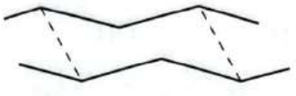
PROBLEM 3-20

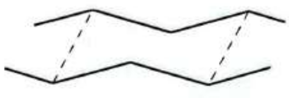
The cyclohexane chair just drawn has the headrest to the left and the footrest to the right. Draw a cyclohexane chair with its axial and equatorial bonds, having the headrest to the right and the footrest to the left.

PROBLEM 3-21

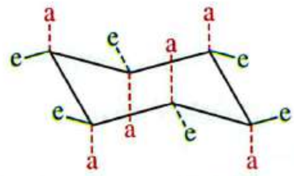
Draw 1,2,3,4,5,6-hexamethylcyclohexane with all the methyl groups
(a) in axial positions. **(b)** in equatorial positions.

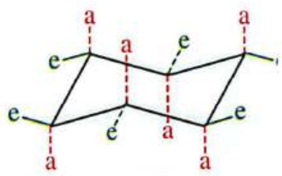
If your cyclohexane rings look awkward or slanted when using the analytical approach just shown, then try the artistic approach:* Draw a wide M, and draw a wide W below it, displaced about half a bond length to one side or the other. Connect the second atoms and the fourth atoms to give the cyclohexane ring with four equatorial bonds.


W displaced to the right


W displaced to the left

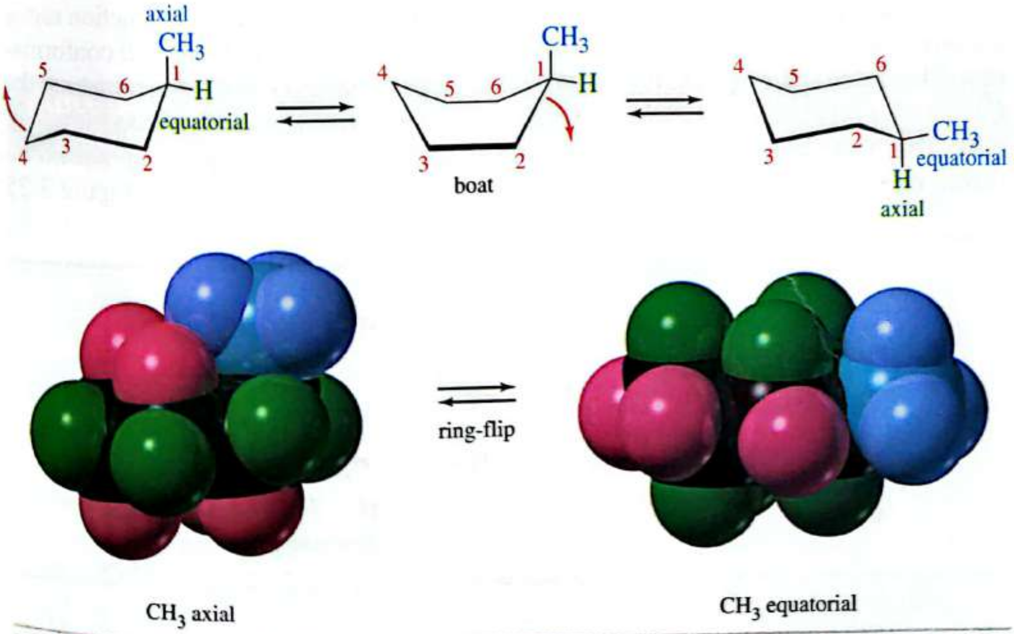
The other two equatorial bonds are drawn parallel to the ring connections. The axial bonds are then drawn vertically.





3-14
Conformations of Monosubstituted Cyclohexanes

A substituent on a cyclohexane ring (in the chair conformation) can occupy either an axial or an equatorial position. In many cases, the reactivity of the substituent depends on whether its position is axial or equatorial. The two possible chair conformations for methylcyclohexane are shown in Figure 3-23. These conformations are in equilibrium because they interconvert at room temperature. The twist boat serves as an intermediate in this **chair–chair interconversion**, sometimes called a "ring-flip." Place different-colored



◀ Figure 3-23
Chair–chair interconversion of methylcyclohexane. The methyl group is axial in one conformation, and equatorial in the other.

