}$ (e.g., HBr, $FeBr_3$, etc.). Cyclopropane reacts rather rapidly with bromine by a radical-chain mechanism, even at −78°, if bromine atoms are formed by light irradiation.

For this reason, compounds such as *cis*-4-*tert*-butylchlorocyclohexane eliminate HCl much more readily by the E2 mechanism than do the corresponding trans isomers.




To have the antarafacial coplanar mechanism operate with the trans isomer, the transition state would have to have the *tert*-butyl group in the highly unfavorable axial position.

---

**Exercise 12-16** Use the data of Table 12-3 and any needed bond energies to calculate $\Delta H^0$ for the following reaction in the vapor state at 25° with $n = 3$, 4, and 5:

$$(CH_2)_n \longrightarrow CH_3(CH_2)_{n-3}CH{=}CH_2$$

What can you conclude about the stability of the cycloalkanes with $n = 3$, 4, and 5 with respect to corresponding open-chain compounds with double bonds? Include consideration of the possible entropy effects, Section 4-4B.

**Exercise 12-17** Use the heats of combustion to liquid water given in Table 12-3 and appropriate bond energies to calculate $\Delta H^0$ (vapor) for ring-opening of the cycloalkanes with bromine in the range $n = 2$ to $n = 6$:

$$(CH_2)_n + Br_2 \longrightarrow (CH_2)_{n-2}(CH_2Br)_2$$

**Exercise 12-18** Investigate the thermodynamic feasibility of the following propagation steps for opening the rings of cycloalkanes with $n = 2$ to $n = 6$ by a radical-chain mechanism:

$$(CH_2)_n + Br\cdot \longrightarrow BrCH_2\text{-}(CH_2)_{n-2}CH_2\cdot$$

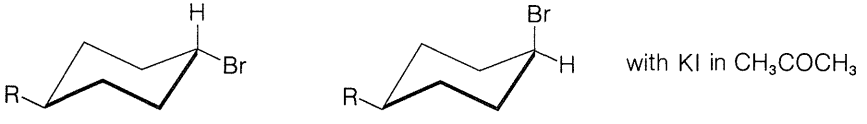
$$BrCH_2\text{-}(CH_2)_{n-2}CH_2\cdot + Br_2 \longrightarrow (CH_2)_{n-2}(CH_2Br)_2 + Br\cdot$$

Use 83 kcal mole$^{-1}$ for the bond-dissociation energy of a normal C–C bond and 68 kcal mole$^{-1}$ for the bond-dissociation energy of a C–Br bond. (An easy way to solve a problem of this type is first to calculate $\Delta H$ of each step for cyclohexane, for which there is no strain, then to make suitable corrections for the strain that is present for smaller values of $n$.)

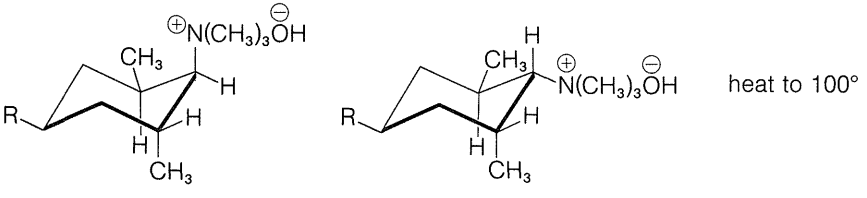
**Exercise 12-19** Show how the reactions described in Table 12-4 could be used to determine whether a hydrocarbon of formula $C_4H_8$ is methylcyclopropane, cyclobutane, or 1-butene ($CH_3CH_2CH{=}CH_2$). Write equations for the reactions used.

**Exercise 12-20** **a.** Consider that all of the following cyclohexane derivatives have R as a very large group so the conformations shown are the most stable ones. Which member of each pair would you expect to react more rapidly under the given conditions and why? Draw the structure and configuration of the major product. (Review Section 8-8.)

1.




2.




**b.** Make sawhorse-type drawings of the possible products of antarafacial addition of bromine to 4-*tert*-butylmethylcyclohexene. Which isomer would you expect to be formed most rapidly? Give your reasoning.

## 12-6 THE LARGER CYCLOALKANES AND THEIR CONFORMATIONS

The Baeyer strain theory suggested that the larger-ring cycloalkanes are difficult to synthesize because of angle strain associated with planar rings, as calculated in Table 12-3. We now know that, except for cyclopropane, none of the cycloalkanes have planar carbon rings and that the higher cycloalkanes have normal or nearly normal bond angles. The reason that the higher cycloalkanes are generally difficult to synthesize from open-chain compounds is not so much angle strain, as Baeyer hypothesized, but the low probability of having reactive groups on the two fairly remote ends of a long hydrocarbon chain come together to effect

cyclization. Usually, coupling of reactive groups on the ends of *different* molecules occurs in preference to cyclization, unless the reactions are carried out in very dilute solutions. This is called the **high-dilution** technique for achieving ring formation when the ring-forming reaction has to compete with rapid intermolecular reactions.

---

**Exercise 12-21*** Formation of a cycloalkane $(CH_2)_n$ by reactions such as

$$Br\text{-}(CH_2)_n\text{-}ZnBr \longrightarrow (CH_2)_n + ZnBr_2$$

occurs in competition with other reactions such as

$$2Br\text{-}(CH_2)_n\text{-}ZnBr \longrightarrow Br\text{-}(CH_2)_{2n}\text{-}ZnBr + ZnBr_2$$

**a.** Explain why cyclization reactions of this kind carried out in *dilute* solutions are likely to give better yields of $(CH_2)_n$ than in *concentrated* solutions.
**b.** Make graphs that show, as a function of $n$ in the range 3 to 15, how the yield of cycloalkane might be expected to depend on (1) the total strain in the ring formed (see Table 12-3), and (2) the probability that at any given instant the reactive ends will be oriented properly with respect to one another so as to permit cyclization.
**c.** Explain how the factors considered in Part b must be balanced relative to one another to account for the reported yields of cyclization products for the following ring sizes: $(CH_2)_3 > 80\%$; $(CH_2)_4 > 7\%$; $(CH_2)_6$ 45%; larger rings $< 10\%$.

