

## CHAPTER 3—STRUCTURE AND STEREOCHEMISTRY OF ALKANES

3-1 (a)  $C_nH_{2n+2}$  where  $n = 28$  gives  $C_{28}H_{58}$

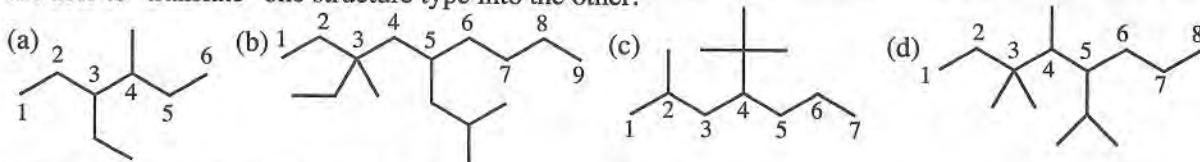
(b)  $C_nH_{2n+2}$  where  $n = 44$  gives  $C_{44}H_{90}$

Note to the student: The IUPAC system of nomenclature has a well-defined set of rules determining how structures are named. You will find a summary of these rules as Appendix 5 in the textbook.

3-2 Use hyphens to separate letters from numbers. Structures might not display their longest chains left to right—you have to search for them. In the name, write substituents in alphabetical order, even though that might be different from the numerical order of position numbers.

- (a) 3-methylpentane (Always find the longest chain; it may not be written in a straight line.)
- (b) 2-bromo-3-methylpentane (Always find the longest chain.)
- (c) 5-ethyl-2-methyl-4-propylheptane ("When there are two longest chains of equal length, use the chain with the greater number of substituents.")
- (d) 4-isopropyl-2-methyldecane ("Number from the end closest to the first substituent." —also for (c))

3-3 This Solutions Manual will present line-angle formulas, or simply "line formulas", where a question asks for an answer including a structure. If you use condensed structural formulas instead, be sure that you are able to "translate" one structure type into the other.



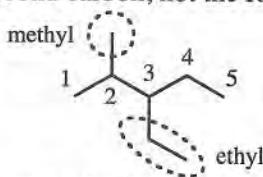
3-4 Separate numbers from numbers with commas. Separate numbers from letters with hyphens.

- |                        |                                       |   |
|------------------------|---------------------------------------|---|
| (a) 2-methylbutane     | (b) 2,2-dimethylpropane               | (c) 3-ethyl-2-methylhexane                |
| (d) 2,4-dimethylhexane | (e) 3-ethyl-2,2,4,5-tetramethylhexane | (f) 4- <i>tert</i> -butyl-3-methylheptane |

3-5 In some cases of an ambiguous or incorrect name, more than one possible structure might be implied. That is often the problem with a wrong name: it does not describe a unique structure.

(a) incorrect: 3-ethyl-4-methylpentane

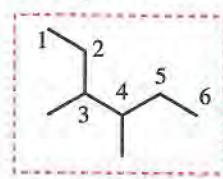
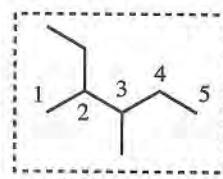
The chain is numbered in the wrong direction. The methyl should be on the second carbon, not the fourth.



correct: 3-ethyl-2-methylpentane

(b) incorrect: 2-ethyl-3-methylpentane

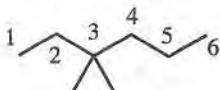
The longest chain was not identified.



correct: 3,4-dimethylhexane

(c) incorrect: 3-dimethylhexane

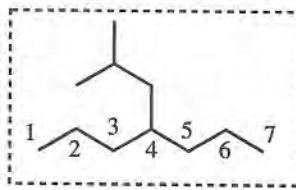
Two substituents require two position numbers; even if they are both 3; that is the example shown below. It is also possible that a different position number was omitted, like "3,4-".



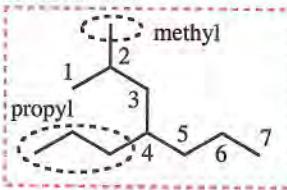
correct: 3,3-dimethylhexane

(d) incorrect: 4-isobutylheptane

This is a more subtle error. If two chains of equal length are possible, select the one that maximizes the number of substituents.



INCORRECT  
one substituent



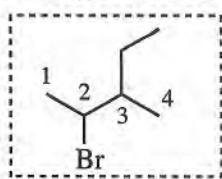
CORRECT  
two substituents

correct: 2-methyl-4-propylhexane

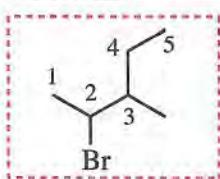
3-5 continued

(e) incorrect: 2-bromo-3-ethylbutane

The longest chain was not identified.



INCORRECT



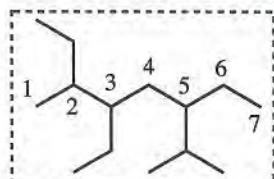
CORRECT

correct: 2-bromo-3-methylpentane

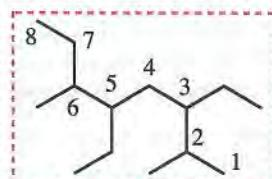
(f) incorrect: 2,3-diethyl-5-isopropylheptane

The longest chain is 8 carbons: octane.

Numbering from the lower right corner as shown below puts the first substituent on carbon-2, and also maximizes the number of substituents.



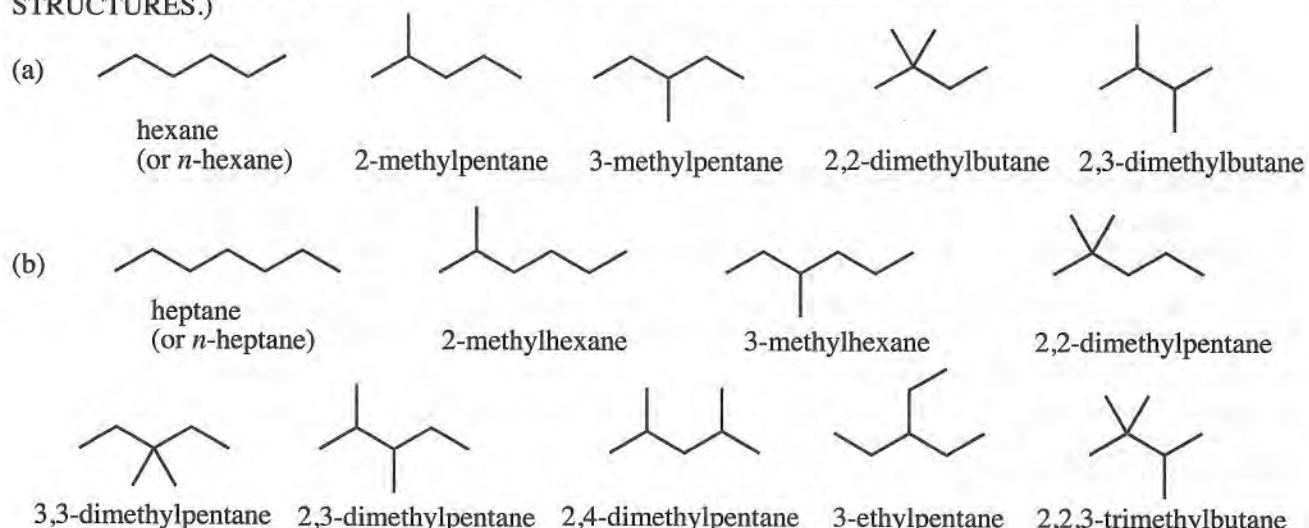
INCORRECT



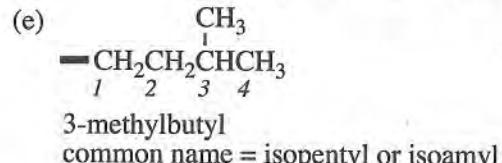
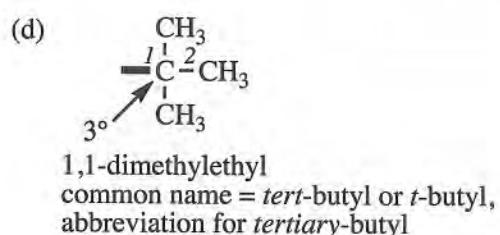
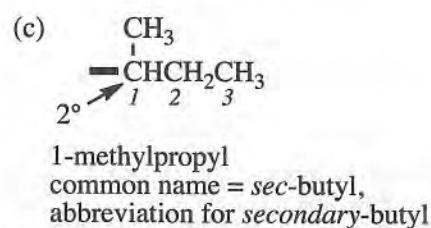
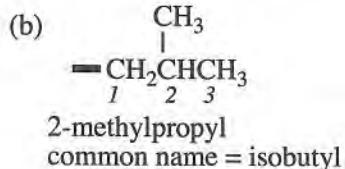
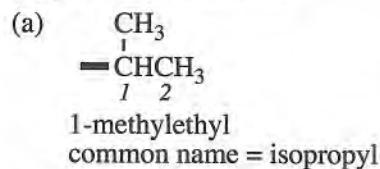
CORRECT

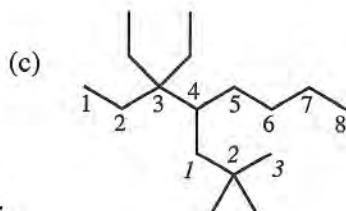
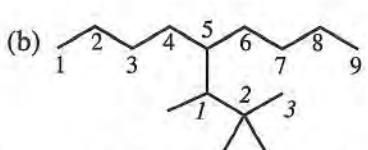
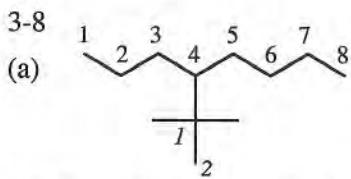
correct: 3,5-diethyl-2,6-dimethyloctane

3-6 (Hints: *systematize* your approach to these problems. For the isomers of a six-carbon formula, for example, start with the isomer containing all six carbons in a straight chain, then the isomers containing a five-carbon chain, then a four-carbon chain, etc. Carefully check your answers to AVOID DUPLICATE STRUCTURES.)



