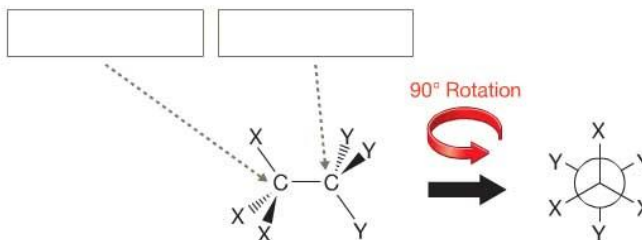


Chapter 4 Isomerism I: Conformational and Constitutional Isomers

YOUR TURN 4.1

Based on the Newman projection given, label the “front carbon” and the “back carbon” in the structure on the left.



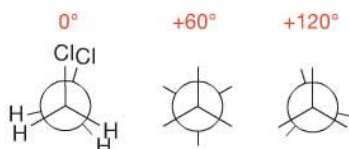
Answers to Your Turns are in the back of the book.

YOUR TURN 4.2

Construct a molecule of 1,1,1-tribromoethane ($\text{H}_3\text{C}-\text{CBr}_3$) using a molecular modeling kit. Rotate the CH_3 and CBr_3 groups relative to each other until the molecule looks like the structure shown in dash-wedge notation on the left side of Figure 4-2. Look down the C—C bonding axis and fill in the missing atoms in the incomplete Newman projection provided here.



Add the substituents to the incomplete Newman projections to represent the molecule at the left after $+60^\circ$ and $+120^\circ$ rotations of the back carbon.



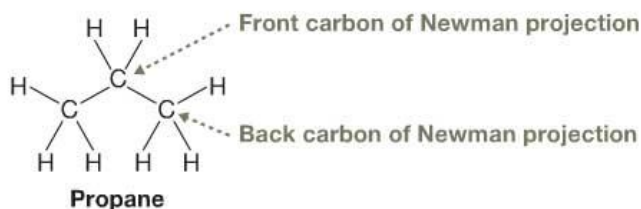
4.3 YOUR TURN

SOLVED problem 4.1 Draw the Lewis structure of the molecule whose Newman projection is as follows:

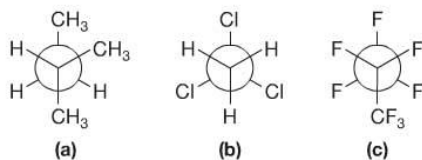


Think Which atoms are connected by the bond not observable in the Newman projection? What atoms or groups are attached to those atoms?

Solve The bond not shown is a C—C single bond. The C atom in the front (represented by the point) is bonded to two H atoms and a CH_3 group, whereas the C in the back (represented by a circle) is bonded to three H atoms. Thus, the structure consists of three C atoms bonded together. The compound is propane.



problem 4.2 Draw the Lewis structure that corresponds to each of the following Newman projections:

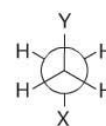


(a)

(b)

(c)

problem 4.3 The Newman projection at the right is of the same generic molecule used in Figure 4-3. Taking this dihedral angle to be -180° , draw Newman projections for each 60° rotation about the C—C single bond, from -180° to $+180^\circ$, in which the back carbon remains frozen in place.



YOUR TURN 4.4

In Figure 4-4, label each of the unlabeled conformations as either “eclipsed” or “staggered.”