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*See V. Dragojlovic, *J. Chem. Educ.* 2001, *78*, 923.

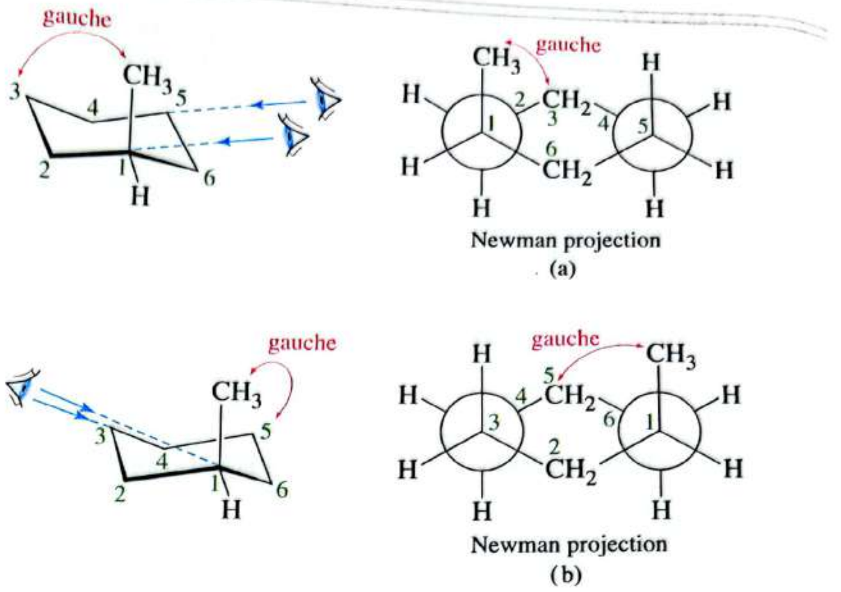


Figure 3-24
(a) When the methyl substituent is in an axial position on C1, it is gauche to C3. (b) The axial methyl group on C1 is also gauche to C5 of the ring.

atoms in the axial and equatorial positions of your cyclohexane model, and notice that the chair–chair interconversion changes axial to equatorial and equatorial to axial.

The two chair conformations of methylcyclohexane interconvert at room temperature, so the one that is lower in energy predominates. Careful measurements have shown that the chair with the methyl group in an equatorial position is the most stable conformation. It is about 7.6 kJ/mol (1.8 kcal/mol) lower in energy than the conformation with the methyl group in an axial position. Both of these chair conformations are lower in energy than any boat conformation. We can show how the 7.6 kJ energy difference between the axial and equatorial positions arises by examining molecular models and Newman projections of the two conformations. First, make a model of methylcyclohexane and use it to follow this discussion.

Consider a Newman projection looking along the armrest bonds of the conformation with the methyl group axial (Figure 3-24a): The methyl group is on C1, and we are looking from C1 toward C2. There is a 60° angle between the bond to the methyl group and the bond from C2 to C3, and the methyl substituent and C3 are in a gauche relationship. In our analysis of torsional strain in butane, we saw that a gauche interaction raises the energy of a conformation by 3.8 kJ/mol (0.9 kcal/mol) relative to the anti conformation. This axial methyl group is also gauche to C5, as you will see if you look along the C1—C6 bond in your model. Figure 3-24b shows this second gauche relationship.

The Newman projection for the conformation with the methyl group equatorial shows that the methyl group has an anti relationship to both C3 and C5. Figure 3-25