---

With regard to conformations of the larger cycloalkanes, we first note that the chair form of cyclohexane is a "perfect" conformation for a cycloalkane. The C–C–C bond angles are close to their normal values, all the adjacent hydrogens are staggered with respect to one another, and the 1,3-axial hydrogens are not close enough together to experience nonbonded repulsions. About the only qualification one could put on the ideality of the chair form is that the trans conformation of butane is somewhat more stable than the gauche conformation (Section 5-2), and that all of the C—C—C—C segments of cyclohexane have the gauche arrangement. Arguing from this, J. Dale[6] has suggested that large cycloalkane rings would tend to have trans C—C—C—C segments to the degree possible and, indeed, cyclotetradecane seems to be most stable in a rectangular conformation with trans C—C—C—C bond segments (Figure 12-16). This conformation has a number of possible substituent positions, but because only single isomers of monosubstituted cyclotetradecanes have been isolated, rapid equilibration of the various conformational isomers must occur. Other evidence indicates that the barrier to interconversion of these conformations is about 7 kcal $mole^{-1}$.

[6]Pronounced Dàlluh.

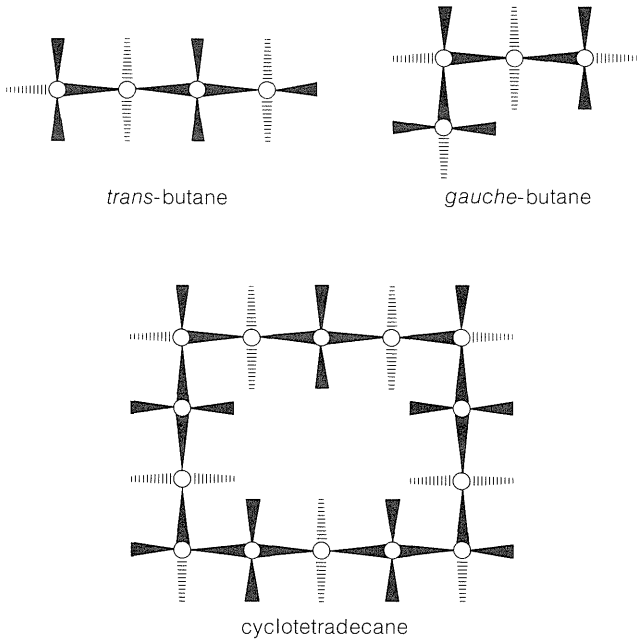


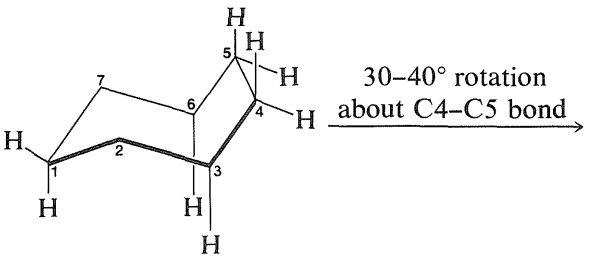

**Figure 12-16** Favored conformation of cyclotetradecane as proposed by Dale. For comparison, the trans and gauche forms of butane are shown by the same convention. (The convention implies that the wedged lines are C–C or C–H bonds projecting out of the plane of the paper, with the wide end closest to you, and the broken lines are C–H bonds projecting behind the plane of the paper. The result is an "aerial" view of the molecule in the most stable staggered conformation.)

With the cycloalkanes having 7 to 10 carbons, there are problems in trying to make either trans or gauche C—C—C—C segments, because the sizes of these rings do not allow the proper bond angles or torsional angles, or else there are more or less serious nonbonded repulsions. Consequently each of these rings assumes a compromise conformation with some eclipsing, some nonbonded repulsions, and some angle distortions. Brief comments on some of these conformations follow. It will be useful to use molecular models to see the interactions involved.

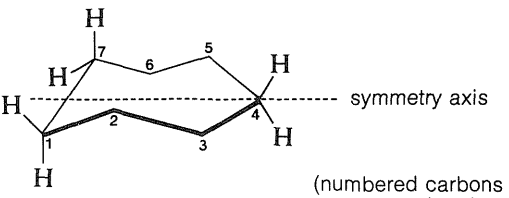
## 12-6A Cycloheptane

Possible conformations for cycloheptane include the "comfortable" appearing chair form, **7**. However, this form has eclipsed hydrogens at C4 and C5 as well as nonbonded interactions between the axial-like hydrogens on C3 and C6. The best compromise conformation is achieved by a 30°–40° rotation around the C4–C5 bond to relieve the eclipsing of the hydrogens. This spreads the interfering hydrogens at C3 and C6 and results in a somewhat less strained conformation called the *twist chair*. The twist chair, **8**, is very flexible and

probably only about 3 kcal mole$^{-1}$ of activation is required to interconvert the various possible monosubstituted cycloheptane conformations.




**7**

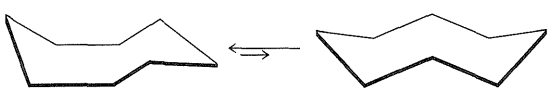



**8**

**Exercise 12-22*** If the twist-chair conformation **8** were rigid rather than flexible, how many different monochlorocycloheptanes would you expect (a) excluding mirror-image isomers and (b) including mirror image isomers?

## 12-6B Cyclooctane

There are several more or less reasonable looking cyclooctane conformations. After much research it now is clear that the favored conformation is the *boat-chair,* **9**, which is in equilibrium with a few tenths percent of the *crown* conformation, **10**:



**9** **10**

The activation energy for interconversion of these two forms is about 10 kcal mole$^{-1}$. The boat-chair conformation **9** is quite flexible and movement of its $CH_2$ groups between the various possible positions occurs with an activation energy of only about 5 kcal mole$^{-1}$.