3-7 For this problem, the carbon numbers in the substituents are indicated in italics. The bold bond shows the point of attachment.





3-9 Once the number of carbons is determined,  $C_nH_{2n+2}$  gives the formula.

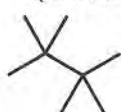
(a) octane = 8C; plus 1,1-dimethylethyl = 4C  $\longrightarrow$  12 C,  $C_{12}H_{26}$

(b) nonane = 9C; plus trimethyl = 3C; plus propyl = 3C  $\longrightarrow$  15 C,  $C_{15}H_{32}$

3-10

(a) (lowest b.p.) hexane < octane < decane (highest b.p.) — molecular weight

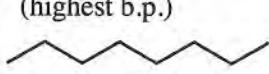
(b)  $(CH_3)_3C-C(CH_3)_3 < CH_3CH_2C(CH_3)_2CH_2CH_2CH_3 <$  octane — branching differences  
 (lowest b.p.) (highest b.p.)



*most branching*  
*actual b.p. 107 °C*



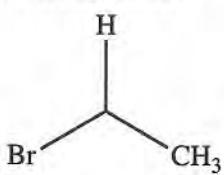
*some branching*  
*actual b.p. 112 °C*



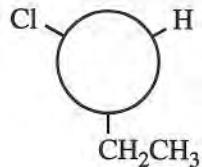
*no branching*  
*actual b.p. 126 °C*

3-11 Part (a) was answered in the text.

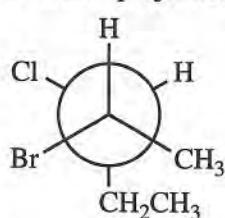
(b) front carbon



back carbon



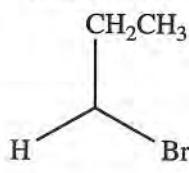
Newman projection



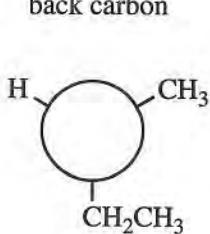
For nomenclature practice,  
 can you name these?

2-bromo-3-chloropentane

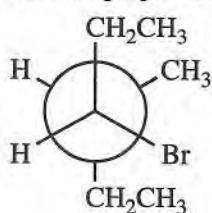
(c) front carbon



back carbon



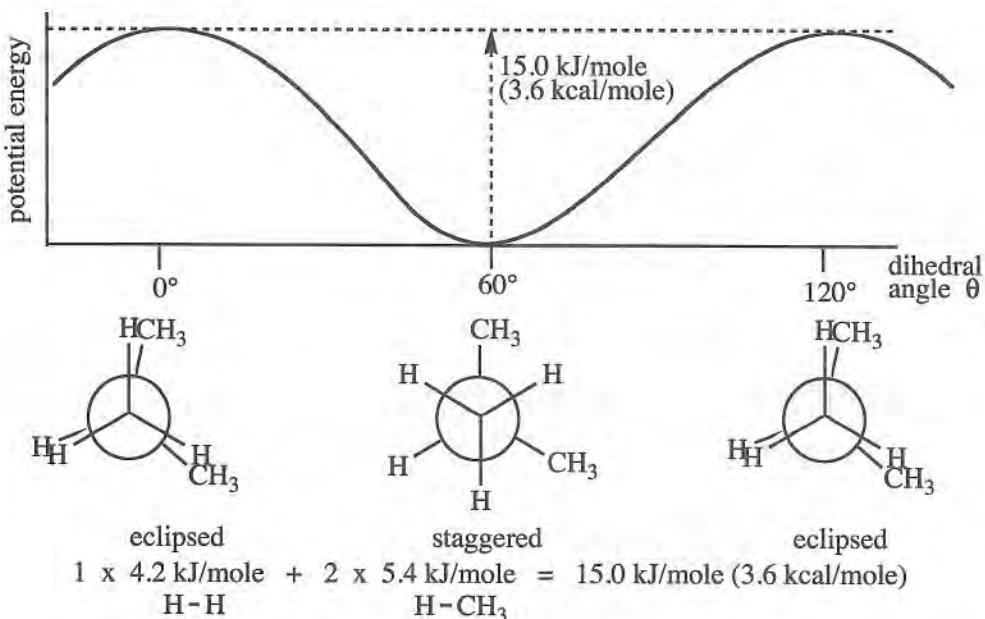
Newman projection



3-bromo-4-methylhexane

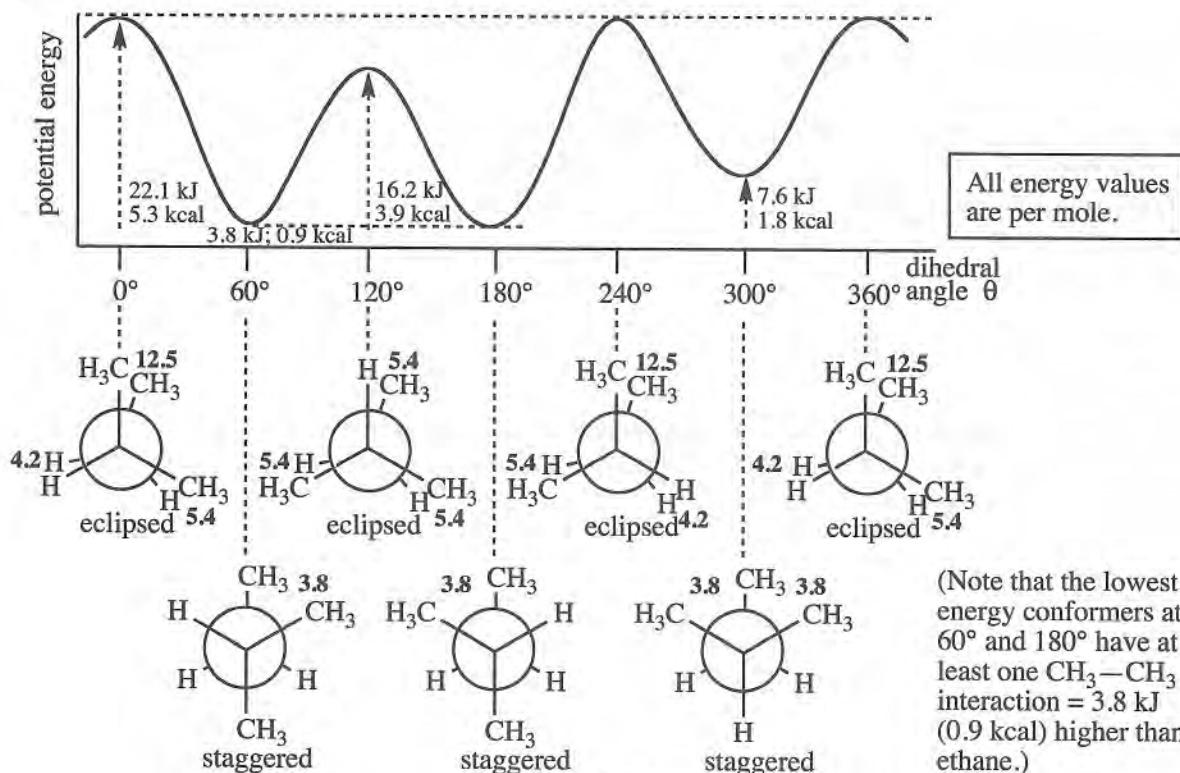
An excellent exercise for your study group is for one person to create a Newman projection, and for the other people in the group to translate that Newman into a line formula, and name it.

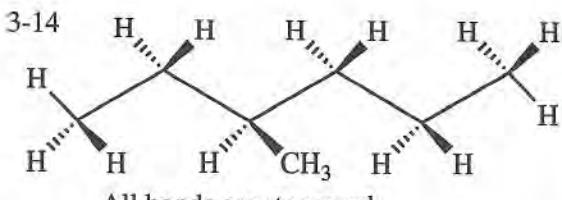
3-12



3-13

Relative energies on the graph on the next page were calculated using these values from the text: 3.8 kJ/mole (0.9 kcal/mole) for a CH<sub>3</sub>–CH<sub>3</sub> gauche (staggered) interaction; 4.2 kJ/mole (1.0 kcal/mole) for a H–H eclipsed interaction; 5.4 kJ/mole (1.3 kcal/mole) for a H–CH<sub>3</sub> eclipsed interaction; 12.5 kJ/mole (3.0 kcal/mole) for a CH<sub>3</sub>–CH<sub>3</sub> eclipsed interaction. These values in kJ/mole are noted on each structure and are summed to give the energy value on the graph. Slight variations between values here and in the text are due to rounding.



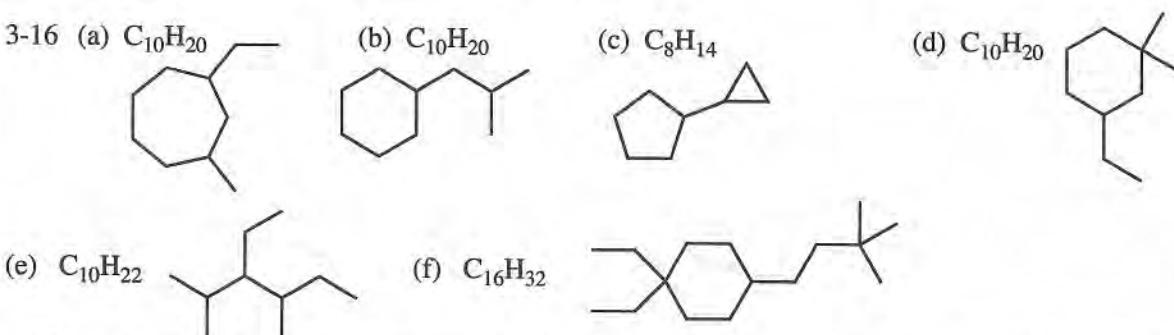


— Wedge bonds are coming toward the reader above the plane of the paper.