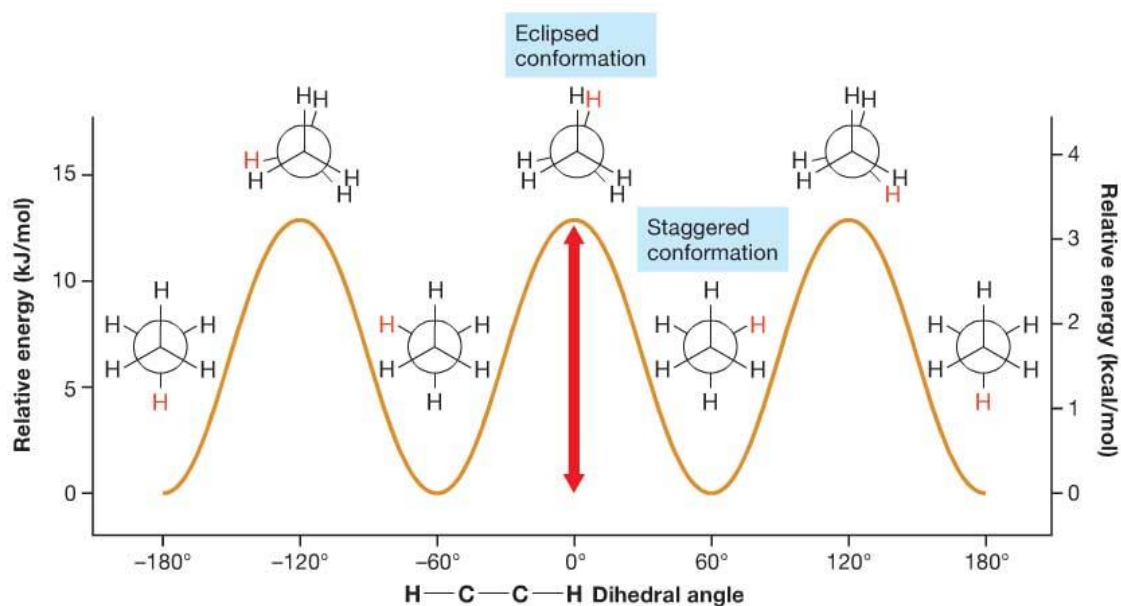


FIGURE 4-4 Conformational analysis of ethane, $\text{H}_3\text{C}-\text{CH}_3$ The plot shows the relative energy of ethane as a function of the C—C dihedral angle. Energies are relative to the lowest-energy conformation. The double-headed arrow represents the energy barrier for rotation about that bond.

Construct a molecule of ethane ($\text{H}_3\text{C}-\text{CH}_3$) using a molecular modeling kit. Rotate the molecule so that the $\text{C}-\text{C}$ bond is in an eclipsed conformation. Now rotate the $\text{C}-\text{C}$ bond so that it is in a staggered conformation. Are the $\text{C}-\text{H}$ bonds closer in the eclipsed conformation or in the staggered conformation?

YOUR TURN 4.6

Use Figure 4-4 to estimate the torsional strain in a molecule of ethane in an eclipsed conformation. _____

YOUR TURN 4.7

Label each unlabeled structure in Figure 4-7 as either "eclipsed" or "staggered."

YOUR TURN 4.8

Use Figure 4-7 to estimate how much higher in energy one eclipsed conformation of 1,2-dibromoethane ($\text{BrCH}_2-\text{CH}_2\text{Br}$) is than the other two.
_____ kJ/mol _____ kcal/mol

Additionally, estimate how much lower in energy one staggered conformation is than the other two.
_____ kJ/mol _____ kcal/mol

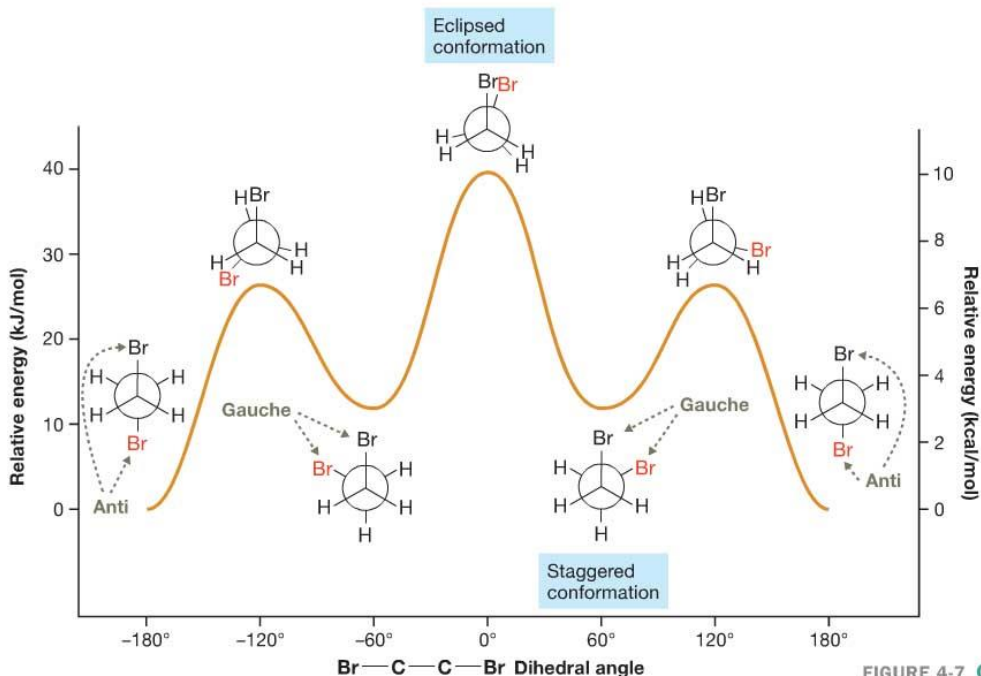
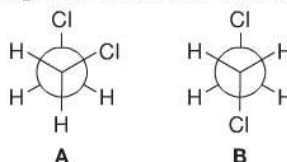


FIGURE 4-7 **Conformational analysis of 1,2-dibromoethane, $\text{Br}-\text{CH}_2-\text{CH}_2-\text{Br}$** The energy of 1,2-dibromoethane is plotted as a function of the $\text{Br}-\text{C}-\text{C}-\text{Br}$ dihedral angle. Energies are relative to that of the most stable conformation. The gauche and anti conformations are labeled.