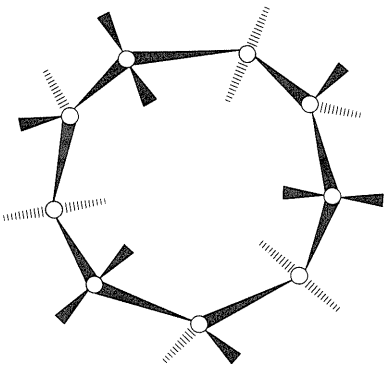


**Figure 12-17** Twist boat-chair conformation of cyclononane (after Dale)

## 12-6C Cyclononane

Several more or less reasonable conformations of cyclononane also can be developed, but the most favorable one is called the *twist-boat-chair,* which has three-fold symmetry (Figure 12-17). The activation energy for inversion of the ring is about 6 kcal $mole^{-1}$.

## 12-6D Cyclodecane

The stable conformation of cyclodecane (Figure 12-18) is similar to that of cyclotetradecane (Figure 12-16). However, there are relatively short H····H distances and the C–C–C bond angles are somewhat distorted because of cross-ring hydrogen-hydrogen repulsions. The most stable position for a substituent on the cyclodecane ring is the one indicated in Figure 12-18. The least stable positions are those in which a substituent replaces any of the six hydrogens shown, because nonbonded interactions are particularly strong at these positions. The activation energy for interconversion of substituent positions is about 6 kcal $mole^{-1}$.

---

**Exercise 12-23*** A conformation of cyclooctane called *boat-boat* can be formed by having two gauche C—C—C—C segments, as shown in Figure 12-19. As drawn, this conformation has all hydrogens staggered and normal C–C–C bond angles. Explain why it is not a favorable conformation. Use of models will be very helpful.

---

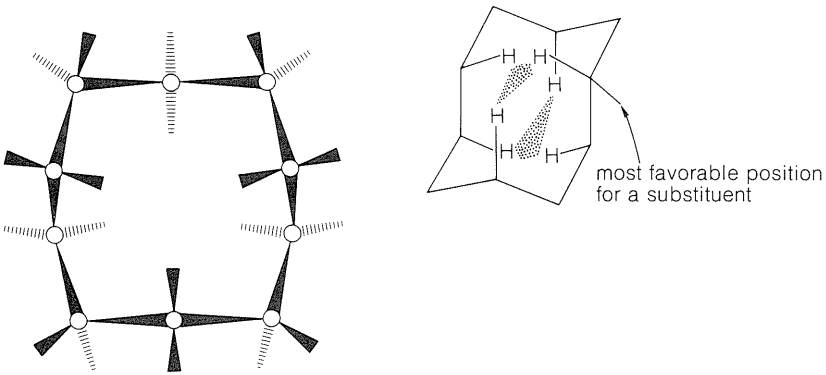



**Figure 12-18** Most stable conformation of cyclodecane; Dale and sawhorse representations. The shaded area in the sawhorse convention indicates substantial nonbonded H · · · · H interactions.

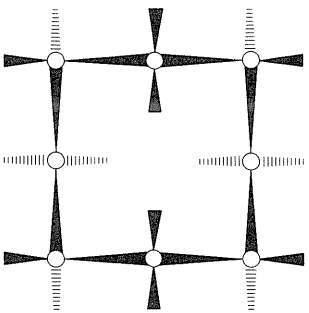


**Figure 12-19** Boat-boat conformation of cyclooctane, based on two gauche forms of butane (see Figure 12-16 and Exercise 12-23).

## 12-7 CYCLOALKENES AND CYCLOALKYNES

The C—C=C angle in alkenes normally is about 122°, which is 10° larger than the normal C—C—C angle in cycloalkanes. This means that we would expect about 20° more angle strain in small-ring cycloalkenes than in the cycloalkanes with the same numbers of carbons in the ring. Comparison of the data for cycloalkenes in Table 12-5 and for cycloalkanes in Table 12-3 reveals that this expectation is realized for cyclopropene, but is less conspicuous for cyclobutene and cyclopentene. The reason for this is not clear, but may be connected in part with the C–H bond strengths (see Section 12-4B).

Cyclopropene has rather exceptional properties compared to the other cycloalkenes. It is quite unstable and the liquid polymerizes spontaneously although slowly, even at −80°. This substance, unlike other alkenes, reacts

**Table 12-5**
Properties of Some Cycloalkenes and Cycloalkynes

| Compound | Mp, °C | Bp, °C | $-\Delta H^0$ of hydrogenation,[a] kcal mole$^{-1}$ | Net strain energy,[b] kcal mole$^{-1}$ |
|---|---|---|---|---|
| "cycloethene" (ethyne) | −81 | −84 | 42[c] | 35 |
| cyclopropene | — | −36 | 54 | 53 |
| cyclobutene | — | 2 | 31 | 28 |
| cyclopentene | −135 | 44 | 27 | 4 |
| cyclohexene | −104 | 83 | 30 | 1 |
| cycloheptene | −56 | 115 | 27 | 4 |
| *cis*-cyclooctene | −12 | 138 | 24 | 5 |
| *trans*-cyclooctene | −59 | 143 | 33 | 14 |
| *cis*-cyclononene | — | 168 | 25 | 9 |
| *trans*-cyclononene | — | $95^{30\ mm}$ | 28 | 12 |
| cyclooctyne | — | $57^{22\ mm}$ | 69[d] | 16[e] |
| cyclononyne | — | $62^{13\ mm}$ | 62[d] | 12[e] |
| cyclodecyne | — | $80^{12\ mm}$ | 56[d] | 5[e] |

[a]For the vapor state, calculated from data summarized by P. von R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.* **92,** 2377 (1970).