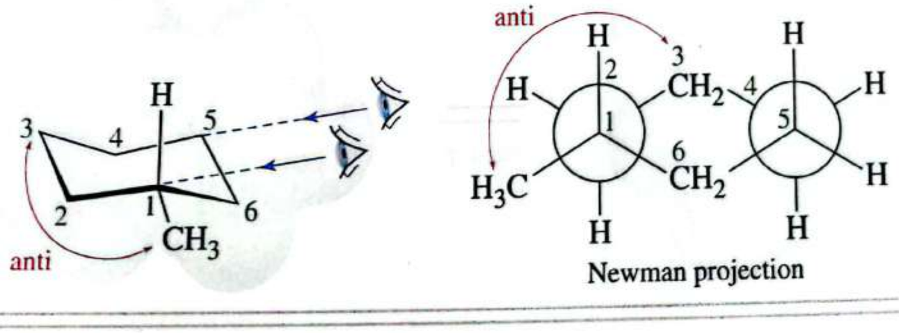
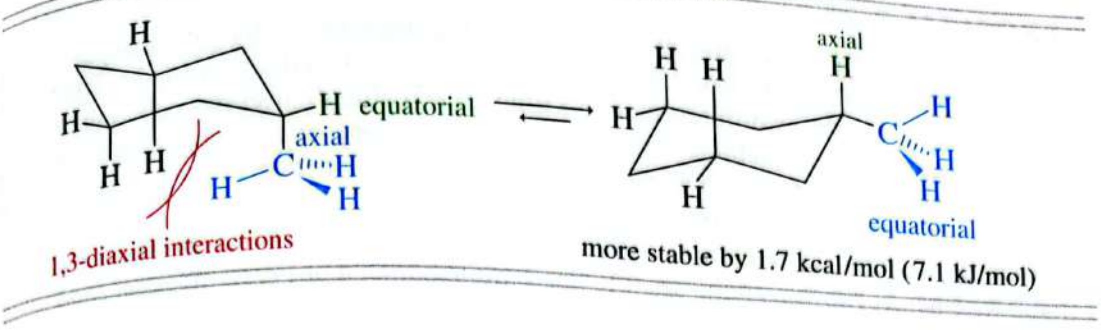


Figure 3-25
ooking down the C1—C2 bond
the equatorial conformation.
otice that the methyl group
anti to C3.



◀ **Figure 3-26**
The axial substituent interferes with the axial hydrogens on C3 and C5. This interference is called a 1,3-diaxial interaction.

shows the Newman projection along the C1—C2 bond, with the anti relationship of the methyl group to C3.

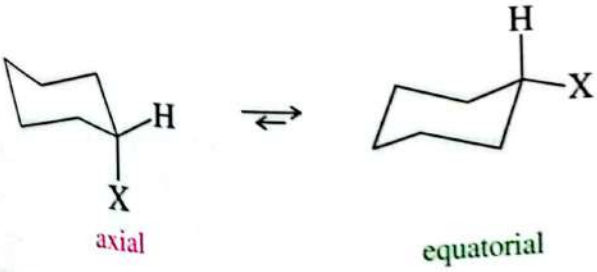
PROBLEM 3-22

Draw a Newman projection, similar to Figure 3-25, down the C1—C6 bond in the equatorial conformation of methylcyclohexane. Show that the equatorial methyl group is also anti to C5. (Using your models will help.)

The axial methylcyclohexane conformation has two gauche interactions, each representing about 3.8 kJ (0.9 kcal) of additional energy. The equatorial methyl group has no gauche interactions. Therefore, we predict that the axial conformation is higher in energy by 7.6 kJ (1.8 kcal) per mole, in good agreement with the experimental value. Figure 3-26 shows that the gauche relationship of the axial methyl group with C3 and C5 places the methyl hydrogens close to the axial hydrogens on these carbons, and their electron clouds begin to interfere. This form of steric hindrance is called a **1,3-diaxial interaction** because it involves substituents on the carbon atom that would be numbered C3 if the carbon bearing the methyl group was numbered C1. These 1,3-diaxial interactions are not present in the equatorial conformation.

A larger group usually has a larger energy difference between the axial and equatorial positions, because the 1,3-diaxial interaction shown in Figure 3-26 is stronger for larger groups. Table 3-6 shows the energy differences between the axial and equatorial positions for several alkyl groups and functional groups. The axial position is higher in energy in each case.