YOUR TURN 4.9

Identify which of the following conformations is anti and which is gauche.

**YOUR TURN 4.10**

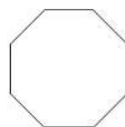
In Figure 4-7, draw a double-headed arrow (\leftrightarrow) to indicate the rotational energy barrier upon going from the anti conformation to one of the gauche conformations. Estimate that energy barrier here: _____ kJ/mol; _____ kcal/mol.

problem 4.4 Perform a conformational analysis of 1,2-dichloroethane ($\text{ClCH}_2\text{—CH}_2\text{Cl}$) by sketching its energy as a function of the dihedral angle about the C—C bond. Make sure the *relative* energies are correct, but do not concern yourself with the exact values. Draw Newman projections for each staggered and eclipsed conformation, and identify the anti and gauche conformations.

problem 4.5 Which molecule do you think has a larger rotational energy barrier about the C—C bond: 1,2-dibromoethane or 1,2-difluoroethane? Why?

YOUR TURN 4.11

The heat of combustion of cyclooctane is 4962.2 kJ/mol (1186.0 kcal/mol).



Cyclooctane

How many CH₂ groups compose cyclooctane? _____

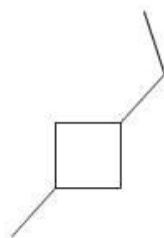
Compute the heat of combustion per CH₂ group. _____

Compute the ring strain per CH₂ group by subtracting cyclohexane's heat of combustion per CH₂ group from that determined for cyclooctane. _____

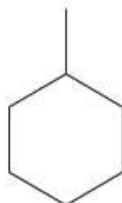
Compute the total ring strain for cyclooctane by taking into account the total number of CH₂ groups in the molecule. _____

How do these values compare to those for the other molecules in Table 4-1?

SOLVED problem 4.6 Rank the following cycloalkanes in order from lowest heat of combustion to highest.



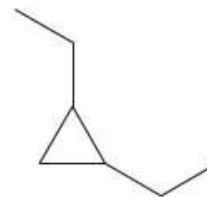
(a)



(b)



(c)

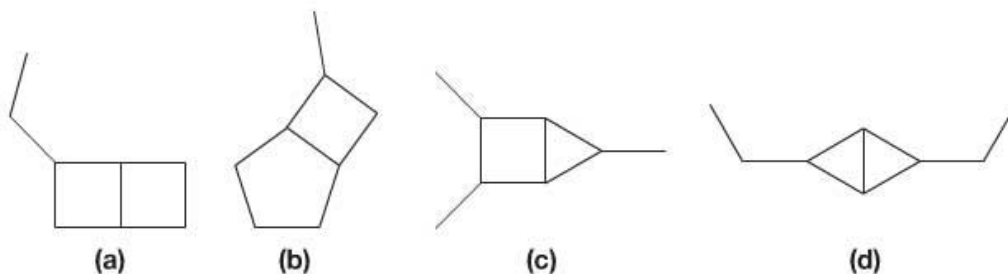


(d)

Think What is the same among these molecules? What is different? How do those differences translate into heats of combustion?

Solve All four of these compounds have the molecular formula C₇H₁₄ and contain only C—C and C—H single bonds. Differences in heats of combustion, therefore, will largely reflect differences in ring strain. The three-membered ring (**D**) is the most strained, so it will give off the most heat during combustion—it will have the highest heat of combustion. Next comes the four-membered ring (**A**), followed by the seven-membered ring (**C**). The six-membered ring (**B**) is the least strained, so it will have the lowest heat of combustion. In order, then, the heats of combustion are: **B** < **C** < **A** < **D**.

problem 4.7 Rank the following cycloalkanes in order from lowest heat of combustion to highest.



YOUR TURN 4.12

Using a molecular modeling kit, build a molecule of cyclohexane in its chair conformation, then rotate it in space until it appears as in Figure 4-12c. Observe the staggered conformation about each C—C bond. Next force all of the carbon atoms to be planar as in Figure 4-13 and observe the eclipsed conformation about each C—C bond.

Identify the C—C bond in Figure 4-14 that is in the eclipsed conformation. It may help if you build a model of cyclopentane in its envelope conformation using a modeling kit.

4.13 YOUR TURN

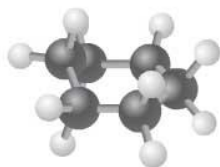
YOUR TURN 4.14

Use a molecular modeling kit to build a molecule of cyclopentane in its envelope conformation. View it so that it appears as shown on the left in Figure 4-19 and move the atoms as indicated in the figure. Identify which C—C bonds rotate and circle those bonds on the drawing on the left in Figure 4-19.