[b]Calculated assuming that the normal heat of hydrogenation of a cis-disubstituted double bond is 29 kcal mole$^{-1}$ (cf. Table 11-2). With cyclopropene as an example, the net strain energy is obtained as $54 - 29 + 28 = 53$ kcal mole$^{-1}$, where 54 kcal is the experimental $-\Delta H^0$ of hydrogenation, −29 kcal is $\Delta H^0$ for hydrogenation of a normal cis-disubstituted alkene, and 28 kcal is the strain energy of cyclopropane, the hydrogenation product.

[c]For hydrogenation to $CH_2{=}CH_2$.

[d]Estimated from the data of R. B. Turner, A. D. Jarrett, P. Goebel, and B. J. Mallon, *J. Amer. Chem. Soc.* **95,** 790 (1973).

[e]Calculated assuming the heat of hydrogenation of a disubstituted alkyne normally is 63 kcal mole$^{-1}$.

rapidly with iodine and behaves like an alkyne in that one of its double-bond hydrogens is replaced in silver–ammonia solution to yield an alkynide-like silver complex.

One of the most interesting developments in the stereochemistry of organic compounds in recent years has been the demonstration that *trans*-cyclooctene (but not the cis isomer) can be resolved into stable chiral isomers (enantiomers, Section 5-1B). In general, a *trans*-cycloalkene would not be expected to be resolvable because of the possibility for formation of achiral conformations with a plane of symmetry. Any conformation with all of the carbons in a plane is such an achiral conformation (Figure 12-20a). However, when the chain connecting the ends of the double bond is short, as in *trans*-cyclooctene, steric hindrance and steric strain prevent easy formation of planar conformations, and both mirror-image forms (Figure 12-20b) are stable and thus resolvable.

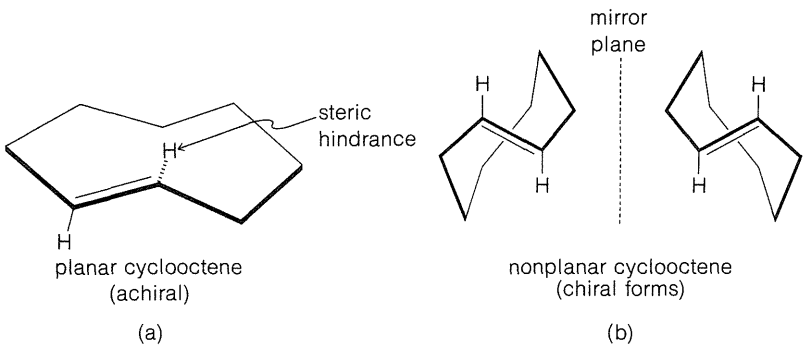



**Figure 12-20** Representation of (a) achiral and (b) chiral conformations of *trans*-cycloalkenes, using *trans*-cyclooctene as a specific example. For *trans*-cyclooctene, the achiral state is highly strained because of interference between the "inside" alkenic hydrogen and the $CH_2$ groups on the other side of the ring. Consequently the mirror-image forms are quite stable. With *trans*-cyclononene, the planar state is much less strained and, as a result, the optical isomers are much less stable. With *trans*-cyclodecene, it has not been possible to isolate mirror-image forms because the two forms corresponding to (b) are interconverted through achiral planar conformations corresponding to (a) about $10^{16}$ times faster than with *trans*-cyclooctene.

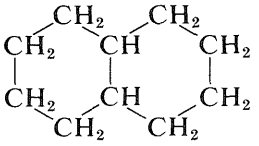
**Exercise 12-24** Space-filling models (Section 2-2B) indicate that the chiral forms of *trans*-cyclopentadecene are likely to be readily interconverted at room temperature. How and where might *trans*-cyclopentadecene be substituted to give stable chiral forms that possess a chiral center but *no* chiral carbon atoms?

The C—C≡C bond angles in alkynes normally are 180° and the angle strain involved in making a small-ring cycloalkyne, such as cyclopropyne, apparently is prohibitive. The smallest reasonably stable member of the series is cyclooctyne, and its properties, along with those of some higher homologs, are shown in Table 12-5. Strong evidence has been adduced for the existence of cyclopentyne, cyclohexyne, and cycloheptyne as unstable reaction intermediates.

## 12-8 NOMENCLATURE OF POLYCYCLOALKANES

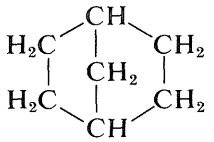
There are many hydrocarbons and hydrocarbon derivatives with two or more rings having common carbon atoms. Such a substance is decalin, which has

ten carbons arranged in two six-membered rings:

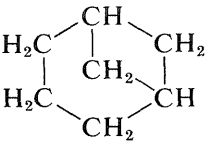


decalin
(bicyclo[4.4.0]decane)
(decahydronaphthalene)

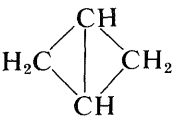
Compounds of this type usually are named by attaching the prefix *bicyclo* to the name of the open-chain hydrocarbon with the *same total number of carbon atoms as in the rings*. Thus decalin, which has ten carbons in the ring system, is a *bicyclodecane*. Next, we have to have a way to specify the sizes of the rings, which is done by counting the number of carbon atoms in each of the chains connecting the two atoms that constitute the **ring junctions or bridgeheads.** Decalin has *four* carbons in each of two chains and *none* in the third. Therefore, decalin is *bicyclo[4.4.0]decane*. Notice that the numbers are enclosed in square brackets after the prefix "bicyclo" and before the name of the hydrocarbon. The numbers are listed in order of decreasing magnitude and are properly separated by periods, not commas. Some other examples follow:



bicyclo[2.2.1]heptane



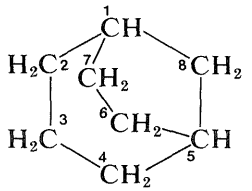
bicyclo[3.1.1]heptane



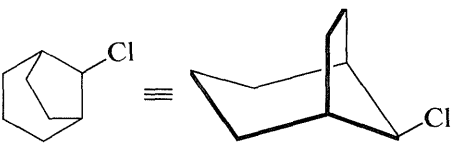
bicyclo[1.1.0]butane

To name substituted polycycloalkanes, a numbering system is required. In the IUPAC system the *main* ring is the one containing the largest number of carbon atoms. Two of the carbons in the main ring serve as junctions for the main bridge, which is chosen to be as large as possible, consistent with the choice of the main ring. Additional rules are required for more complex cases, but these are not of interest to us here.