TABLE 3-6 Energy Differences Between the Axial and Equatorial Conformations of Monosubstituted Cyclohexanes



X	ΔG (axial–equatorial) (kJ/mol)	ΔG (axial–equatorial) (kcal/mol)
—F	0.8	0.2
—CN	0.8	0.2
—Cl	2.1	0.5
—Br	2.5	0.6
—OH	4.1	1.0
—COOH	5.9	1.4
$—CH_3$	7.6	1.8
$—CH_2CH_3$	7.9	1.9
$—CH(CH_3)_2$	8.8	2.1
$—C(CH_3)_3$	23	5.4

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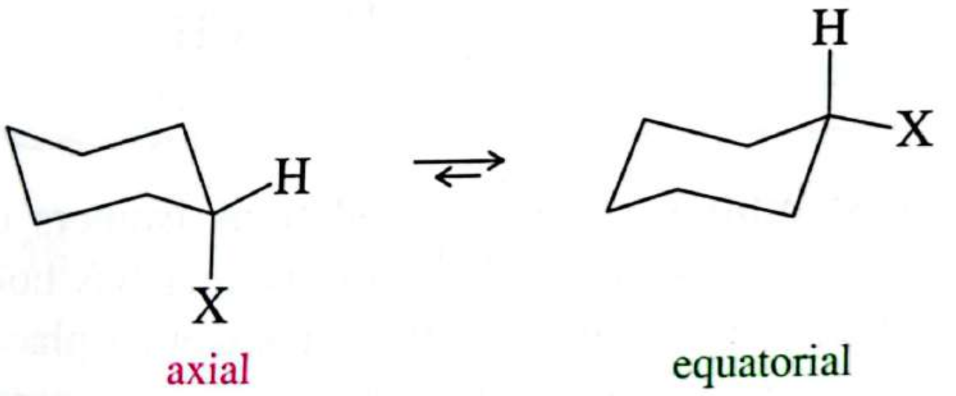

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$—C(CH_3)_3$	23	5.4

PROBLEM 3-23

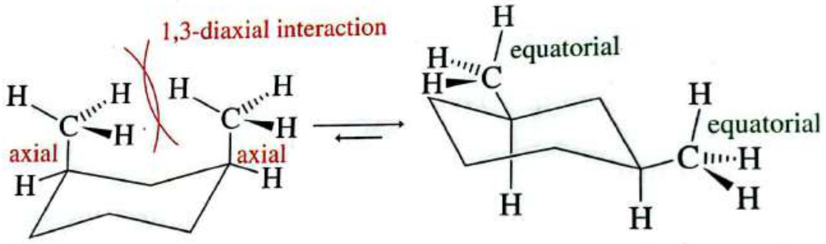
Table 3-6 shows that the axial–equatorial energy difference for methyl, ethyl, and isopropyl groups increases gradually: 7.6, 7.9, and 8.8 kJ/mol (1.8, 1.9, and 2.1 kcal/mol). The *t*-butyl group jumps to an energy difference of 23 kJ/mol (5.4 kcal/mol), over twice the value for the isopropyl group. Draw pictures of the axial conformations of isopropylcyclohexane and *t*-butylcyclohexane, and explain why the *t*-butyl substituent experiences such a large increase in axial energy over the isopropyl group.

PROBLEM 3-24

Draw the most stable conformation of
(a) ethylcyclohexane **(b)** isopropylcyclohexane **(c)** *t*-butylcyclohexane

3-15 Conformations of Disubstituted Cyclohexanes

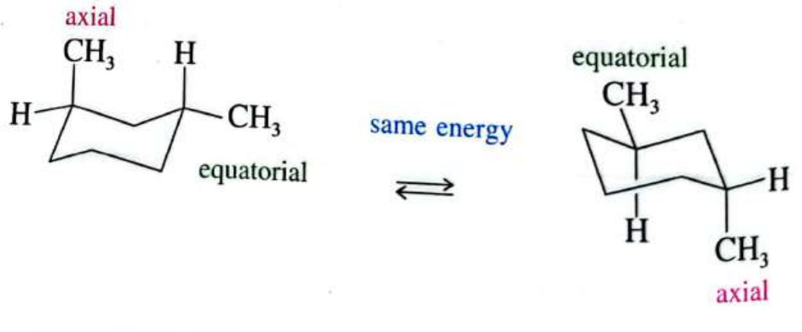
The steric interference between substituents in axial positions is particularly severe when there are large groups on two carbon atoms that bear a 1,3-diaxial relationship (*cis* on C1 and C3, or C1 and C5), as in the two chair conformations of *cis*-1,3-dimethylcyclohexane shown here. The less stable conformation has both methyl groups in axial positions. The more stable conformation has both methyl groups in equatorial positions. Note the strongly unfavorable 1,3-diaxial interaction between the two methyl groups in the diaxial conformation. The molecule can relieve this 1,3-diaxial interference by flipping to the diequatorial conformation. Use your models to compare the diaxial and diequatorial forms of *cis*-1,3-dimethylcyclohexane.