···· Dashed bonds are going away from the reader behind the plane of the paper.

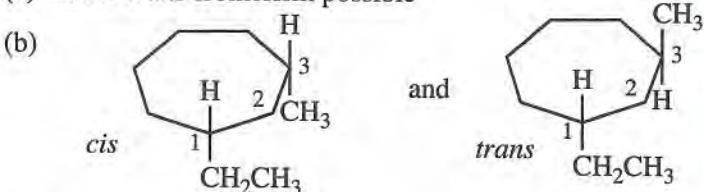
3-15 Note that in rings, parts (a) and (b), two substituents on one carbon indicate where to begin numbering.

- (a) 3-sec-butyl-1,1-dimethylcyclopentane
- (b) 3-cyclopropyl-1,1-dimethylcyclohexane
- (c) 4-cyclobutylnonane (The chain is longer than the ring.)

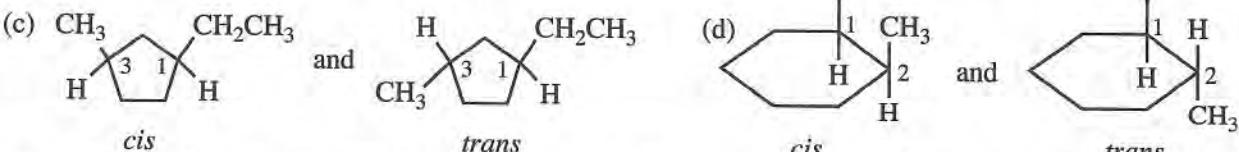


3-17 It helps to visualize *cis-trans* isomerism by putting in the H atoms on the carbons with substituents.

- (a) no *cis-trans* isomerism possible



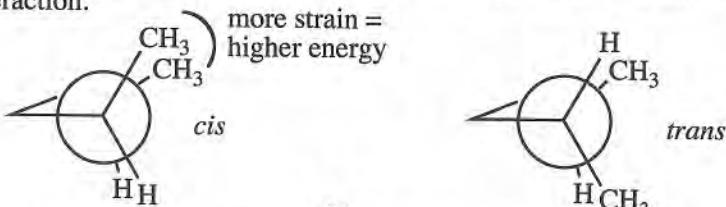
The terms *cis* and *trans* designate *relative position*. For *cis*, both substituents have to be on the same side; it does not matter if both are up or both down. For *trans*, one must be up and the other down; it does not matter which is which.



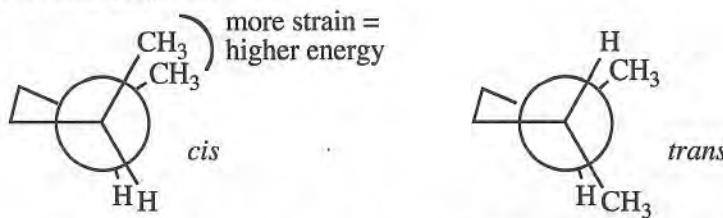
3-18 In (a) and (b), numbering of the ring is determined by the first group *alphabetically* being assigned to ring carbon 1.

- (a) *cis*-1-methyl-3-propylcyclobutane ("M" comes before "p"—practice that alphabet!)
- (b) *trans*-1-*tert*-butyl-3-ethylcyclohexane (*Tert*, *sec*, and *n* are ignored in assigning alphabetical priority.)
- (c) *trans*-1,2-dimethylcyclopropane (Either carbon with a  $CH_3$  could be carbon-1; the same name results.)

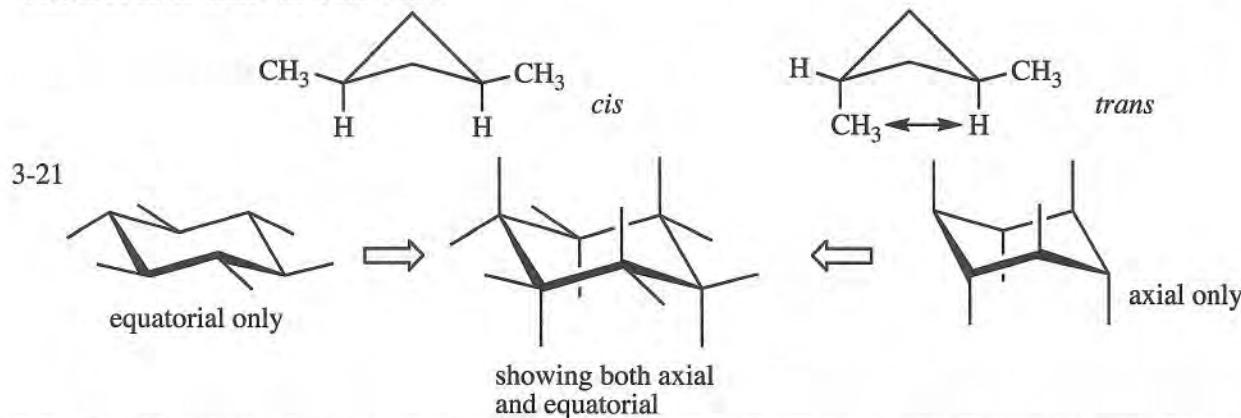
3-19 Combustion of the *cis* isomer gives off more energy, so *cis*-1,2-dimethylcyclopropane must start at a higher energy than the *trans* isomer. The Newman projection of the *cis* isomer shows the two methyls are eclipsed with each other; in the *trans* isomer, the methyls are still eclipsed, but with hydrogens, not each other—a lower energy interaction.



3-20 *trans*-1,2-Dimethylcyclobutane is more stable than *cis* because the two methyls can be farther apart when *trans*, as shown in the Newman projections.



In the 1,3-dimethylcyclobutanes, however, the *cis* allows the methyls to be farther from other atoms and therefore more stable than the *trans*.

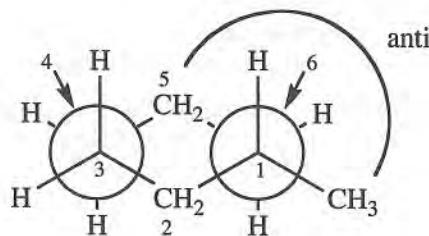


3-22 The abbreviation for a methyl group,  $\text{CH}_3$ , is "Me". Ethyl is "Et", propyl is "Pr", and butyl is "Bu".

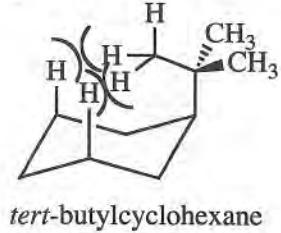
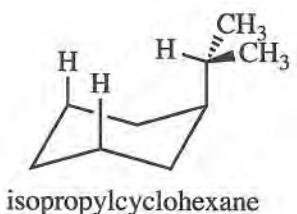


Note that axial groups alternate up and down around the ring.

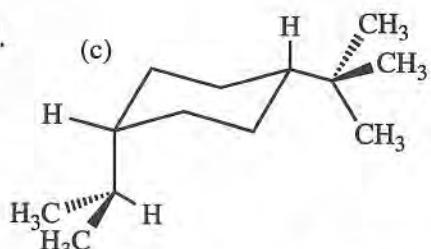
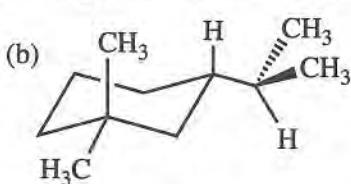
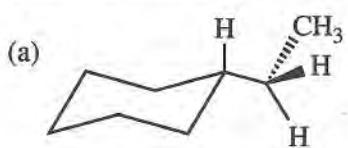
3-23 Carbons 4 and 6 are the back carbons.



3-24 The isopropyl group can rotate so that its hydrogen is near the axial hydrogens on carbons 3 and 5, similar to a methyl group's hydrogen, and therefore similar to a methyl group in energy. The *tert*-butyl group, however, must point a methyl group toward the hydrogens on carbons 3 and 5, giving severe diaxial interactions, causing the energy of this conformer to jump dramatically.



3-25 The most stable conformers have larger substituents equatorial.



The *cis*-1,4 isomer must have one group axial and the other equatorial. The *tert*-butyl group is larger and will take the equatorial position.

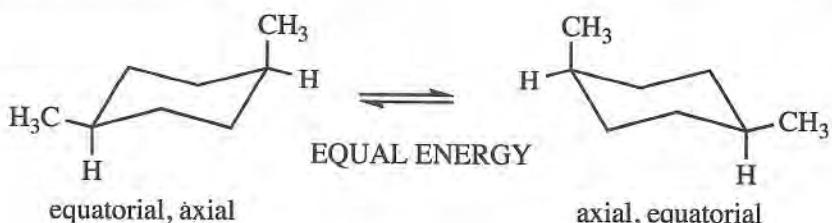
3-26 The key to determining *cis* and *trans* around a cyclohexane ring is to see whether a substituent group is "up" or "down" relative to the H at the same carbon. Two "up" groups or two "down" groups will be *cis*; one "up" and one "down" will be *trans*. This works independent of the conformation the molecule is in!