In numbering bicyclic ring systems that have two ring junctions, one of them is chosen as C1. The numbering proceeds along the *longest* chain of carbons to the next junction, then continues along the next longest chain, and finally is completed along the shortest chain. For example,



bicyclo[3.2.1]octane

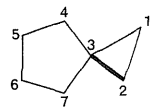


8-chlorobicyclo[3.2.1]octane

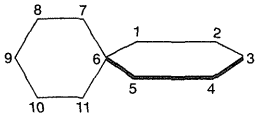
11

Here, the main ring has seven carbons (C1 to C7) and there is a one-carbon bridge (C8).

When the hydrocarbon rings have only one carbon in common, they are called *spiranes* and are given systematic names in accord with the following examples:



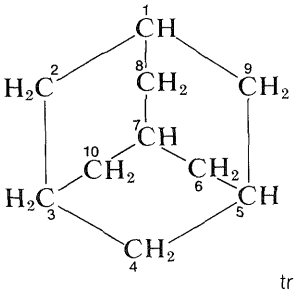

spiro[4.2]heptane



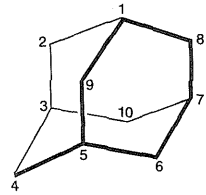

spiro[5.5]undecane

Notice that for spiranes the numbering starts next to the junction point in the *smaller* ring.

The naming of tricycloalkanes follows the same general system.[7] The largest ring and its main linkage form a bicyclic system, and the location of the fourth or *secondary* linkage is shown by superscripts. The systematic name of the interesting hydrocarbon adamantane is given below as an example; its conformation also is shown. The largest ring in adamantane is eight-membered and the carbons that constitute it could be selected in several different ways. The carbon chosen as C9 lies between C1 and C5, not between the higher-numbered C3 and C7:



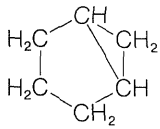

≡



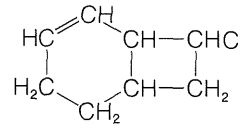

tricyclo(3.3.1.1$^{3,7}$)decane
(adamantane)

**Exercise 12-25** Name each of the following compounds by an accepted system:

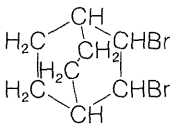
**a.**

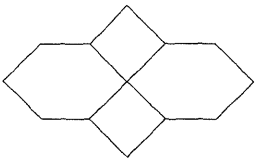


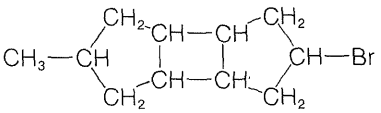

**b.**

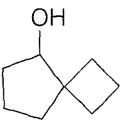



[7]To determine whether a given bridged polycyclic ring system should be *bicyclo-*, *tricyclo-*, and so on, use the rule that the number of rings is equal to the minimum number of bond cleavages to convert the ring system into an *acyclic* hydrocarbon having the same number of carbons.

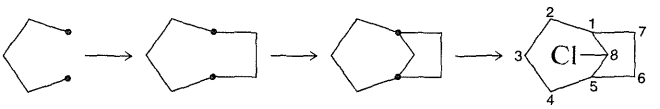
c. 

e. 

d. 

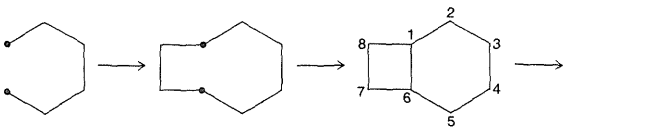
f. 

To generate a structure from a name such as 8-chlorobicyclo[3.2.1]octane, **11**, start with a pair of junction atoms, connect them as prescribed, then number the initial skeleton, make the final connections, and locate the substituents. The steps follow:

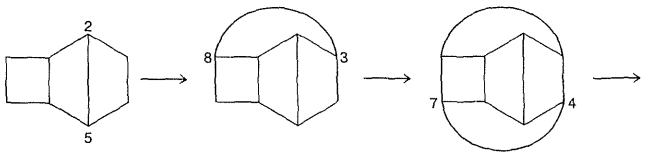


[3. [3.2. [3.2.1] 8-chlorobicyclo-[3.2.1]octane, **11**

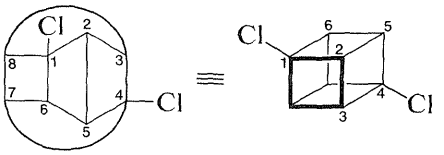
A further and more complicated example is 1,4-dichloropentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane:



[4. [4.2 [4.2.0.



[4.2.0.$0^{2,5}$. [4.2.0.$0^{2,5}$.$0^{3,8}$. [4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]



1,4-dichloropentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane

The most difficult part of the whole procedure may be generating the final structure in appropriate perspective. The task of doing this can be simplified greatly by the use of molecular models.

## 12-9 CONFORMATIONS OF DECALIN

The six-membered rings of decalin, like those of cyclohexane, are expected to be most stable in the chair form. However, there are two possible ways in which two chairs can be joined (Figure 12-21). The ring-junction hydrogens may be either on the same side of the molecule (*cis*-decalin) or on opposite sides (*trans*-decalin). When the two rings are joined through two equatorial-type bonds, *trans*-decalin results, whereas an axial-equatorial union gives *cis*-decalin. Both isomers are known, and the trans isomer is about 2 kcal mole$^{-1}$ more stable than the cis isomer, largely because of relatively unfavorable nonbonded interactions within the concave area of *cis*-decalin (see Figure 12-22).