diaxial—very unfavorable diequatorial—much more stable

Either of the chair conformations of *trans*-1,3-dimethylcyclohexane has one methyl group in an axial position and one in an equatorial position. These conformations have equal energies, and they are present in equal amounts.

Chair conformations of trans-*1,3-dimethylcyclohexane*



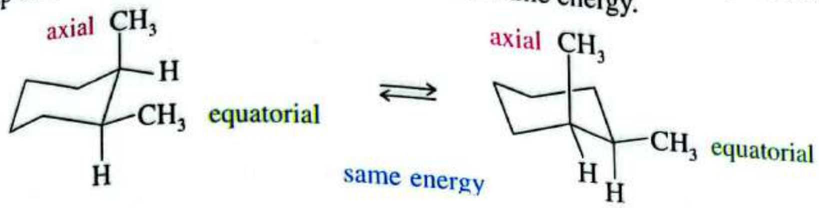
Now we can compare the relative stabilities of the cis and trans isomers of 1,3-dimethylcyclohexane. The most stable conformation of the cis isomer has both methyl groups in equatorial positions. Either conformation of the trans isomer places one methyl group in an axial position. The trans isomer is therefore higher in energy than the cis isomer by about 7.6 kJ/mol (1.8 kcal/mol), the energy difference between axial and equatorial methyl groups. Remember that the cis and trans isomers cannot interconvert, and there is no equilibrium between these isomers.

SOLVED PROBLEM 3-3

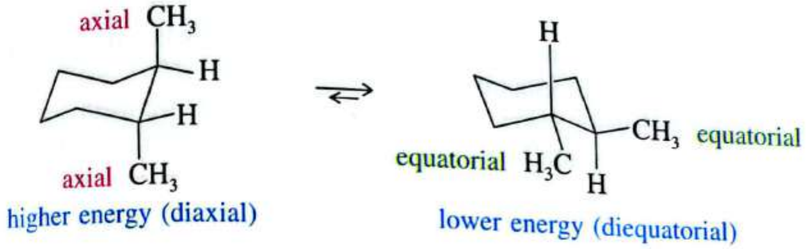
(a) Draw both chair conformations of *cis*-1,2-dimethylcyclohexane, and determine which conformer is more stable.
(b) Repeat for the trans isomer.
(c) Predict which isomer (cis or trans) is more stable.

SOLUTION

(a) There are two possible chair conformations for the cis isomer, and these two conformations interconvert at room temperature. Each of these conformations places one methyl group axial and one equatorial, giving them the same energy.



(b) There are two chair conformations of the trans isomer that interconvert at room temperature. Both methyl groups are axial in one, and both are equatorial in the other. The diequatorial conformation is more stable because neither methyl group occupies the more hindered axial position.



(c) The trans isomer is more stable. The most stable conformation of the trans isomer is diequatorial and therefore about 7.6 kJ/mol (1.8 kcal/mol) lower in energy than either conformation of the cis isomer, each having one methyl axial and one equatorial. Remember that cis and trans are distinct isomers and cannot interconvert.

PROBLEM-SOLVING Hint

Ring-flips change the axial or equatorial positioning of groups, but they cannot change their cis-trans relationships. Converting cis into trans would require breaking and re-forming bonds.

PROBLEM-SOLVING Hint

If you number the carbons in a cyclohexane, the odd-numbered carbons are similar, as are the even-numbered carbons. If the odd-numbered carbons all have their *up* bond axial and their *down* bond equatorial, the even-numbered carbons will all have their *down* bond axial and their *up* bond equatorial. For example, *cis*-1,3 (both up, both odd) will be both axial or both equatorial; *cis*-1,2 (both up, one odd, one even) will be one axial, one equatorial. This tip allows you to predict the answers before you draw them.