- (a) *cis*-1,3-dimethylcyclohexane
- (b) *cis*-1,4-dimethylcyclohexane
- (c) *trans*-1,2-dimethylcyclohexane

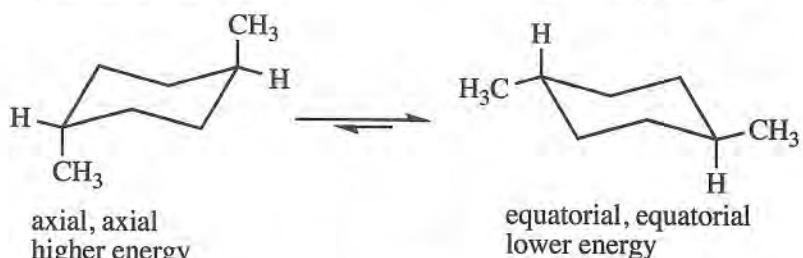
- (d) *cis*-1,3-dimethylcyclohexane
- (e) *cis*-1,3-dimethylcyclohexane
- (f) *trans*-1,4-dimethylcyclohexane

3-27

(a) *cis*



(b) *trans*

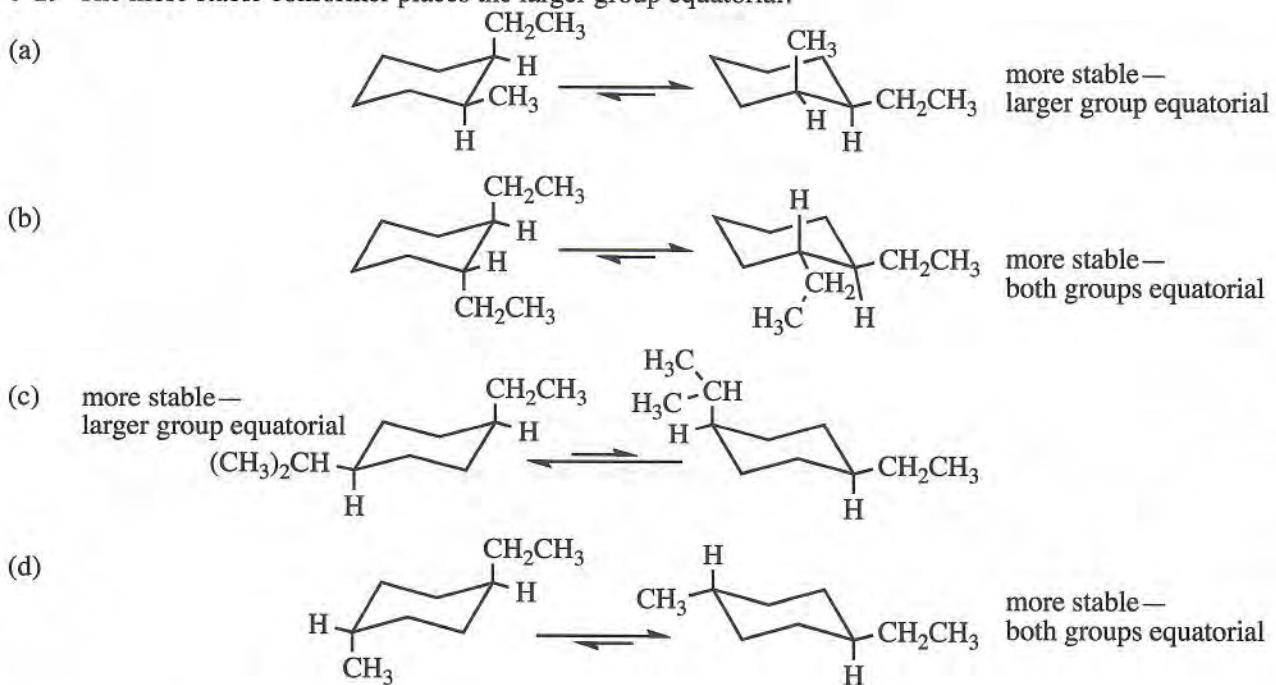


(c) The *trans* isomer is more stable because BOTH substituents can be in the preferred equatorial positions.

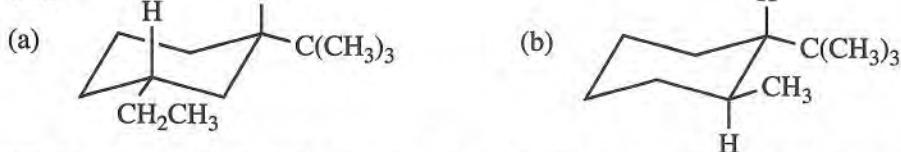
3-28

Positions	<i>cis</i>	<i>trans</i>
1,2	(e,a) or (a,e)	(e,e) or (a,a)
1,3	(e,e) or (a,a)	(e,a) or (a,e)
1,4	(e,a) or (a,e)	(e,e) or (a,a)

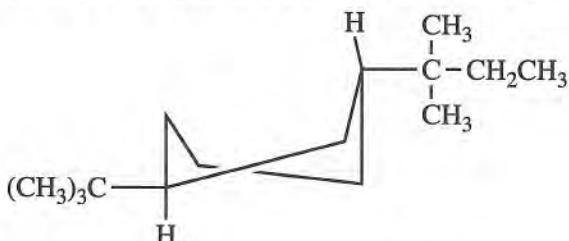
3-29 The more stable conformer places the larger group equatorial.



3-30



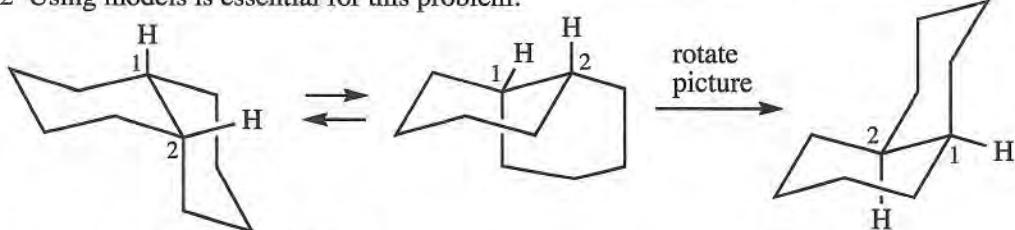
(c) Bulky substituents like *tert*-butyl adopt equatorial rather than axial positions, even if that means altering the conformation of the ring. The twist boat conformation allows both bulky substituents to be "equatorial".



3-31 The nomenclature of bicyclic alkanes is summarized in Appendix 5 in the textbook.

- (a) bicyclo[3.1.0]hexane (b) bicyclo[3.3.1]nonane (c) bicyclo[2.2.2]octane (d) bicyclo[3.1.1]heptane

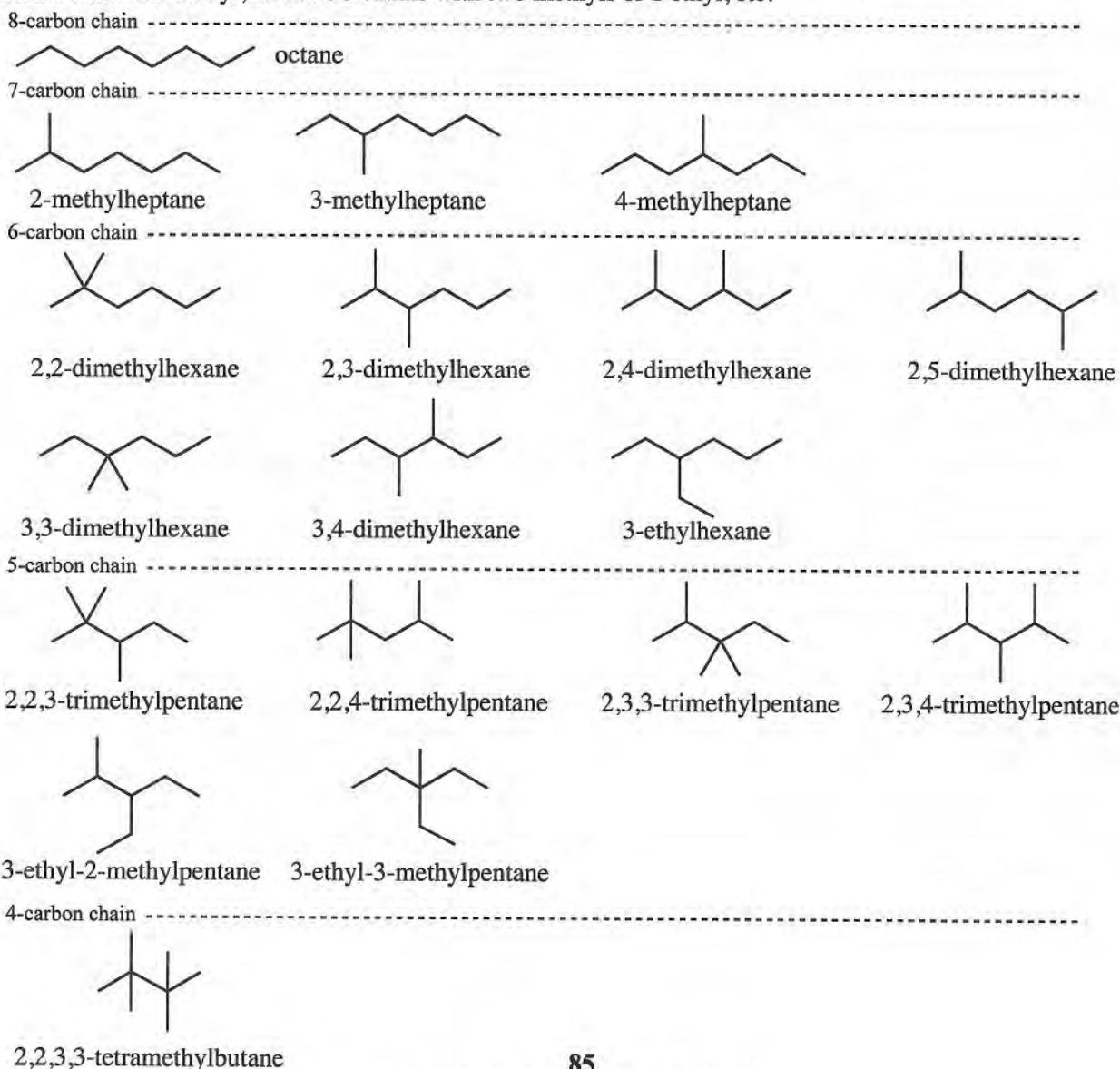
3-32 Using models is essential for this problem.