**Exercise 12-26** Use ball-and-stick models to assess the degree of stability to be expected for a decalin with chair-form rings and an axial-axial ring fusion.

It is of historical interest to note that the Baeyer strain theory with its planar rings predicts only one form of decalin with the ring-junction hydrogens on the same side of the molecule (Figure 12-23). The Sachse–Mohr concept of puckered strain-free rings allows for two isomers. In fact, Mohr predicted that the two isomers of decalin should exist before W. Hückel (1925) succeeded in preparing them. Both isomers occur in petroleum.

At this point, it probably will be helpful to construct models of *cis*- and *trans*-decalins to appreciate the following: (a) The two compounds cannot interconvert unless C–C or C–H bonds first are broken. (b) *trans*-Decalin is a relatively rigid system and, unlike cyclohexane, the two rings cannot flip from one chair form to another. Accordingly, the orientation of the substituent is fixed in the chair-chair conformation of *trans*-decalin. (c) The chair-chair forms of *cis*-decalin are relatively flexible, and inversion of both rings at once occurs fairly easily (the barrier to inversion is about 14 kcal mole$^{-1}$). A substituent therefore can interconvert between axial and equatorial conformations (Figure 12-24).

The ramifications of conformational analysis of flexible and rigid ring systems are of considerable importance to the understanding of stability and reactivity in polycyclic systems. This will become increasingly evident in later discussions.

**Exercise 12-27** The equatorial form of methylcyclohexane is 1.5 kcal mole$^{-1}$ more stable than the axial form because the axial form has steric hindrance between the methyl and two hydrogens, one in the 3- and the other in the 5-position. Knowing that *cis*-decalin is about 2 kcal mole$^{-1}$ less stable than *trans*-decalin, what would you estimate for the relative stabilities of *cis*- and *trans*-9-methyldecalin (numbering as in Figure 12-22)?

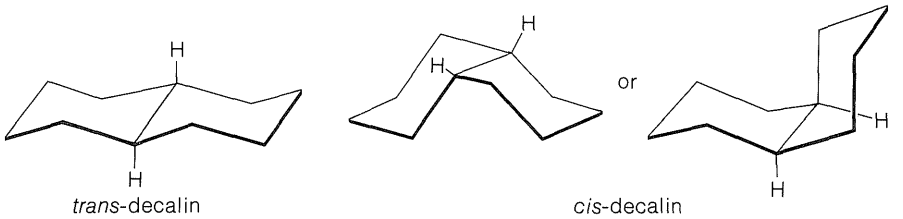



**Figure 12-21** Chair conformations of the decalins. The two drawings of the cis conformation represent the same arrangement of atoms but different perspectives.

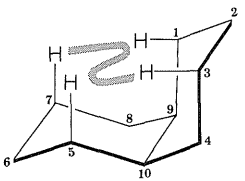



**Figure 12-22** Representation of *cis*-decalin showing nonbonded interactions (shaded areas). The numbering of the decalin ring is the currently accepted convention, which is not the same as the numbering system used generally for bicyclic systems, as described in Section 12-8.

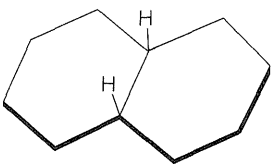



**Figure 12-23** Baeyer formulation of decalin which, with planar rings, allows for only the cis configuration at the ring conjunction.

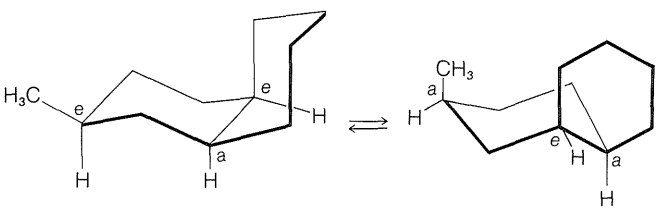


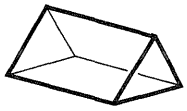

**Figure 12-24** Ring inversion in *cis*-decalin, which takes a substituent from the equatorial to the axial position. In both conformations, each ring is a chair form. You should check this process with ball-and-stick models.

## 12-10 STRAIN IN POLYCYCLIC MOLECULES

Knowing the importance of angle and eclipsing strain in the small-ring cycloalkanes, we should expect that these strains would become still more important in going from cyclobutane to bicyclo[1.1.0]butane or from cyclooctane to pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane (cubane). This expectation is borne out by the data in Table 12-6, which gives the properties of several illustrative small-ring polycyclic molecules that have been synthesized only in recent years.

The extraordinary strain energy of cubane (~142 kcal mole$^{-1}$) is worthy of special note. It is roughly equal to six times the strain energy of a single cyclobutane ring (~26 kcal mole$^{-1}$) as befits a molecule made up of six cyclobutane rings as faces. Despite this, cubane is surprisingly stable to spontaneous decomposition processes, although it will rearrange under the influence of metal or acid catalysts.

Another extraordinarily strained polycyclic hydrocarbon that has been prepared in recent years is prismane (the Ladenburg structure for benzene, see Exercise 1-6).



prismane

This substance is a liquid that decomposes explosively when heated. In *dilute* solution at 100°, it is converted slowly to benzene.

---

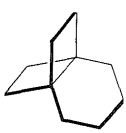
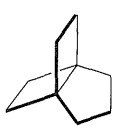
**Exercise 12-28** Name prismane according to the system described in Section 12-8.

**Exercise 12-29** Draw a sawhorse-style formula for bicyclo[1.1.0]butane and formulas for all of the eight possible dichlorobicyclo[1.1.0]butanes (including chiral forms).