PROBLEM 3-25

(a) Draw both chair conformations of *cis*-1,4-dimethylcyclohexane, and determine which conformer is more stable.
(b) Repeat for the trans isomer.
(c) Predict which isomer (cis or trans) is more stable.

PROBLEM 3-26

Use your results from Problem 3-25 to complete the following table. Each entry shows the positions of two groups arranged as shown. For example, two groups that are trans on adjacent carbons (*trans*-1,2) must be both equatorial (e,e) or both axial (a,a).

Positions	cis	trans
1,2	(e,a) or (a,e)	(e,e) or (a,a)
1,3		
1,4		

3-15A Substituents of Different Sizes

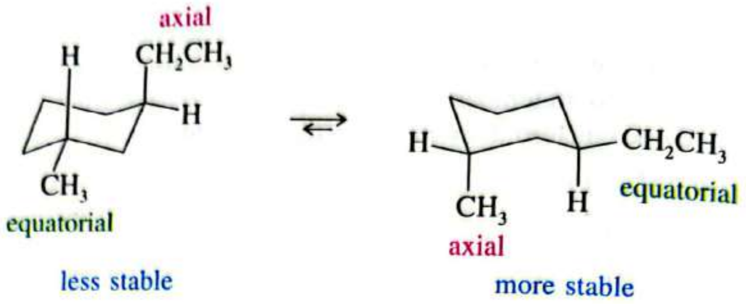
In many substituted cyclohexanes, the substituents are different sizes. As shown in Table 3-6 (p. 113), the energy difference between the axial and equatorial positions for a larger group is greater than that for a smaller group. In general, if both groups cannot be equatorial, the most stable conformation has the larger group equatorial and the smaller group axial.

SOLVED PROBLEM 3-4

Draw the most stable conformation of *trans*-1-ethyl-3-methylcyclohexane.

SOLUTION

First, we draw the two conformations.



Both of these conformations require one group to be axial while the other is equatorial. The ethyl group is bulkier than the methyl group, so the conformation with the ethyl group equatorial is more stable. These chair conformations are in equilibrium at room temperature, and the one with the equatorial ethyl group predominates.

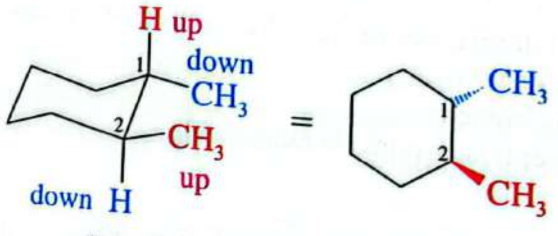
PROBLEM 3-27

Draw the two chair conformations of each of the following substituted cyclohexanes. In each case, label the more stable conformation.

(a) *cis*-1-ethyl-2-methylcyclohexane
(b) *trans*-1-ethyl-2-methylcyclohexane
(c) *cis*-1-ethyl-4-isopropylcyclohexane
(d) *trans*-1-ethyl-4-methylcyclohexane

PROBLEM-SOLVING STRATEGY
Recognizing cis and trans Isomers

Some students find it difficult to look at a chair conformation and tell whether a disubstituted cyclohexane is the cis isomer or the trans isomer. In the following drawing, the two methyl groups appear to be oriented in similar directions. They are actually trans but are often mistaken for cis.



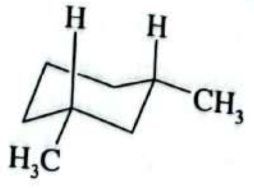
trans-1,2-dimethylcyclohexane

This ambiguity is resolved by recognizing that each of the ring carbons has two available bonds, one upward and one downward. In this drawing, the methyl group on C1 is on the downward bond, and the methyl on C2 is on the upward bond. Because one is down and one is up, their relationship is trans. A cis relationship would require both groups to be upward or both to be downward.

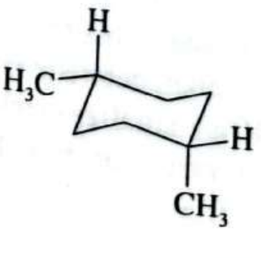
PROBLEM 3-28

Name the following compounds. Remember that two *up* bonds are cis; two *down* bonds are cis; one *up* bond and one *down* bond are trans.