from text Figure 3-27

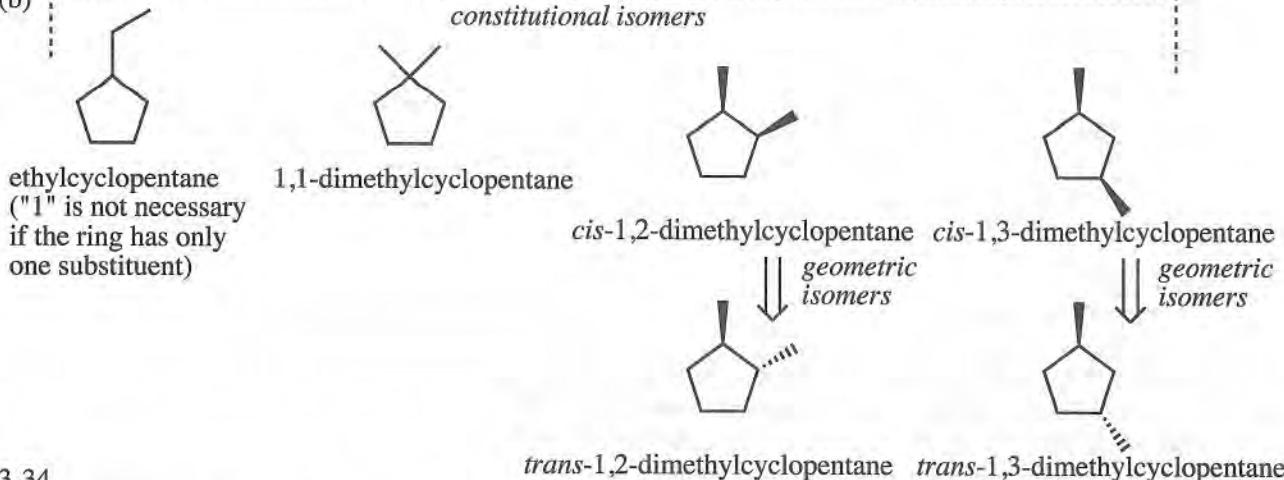
3-33

(a) Here are eighteen isomers of  $C_8H_{18}$ . An easy way to compare is to name yours and see if the names match. Note how these isomers were generated systematically: 8C chain (only one), all the possible 7C chains with one methyl, all the 6C chains with two methyls or 1 ethyl, etc.



3-33 continued

(b)



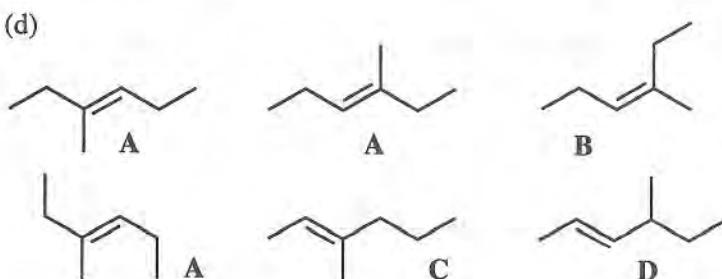
3-34

(a) The third structure is 2-methylpropane (isobutane). The other four structures are all butane (*n*-butane). Remember that a compound's identity is determined by how the atoms are connected, not by the position of the atoms when a structure is drawn on a page.

(b) The first and fourth structures are both *cis*-but-2-ene. The second and fifth structures are both but-1-ene. The third structure is *trans*-but-2-ene. The last structure is 2-methylpropene.

(c) The first two structures are both *cis*-1,2-dimethylcyclopentane. The next two structures are both *trans*-1,2-dimethylcyclopentane. The last structure, *cis*-1,3-dimethylcyclopentane, is different from all the others.

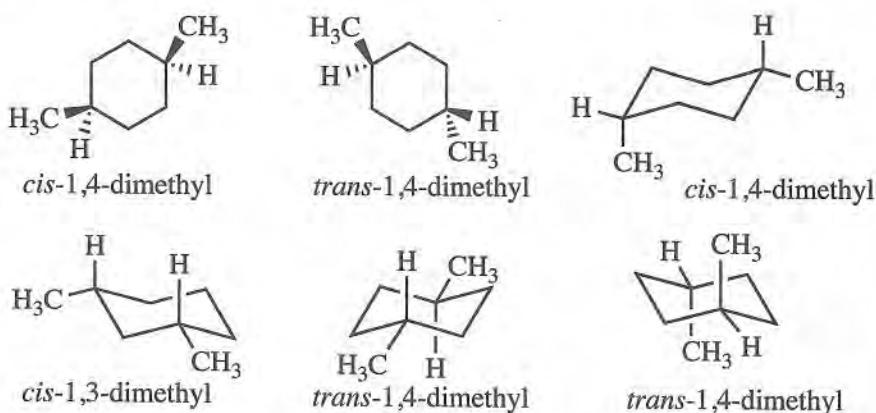
(d)



Analysis of the structures shows that some double bonds begin at carbon-2 and some at carbon-3 of the longest chain.

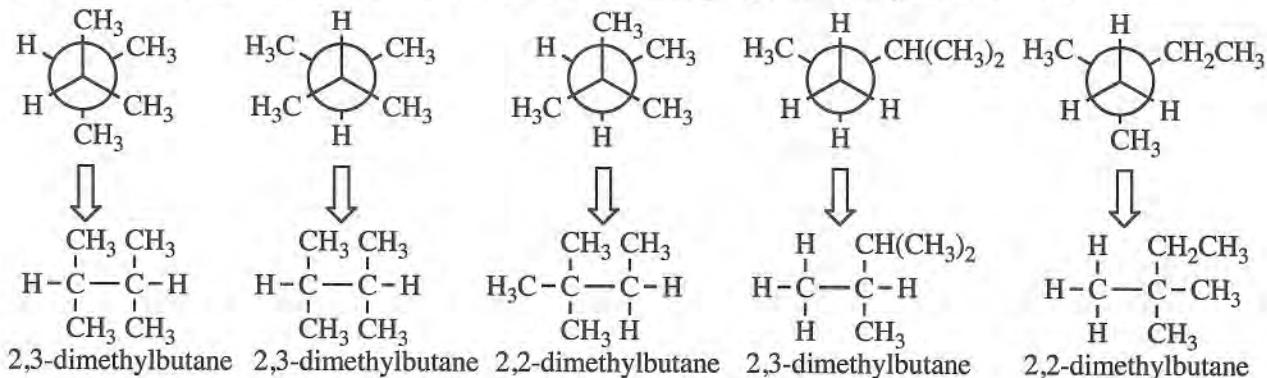
The three structures labeled A are the same, with the double bond *trans*; B is a geometric isomer (*cis*) of A. C and D are constitutional isomers of the others.

(e) Naming the structures shows that three of the structures are *trans*-1,4-dimethylcyclohexane, two are the *cis* isomer, and one is *cis*-1,3-dimethylcyclohexane. Although a structure may be shown in two different conformations, it still represents only one compound.



3-34 continued

(f) An important and useful skill is the ability to translate Newman projections into other structural formulas and *vice versa*. The way to do this is to start with the two carbons that represent the front and back carbons in the middle of the Newman projections, then attach the three groups emanating from each one.

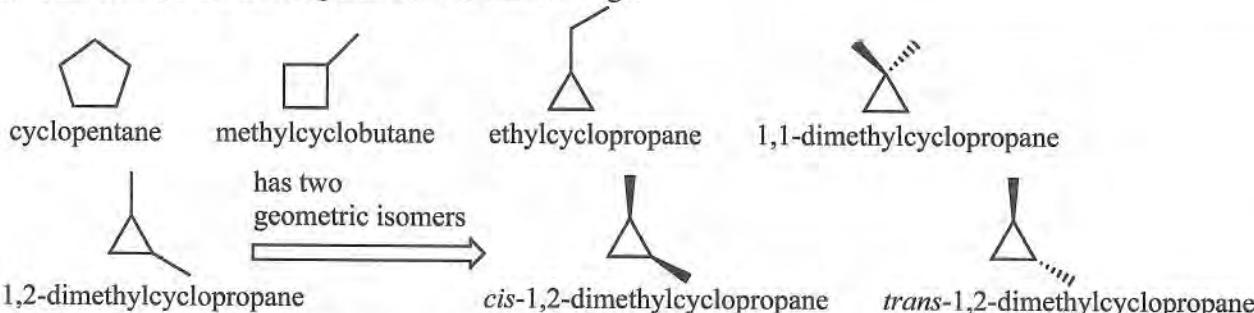


What may not be clear in the Newman projections is revealed in the structural formulas and especially in the names. There are only two compounds represented here: the first, second, and fourth are the same; the third and fifth are the same.

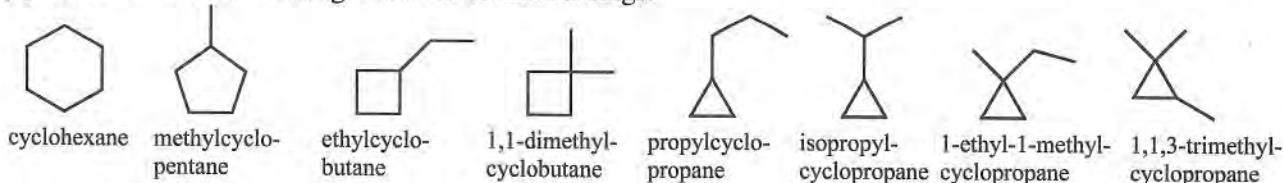
(g) Names have been incorporated into the other solutions.