---

One of the most interesting types of polycyclic carbon compounds prepared in recent years is the group of tricyclic substances known as "propellanes." A typical example is tricyclo[3.2.2.$0^{1,5}$]nonane, which sometimes is called [3.2.2]propellane, **12**. The physical properties of several of these are included in Table 12-6. A quick look at formula **12** probably does not suggest any great structural difference from the bicyclic compounds we have discussed previously. However, if one tries to construct a ball-and-stick model of **12**, one soon concludes that the propellanes are truly extraordinary substances in that all four carbon bonds at the bridgehead carbons extend, not to the corners of a tetrahedron, or even a distorted tetrahedron as for a cyclopropane ring, but

**Table 12-6**
Properties of Some Small-Ring Polycyclic Hydrocarbons

| Name | Structure | Mp, °C | Bp, °C | Heat of formation[a] $\Delta H^0$, kcal mole$^{-1}$ | Strain energy,[b] kcal mole$^{-1}$ |
|---|---|---|---|---|---|
| bicyclo[1.1.0]butane | | – | 8 | 51.9 | 59 |
| spiro[2.2]pentane | | −107 | 39 | 44.2 | 56 |
| bicyclo[2.1.0]pentane | | – | 45.5 | 37.6 | 50 |
| cubane | | 130–131 | – | 148.7 | 143 |
| tricyclo[4.2.2.0$^{1,6}$] |  | 32 | 109$^{11}$ mm | – | – |
| tricyclo[3.2.2.0$^{1,5}$]nonane |  | 11 | – | – | – |
| tricyclo[3.2.1.0$^{1,5}$]octane | | – | 45$^{25}$ mm | – | ~60[c] |
| bicyclo[3.3.1]-1-nonene | | – | ~60$^{5}$ mm | – | ~12[d] |

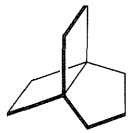
[a]These values are for formation of the respective compound from C(*s*) and $H_2$(*g*) at 25°C.

[b]The strain energies are calculated as the difference in heats of formation in the preceding column and the heats of formation of an imaginary strainless compound with the same number of C–H and C–C bonds, having bond energies as given in Table 4-3, and C(s) ⟶ C(*g*) with $\Delta H^0 = +171.3$ kcal mole$^{-1}$.

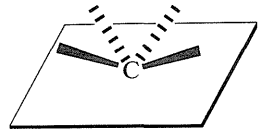
[c]Estimated from heats of combustion of similarly constituted compounds.

[d]Estimated from the heat of hydrogenation.

away from the carbon on the *same side* of a plane through the carbon as in **13**:

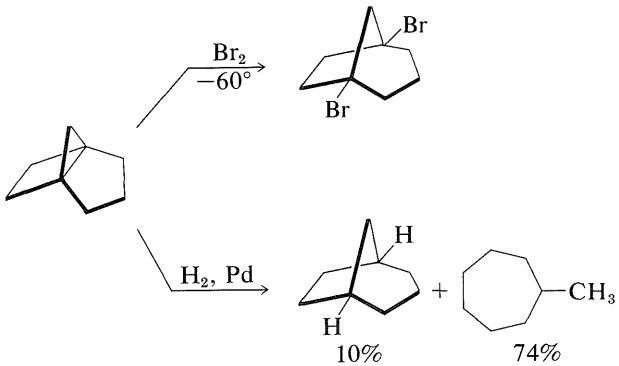


**12**

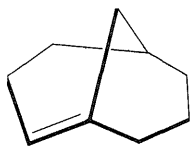



**13**

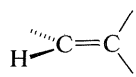
Angle strain is severe. Accordingly, [3.2.1]propellane reacts rapidly with bromine at −60° and with hydrogen over palladium at room temperature:




Still another way to torture the valence angles of carbon is to twist a double bond by connecting it to the bridgehead carbon of a bicyclic system with reasonably small rings, as in bicyclo[3.3.1]-1-nonene, **14**:

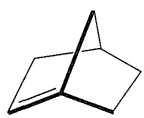


**14**




**15**

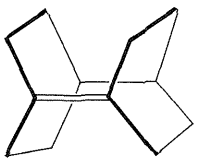
As with **12**, it might appear that there is nothing unusual about **14**. But a ball-and-stick model of **14** reveals that the carbon–carbon double bond is in a strained configuration like **15**. Some of the properties of **14** are given in Table 12-6. That compounds with a double bond to a bridgehead carbon, such as **14**, should be highly strained is known as "Bredt's Rule." The most spectacular example of this form of molecular distortion reported so far is bicyclo[2.2.1]-1-heptene, **16**, for which evidence has been adduced that it is an unstable reaction intermediate:



**16**

**Exercise 12-30*** How could you phrase Bredt's rule so it could distinguish between the lack of stability of **16** and the stability of bicyclo[5.5.0]-1,2-decene, both compounds having a double-bonded carbon at a ring junction?

**Exercise 12-31*** Using the system described in Section 12-8, name the following compound:



To what degree do you think this compound violates Bredt's rule? (Use of ball-and-stick models will be helpful here.) By what kind of mechanism would you expect bromine to add to the double bond? (Review Sections 12-3A, 12-5, 10-6, and 10-7.)

## Additional Reading

P. von R. Schleyer, J. E. Williams, and K. R. Blanchard, "The Evaluation of Strain in Hydrocarbons. The Strain in Adamantane and its Origin," *J. Amer Chem. Soc.* **92,** 2377 (1970).

D. R. Eckroth, "A Method for Manual Generation of Correct von Baeyer Names of Polycyclic Hydrocarbons," *J. Org. Chem.* **32,** 3362 (1967).

E. L. Eliel, *Stereochemistry of Carbon Compounds,* McGraw-Hill Book Company, New York, 1962.

E. L. Eliel, *Conformational Analysis,* McGraw-Hill Book Company, New York, 1965.

M. Hanack, *Conformation Theory,* Academic Press, New York, 1965.

J. Dale, "Exploratory Calculations of Medium and Large Rings. Part 1. Conformational Minima of Cycloalkanes," *Acta Chem. Scand.* **27,** 1115 (1973).

J. Dale, "Exploratory Calculations of Medium and Large Rings. Part 2. Conformational Interconversions in Cycloalkanes," *Acta Chem. Scand.* **27,** 1130 (1973).