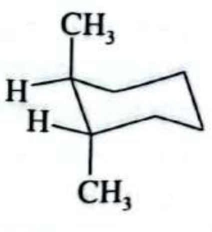
(a)



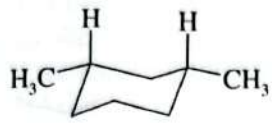
(b)



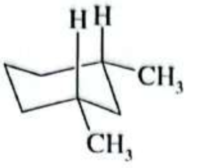
(c)



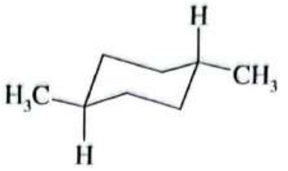
(d)



(e)

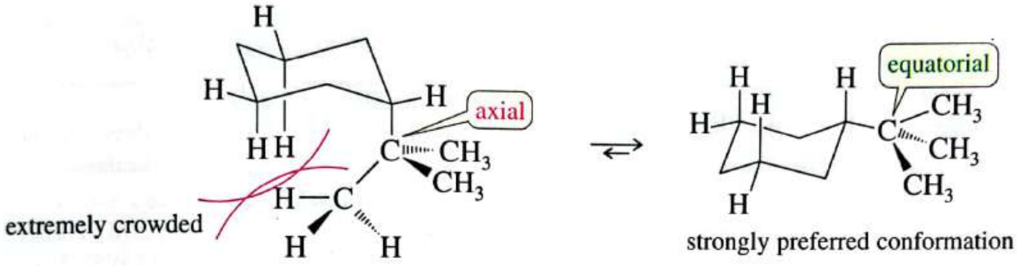


(f)

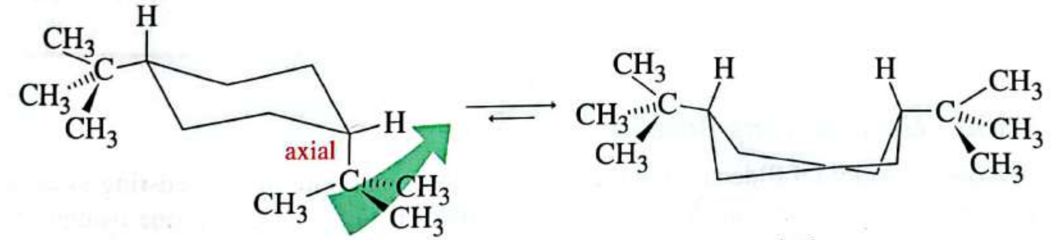


3-15B Extremely Bulky Groups

Some groups, such as *tertiary*-butyl groups, are so bulky that they are extremely strained in axial positions. Regardless of the other groups present, cyclohexanes with *t*-butyl substituents are most stable when the *t*-butyl group is in an equatorial position. The following figure shows the severe steric interactions in a chair conformation with a *t*-butyl group axial.



If two *t*-butyl groups are attached to the ring, both of them are much less strained in equatorial positions. When neither chair conformation allows both bulky groups to be equatorial, they may force the ring into a twist boat conformation. For example, either chair conformation of *cis*-1,4-di-*t*-butylcyclohexane requires one of the bulky *t*-butyl groups to occupy an axial position. This compound is more stable in a twist boat conformation that allows both bulky groups to avoid axial positions.



t-butyl group moves out of the axial position

twist boat

PROBLEM 3-29

Draw the most stable conformation of
(a) *cis*-1-*t*-butyl-3-ethylcyclohexane
(b) *trans*-1-*t*-butyl-2-methylcyclohexane
(c) *trans*-1-*t*-butyl-3-(1,1-dimethylpropyl)cyclohexane

3-16 Bicyclic Molecules

Two or more rings can be joined into *bicyclic* or *polycyclic* systems. There are three ways that two rings may be joined. **Fused rings** are most common, sharing two adjacent carbon atoms and the bond between them. **Bridged rings** are also common, sharing two nonadjacent carbon atoms (the **bridgehead carbons**) and one or more carbon atoms (the bridge) between them. **Spirocyclic compounds**, in which the two rings share only one carbon atom, are relatively rare.