3-35

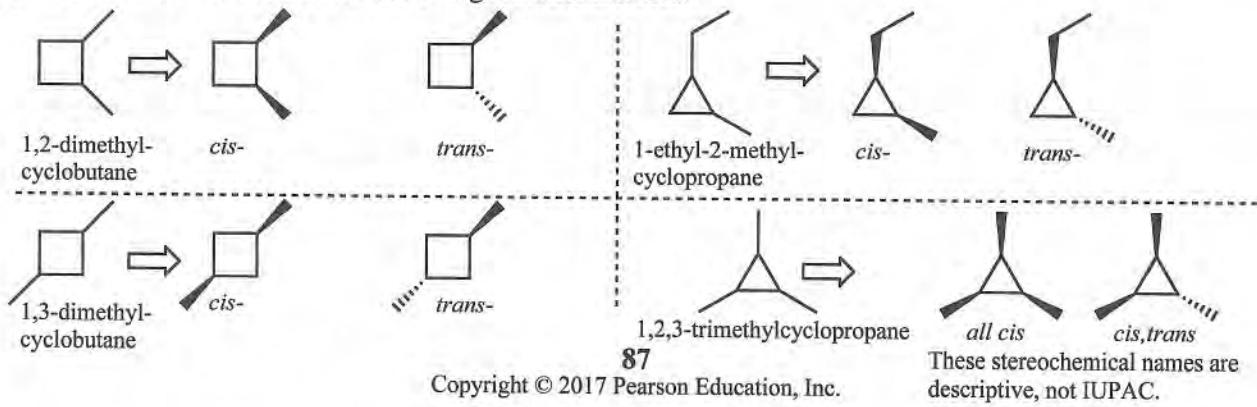
(a) Start with a 5-carbon ring and work to smaller rings:



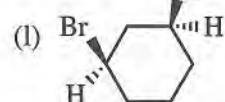
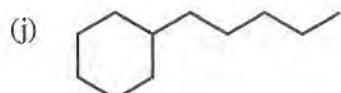
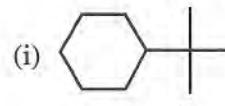
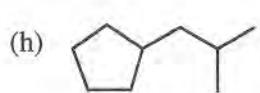
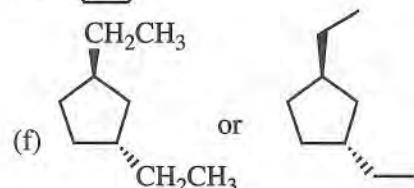
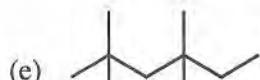
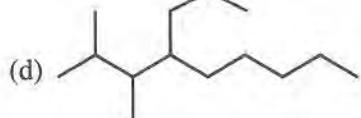
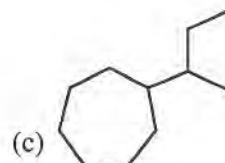
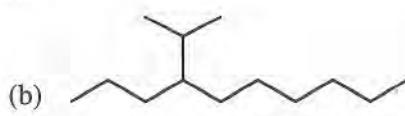
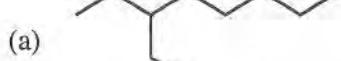
(b) Start with a 6-carbon ring and work to smaller rings:



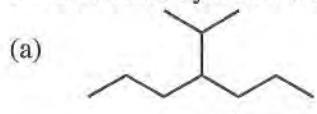
(c) Each of these four structures has two geometric isomers.



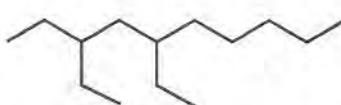
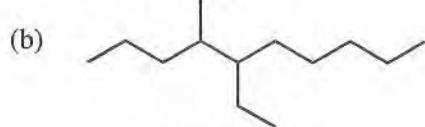
3-36 Line-angle formulas are shown.



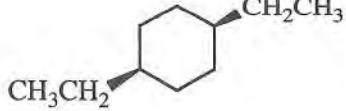
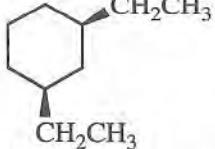
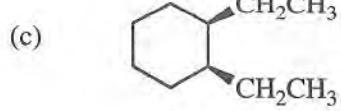
3-37 There are often many possible answers to this type of problem, although some can have unique solutions. The ones shown here are examples of correct answers. Your answers may be different AND correct. Check your answers in your study group.



4-Isopropylheptane is the only possible answer. Why not 1- or 2- or 3-? Draw these structures in your study group, and name them.



(Any combination is correct except using position numbers 1 or 2 or 9 or 10. Why won't these work?)



*cis*-1,2-diethylcyclohexane

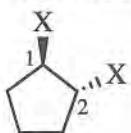
*cis*-1,3-diethylcyclohexane

*cis*-1,4-diethylcyclohexane

NOT 1,5—same as 1,3; NOT 1,6—same as 1,2

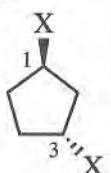
(d) "Halo" is the abbreviation for any of the four halogens (F, Cl, Br, I), and "X" is the symbol used in organic structures. If unspecified, any of the four elements will satisfy the "halo" group. However, on a 5-membered ring, the substitution can be only two possibilities: 1,2- or 1,3-.

*trans*-1,2-dihalocyclopentane

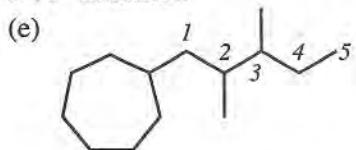


"X" stands for any of the four halogen elements.

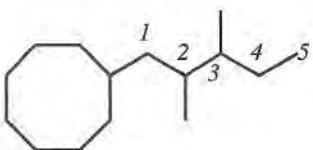
*trans*-1,3-dihalocyclopentane



3-37 continued

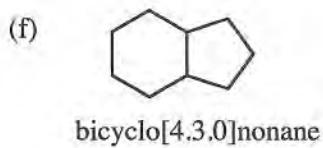


(2,3-dimethylpentyl)cycloheptane



(2,3-dimethylpentyl)cyclooctane

Other ring sizes are possible, although they must have 6 or more carbons to be longer than the 5 carbons of the substituent chain.



bicyclo[4.3.0]nonane

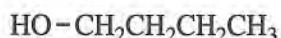
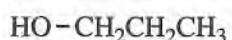
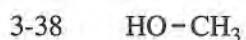


bicyclo[3.2.2]nonane



bicyclo[3.3.1]nonane

Any combination where the number of carbons in the bridges sums to 7 will work. (Two carbons are the bridgehead carbons.)



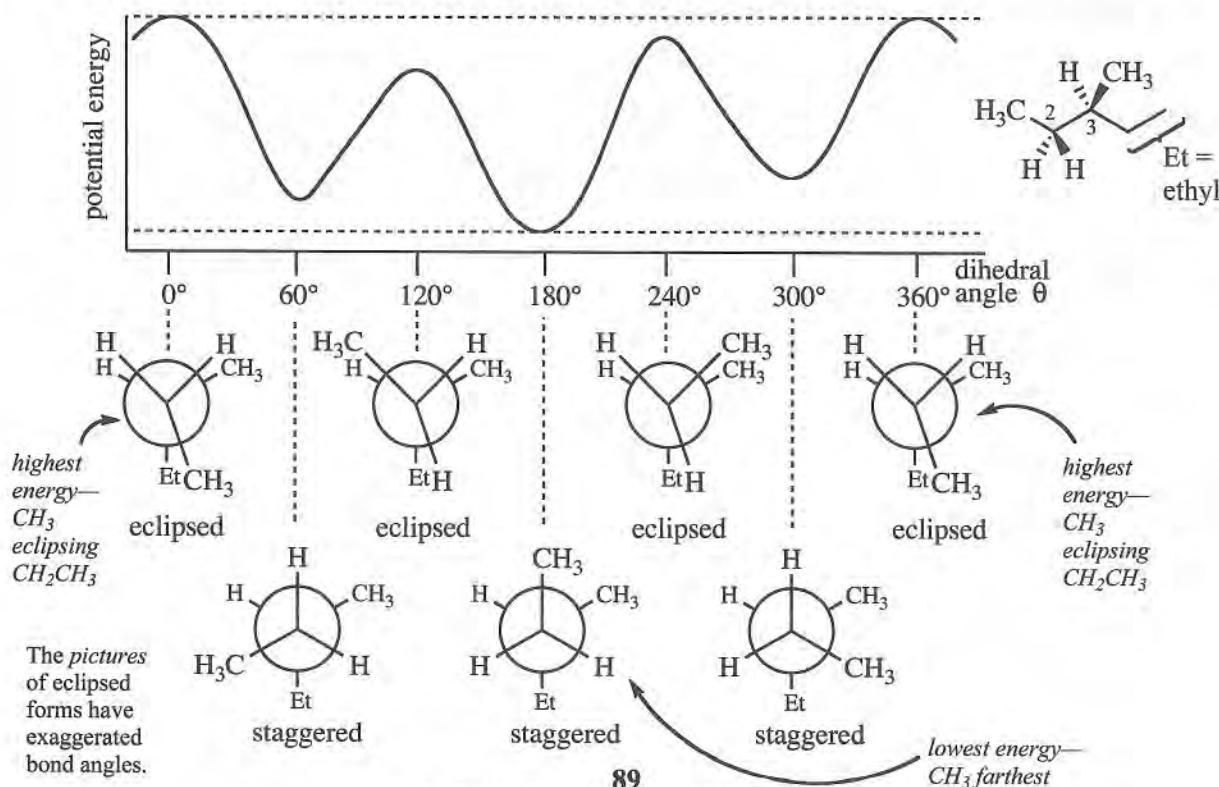
3-39

- (a) 3-ethyl-2,2,6-trimethylheptane
- (c) 3,7-diethyl-2,2,8-trimethyldecane
- (e) bicyclo[4.1.0]heptane
- (g) (1,1-diethylpropyl)cyclohexane

- (b) 3-ethyl-2,6,7-trimethyloctane
- (d) 1,1-diethyl-2-methylcyclobutane
- (f) *cis*-1-ethyl-3-propylcyclopentane
- (h) *cis*-1-ethyl-4-isopropylcyclodecane

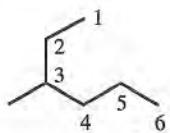
3-40 The ethyl group, —CH<sub>2</sub>CH<sub>3</sub>, is abbreviated Et. The back carbon is kept constant while the front carbon is rotated clockwise. The problem asks for relative energies, not calculations; the ethyl group is slightly larger than a methyl group, causing a higher energy than methyl in eclipsed conformations.