R. W. Hoffman, *Dehydrobenzene and Cycloalkynes,* Academic Press, New York, 1967.

## Supplementary Exercises

**12-32** Write structural formulas for substances (one for each part) that fit the following descriptions. Make sawhorse drawings of the substances for which conformational problems are involved.

**a.** a compound of formula $C_4H_8$ that reacts slowly with sulfuric acid and also with bromine (light induced)
**b.** the most highly strained isomer of $C_5H_{10}$
**c.** the possible products from treatment of 1-ethyl-2-methylcyclopropane with bromine (light induced)
**d.** the least-stable chair and the least-stable boat conformations of *cis*-1,4-dichlorocyclohexane
**e.** the most stable geometrical isomer of 1,3-di-*tert*-butylcyclobutane
**f.** a compound with a six-membered ring that is most stable with the ring in a boat form
**g.** *trans*-bicyclo[7.1.0]decane
**h.** the most stable conformation of *trans*-1,3-di-*tert*-butylcyclohexane
**i.** the most stable conformation of *cis*-2-*tert*-butyl-*cis*-decalin
**j.** a boat-boat conformation of *cis*-decalin
**k.** *trans,trans,trans*-tricyclo[8.4.0.$0^{2,7}$]tetradecane

**12-33** The $\Delta H^0$ value for hydrogenation of cyclopropane to propane at 25° in the vapor state is −37.5 kcal $mole^{-1}$. Use this value and any other bond energies to calculate the bond energies of the C–C bonds in cyclopropane on the assumption that all of its C–C bonds are equally strong and the C–H bonds are 6 kcal $mole^{-1}$ stronger than normal. Notice that, by definition, the bond energies must give the proper value of $\Delta H^0$ for the following reaction:

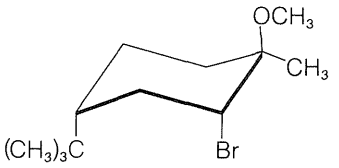
$$(CH_2)_3(g) \longrightarrow 3C(g) + 6H(g)$$

Use your cyclopropane bond energies to calculate $\Delta H^0$ values for the following reactions:
**a.** $(CH_2)_3 \longrightarrow \cdot CH_2—CH_2—CH_2\cdot$ (normal C–C bonds)
**b.** $2(CH_2)_3 \longrightarrow (CH_2)_6$

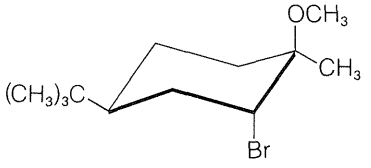
**12-34** Draw structural formulas in reasonable perspective for each of the following substances:
**a.** the cis and trans isomers of bicyclo[3.3.0]octane
**b.** *trans*-tricyclo[3.1.0.$0^{2,6}$]hexane
**c.** tricyclo[3.1.$0^{2,6}$]hexane
**d.** *trans*-2,6-dichlorobicyclo[2.2.2]octane
**e.** quinquecyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane

**12-35** Draw each of the following compounds in perspective to show the preferred conformation. Construct models if in doubt.
**a.** 2-*tert*-butyl-*trans*-decalin
**b.** bicyclo[2.2.2]octane
**c.** spiro[5.4]decane
**d.** *trans*-3-phenyl-1-methylcyclohexane

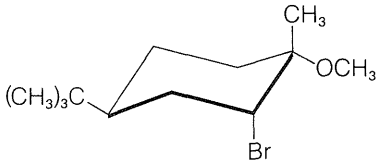
**12-36** When bromine adds to 4-*tert*-butyl-1-methylcyclohexene in $CH_3OH$ solution, which of the following structures, A–F, would be the major product? Give your reasoning in detail.



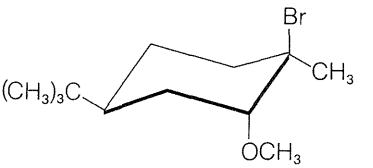

A



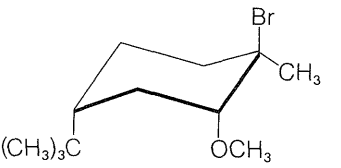

B



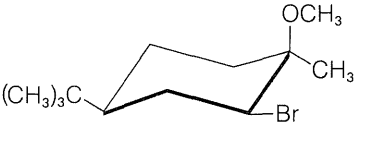

C




D



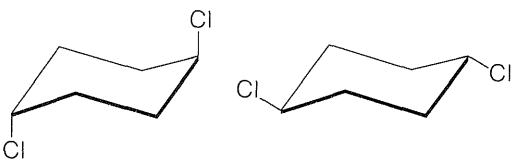

E



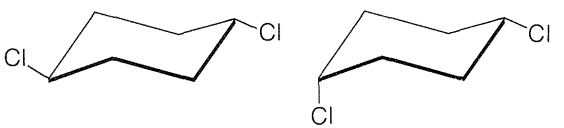

F

**12-37** Which conformational or position isomer in each of the following pairs would you expect to be the most stable (of lowest energy)? (Models will be helpful.)

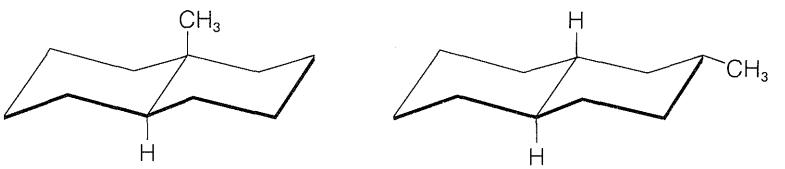
**a.**

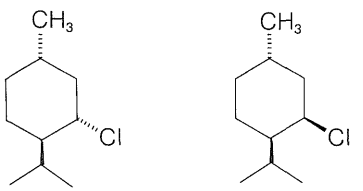



**b.**




**c.**




**d.**