Interestingly, all of the minima and all of the maxima are at different energies; this arises because the three groups on the back carbon (H, CH<sub>3</sub>, CH<sub>2</sub>CH<sub>3</sub>) are all different.



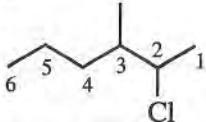
3-41

(a)



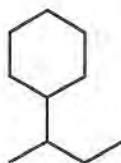
correct name: 3-methylhexane  
(longer chain)

(c)



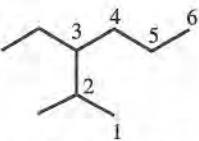
correct name: 2-chloro-3-methylhexane  
(Begin numbering at end closest to substituent.)

(e)



correct name: *sec*-butylcyclohexane or  
(1-methylpropyl)cyclohexane  
(The longer chain or ring is the base name.)

(b)



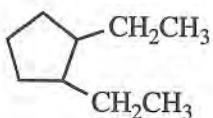
correct name: 3-ethyl-2-methylhexane  
(more branching with this numbering)

(d)



correct name: 2,2-dimethylbutane (Include  
a position number for each substituent,  
regardless of redundancies.)

(f)

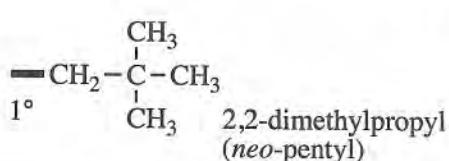
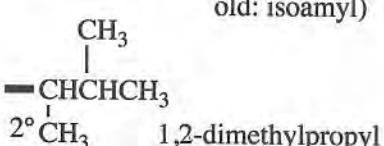
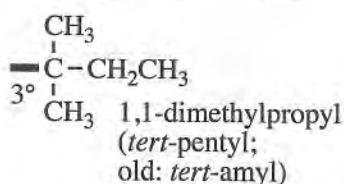
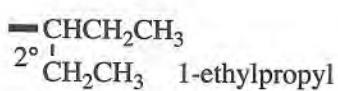
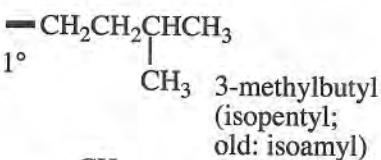
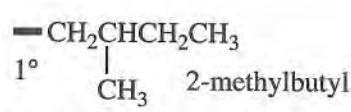
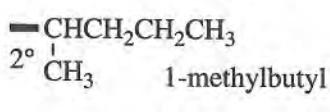
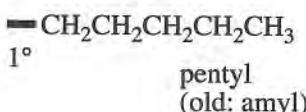


correct name: 1,2-diethylcyclopentane  
(Position numbers are the lowest possible.)  
*cis*- or *trans*- is not specified.

3-42

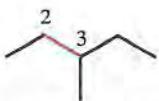
- (a) Octane has a higher boiling point than 2,2,3-trimethylpentane because linear molecules boil higher than branched molecules of the same molecular weight (increased van der Waals interaction).
- (b) Nonane has a higher boiling point than 2-methylheptane because nonane has a higher molecular weight and it is a linear structure as opposed to the lighter, branched 2-methylheptane.
- (c) Nonane boils higher than 2,2,5-trimethylhexane for the same reason as in (a).

3-43 The point of attachment is shown by the bold bond at the left of each structure.

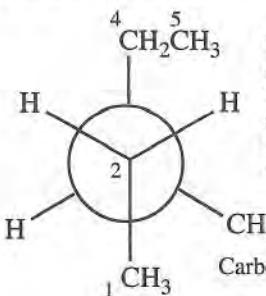


3-44 In each case, put the largest groups on adjacent carbons in anti positions to make the most stable conformations.

(a) 3-methylpentane



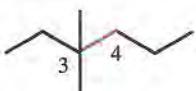
C-2 is the front carbon with H, H, and CH<sub>3</sub>  
C-3 is the back carbon with H, CH<sub>3</sub>, and CH<sub>2</sub>CH<sub>3</sub>



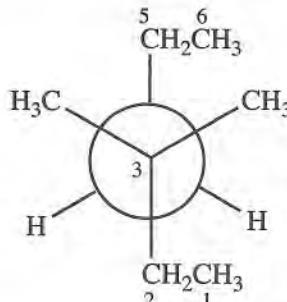
Newman projections were introduced in text section 3-7. They are used extensively to show the three-dimensional arrangement of atoms in a molecule.

Carbon-3 is behind carbon-2.

(b) 3,3-dimethylhexane



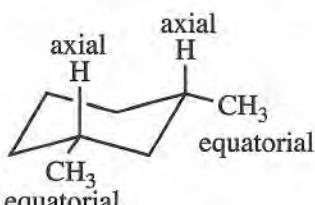
C-3 is the front carbon with CH<sub>3</sub>, CH<sub>3</sub>, and CH<sub>2</sub>CH<sub>3</sub>  
C-4 is the back carbon with H, H, and CH<sub>2</sub>CH<sub>3</sub>



Carbon-4 is behind carbon-3.

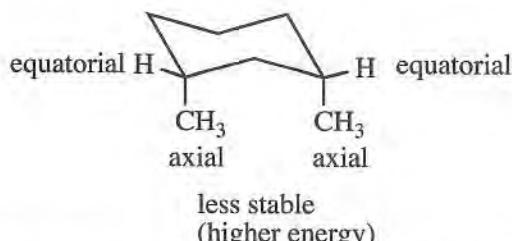
3-45

(a)



(b)

more stable  
(lower energy)

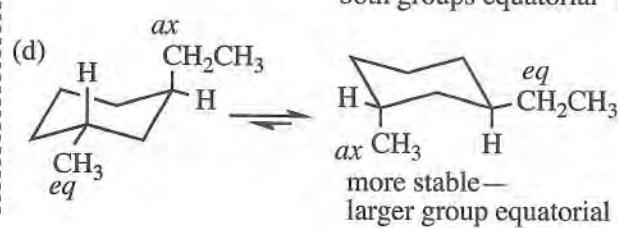
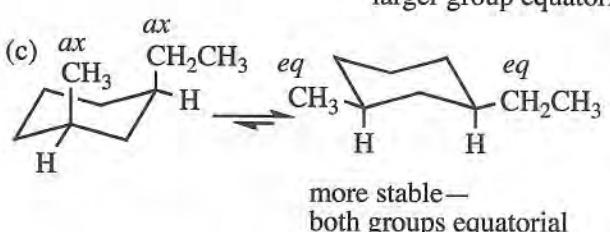
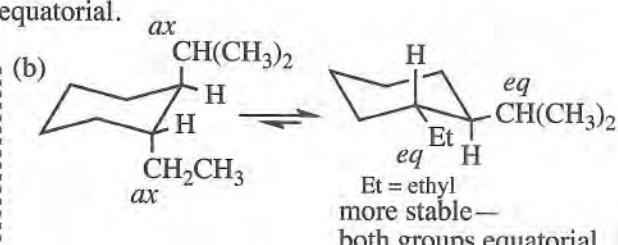
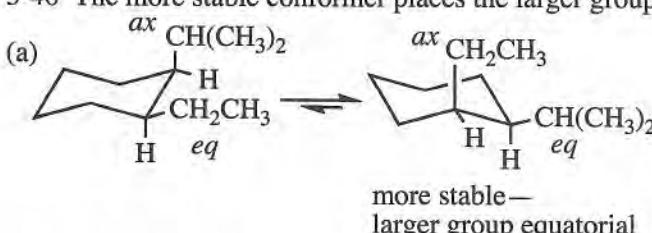


(c) From Section 3-14 of the text, each gauche interaction raises the energy 3.8 kJ/mole (0.9 kcal/mole), and each axial methyl has two gauche interactions, so the energy is:

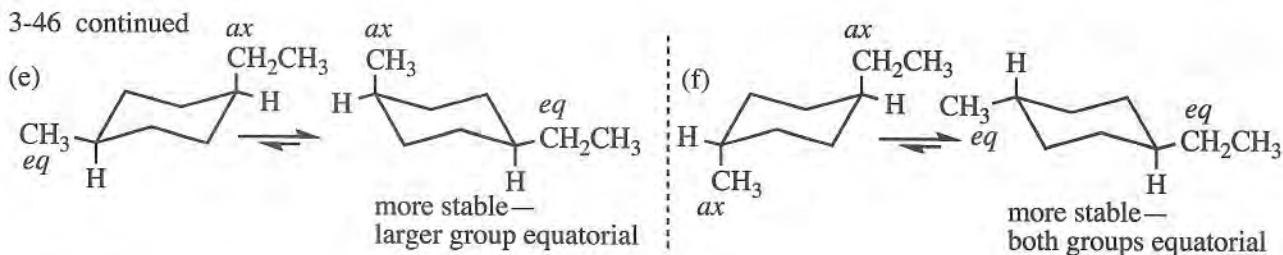
2 methyls x 2 interactions per methyl x 3.8 kJ/mole per interaction = 15.2 kJ/mole (3.6 kcal/mole)

(d) The steric strain from the 1,3-diaxial interaction of the methyls must be the difference between the total energy and the energy due to gauche interactions: 23 kJ/mole - 15.2 kJ/mole = 7.8 kJ/mole (5.4 kcal/mole - 3.6 kcal/mole = 1.8 kcal/mole)

3-46 The more stable conformer places the larger group equatorial.

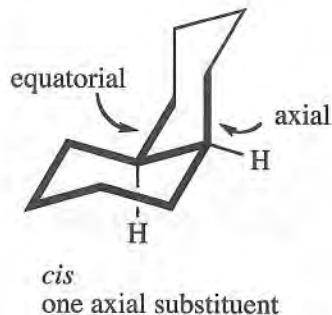
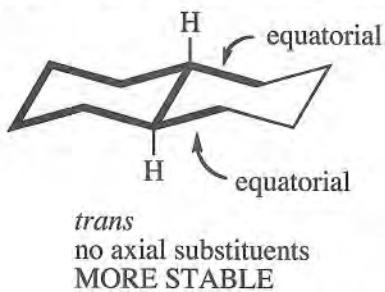


3-46 continued

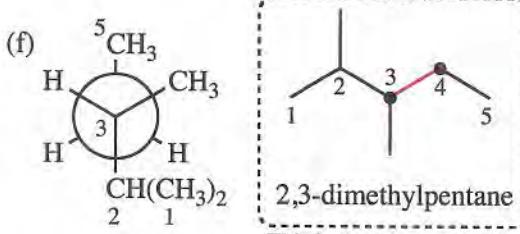
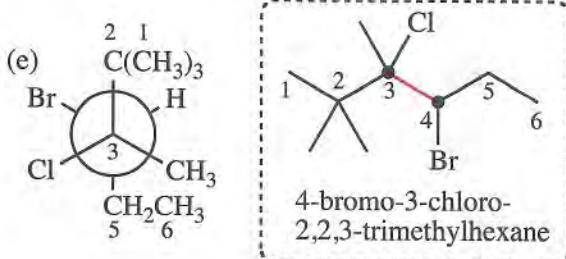
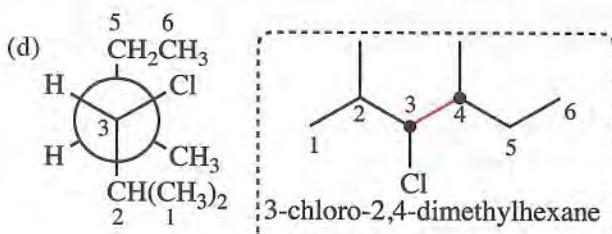
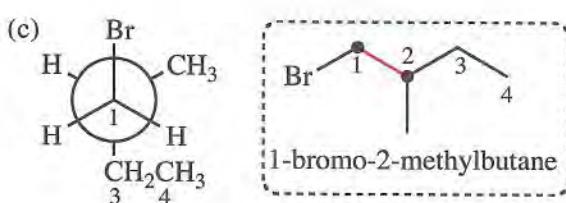
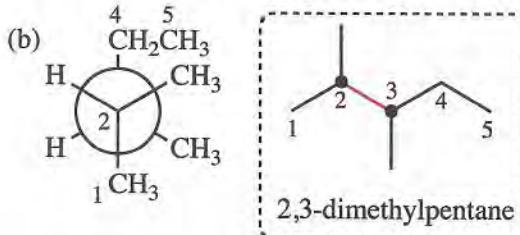
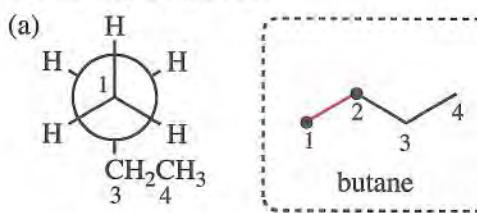


3-47 (Using models is essential to this problem.)

In both *cis*- and *trans*-decalin, the cyclohexane rings can be in chair conformations. The relative energies will depend on the number of axial substituents.

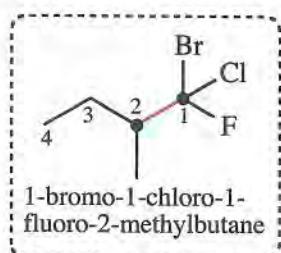
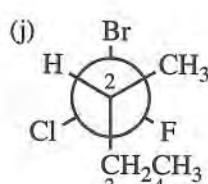
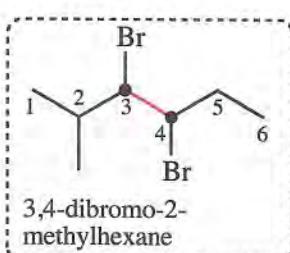
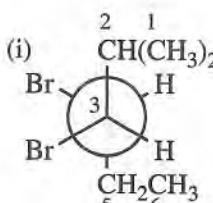
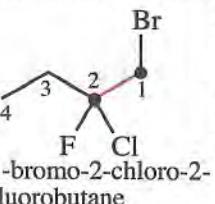
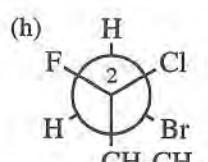
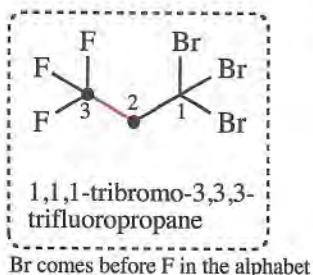
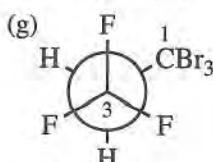


3-48 Solutions are given in the boxes. The front and back carbons from the Newman projection are denoted by a dark dot.

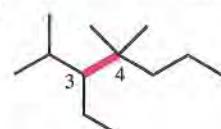


This is the same structure as part (b), sighted down a different bond.

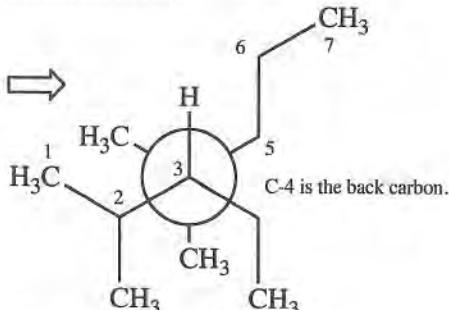
3-48 continued



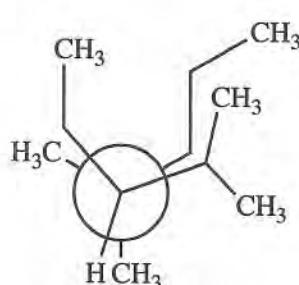
3-49



3-ethyl-2,4,4-trimethylheptane

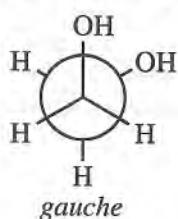
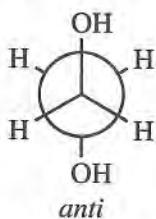


most stable conformation—  
two largest groups anti in a  
staggered conformation

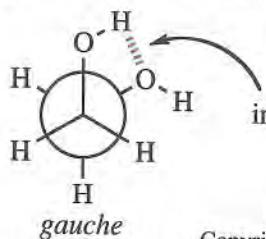


least stable conformation—  
two largest groups eclipsed

3-50 Usually, the anti conformation is more stable than the gauche because the two larger groups are farther away in the anti conformer. There must be something special about the gauche conformer, some attractive force that overcomes the normal repulsion between groups in the gauche conformation. What could it be?

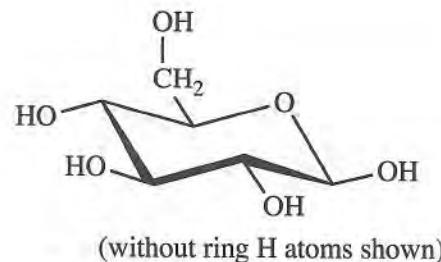
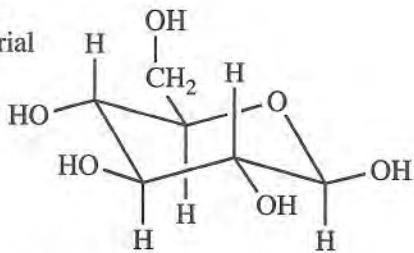


Hydrogen bonding! Moving the two OH groups closer together permits the H of one to come close to the O of the other, as can be seen in the picture below. Such intramolecular (within one molecule) hydrogen bonding cannot take place in the anti conformation where the two OH groups are too far apart.



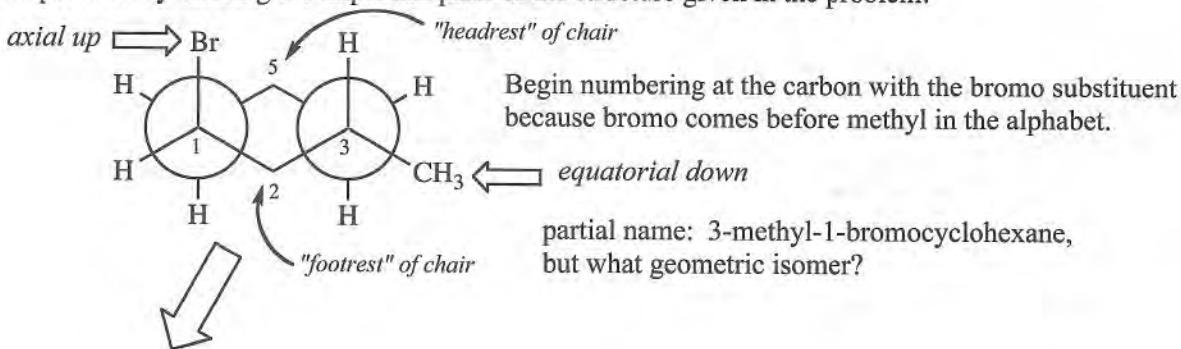
intramolecular hydrogen bonding, a strong attractive force

3-51 chair form of glucose with all substituents equatorial

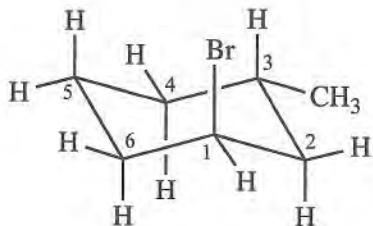


3-52

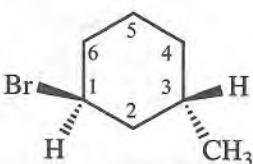
Begin this problem by labeling the important parts of the structure given in the problem.



(a)



(b)



(c) *trans*-1-bromo-3-methylcyclohexane

Note to the student: Creating practice problems for your study group is very helpful in learning new material, and in some areas, it is not difficult. For example, to create nomenclature problems, draw a cyclopentane, add three substituents, and name it. Then erase one of the ring bonds and name that acyclic structure. Go around the ring, erasing one bond at a time, and you have generated five new nomenclature problems for your group to practice naming!