YOUR TURN 4.15

Use a molecular modeling kit to construct a model of cyclohexane and view it so that it parallels the structure on the left in Figure 4-22. Perform a chair flip by moving the two carbon atoms indicated by the red arrows to obtain the conformation on the right in the figure. Reverse and repeat this procedure several more times. As you flip the chair back and forth, identify the bonds of the ring that rotate and the direction in which they rotate. Circle and label those bonds in the drawing on the left in Figure 4-22.

Use a molecular modeling kit to build the following half-chair conformation:



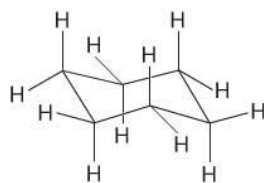
Examine the model from different points of view, and note the different types of strain. In the figure provided here, indicate where the strain exists, as well as the type of strain (i.e., angle, steric, or torsional). With these observations, can you justify why the half-chair conformation is so high in energy?

4.16 YOUR TURN

Draw the chair conformation of cyclohexane in Figure 4-28 using the steps described above. Practice doing so until you can draw it without having to refer to the figure.

4.17 YOUR TURN

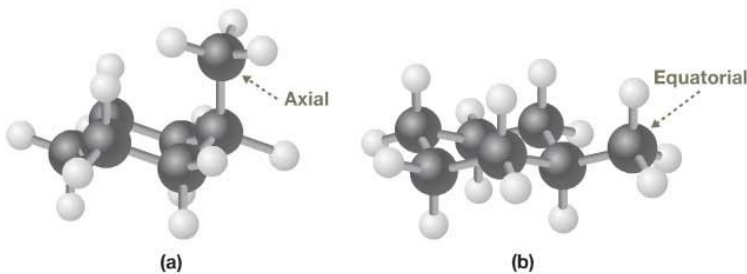
The following chair conformation of cyclohexane is obtained after the one in Figure 4-28 has undergone a chair flip:



Use the steps in Figure 4-28 to practice drawing this chair conformation until you can draw it without having to refer to the figure.

4.18 YOUR TURN

FIGURE 4-29 The two chair conformations of methylcyclohexane The two chair conformations of monosubstituted cyclohexanes are not equivalent. (a) The methyl group occupies an axial position. (b) The methyl group occupies an equatorial position.



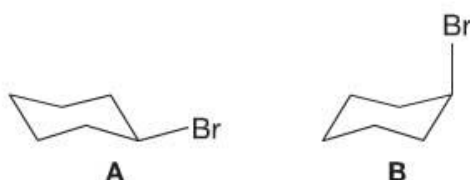
YOUR TURN 4.19

In Figure 4-29a, label each of the 11 hydrogen atoms bonded to the ring as either axial or equatorial. Do the same for Figure 4-29b.

The model of methylcyclohexane below corresponds to the top structure in Figure 4-30a. It shows two hydrogen atoms on the ring involved in 1,3-diaxial interactions with the CH_3 group. Identify these two hydrogens. Also, two different CH_2 groups are gauche to the CH_3 group. One is indicated in Figure 4-30a. Identify the second one in the structure below. (*Hint*: Build a molecular model of methylcyclohexane.)

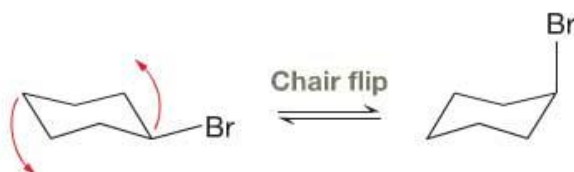


SOLVED problem 4.8 Which species below is more stable?



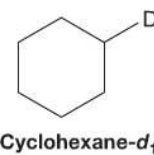
Think How are the two molecules related? How are they different? How do those differences translate into stabilities?

Solve The two species are related by a simple chair flip:

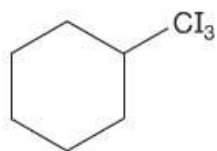


The Br atom occupies an equatorial position in **A**, whereas it occupies an axial position in **B**. Bromine is much larger than any of the 11 H atoms also bonded to the cyclohexane ring, so it requires more room. Because the equatorial position provides more room than the axial position, conformation **A** is more stable.

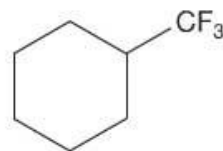
problem 4.9 Draw both chair conformations of cyclohexane- d_1 , in which a hydrogen atom on cyclohexane has been replaced by a deuterium atom. Which conformation would you expect to be in greater abundance, if any? Explain. (*Hint*: Deuterium is an isotope of hydrogen, possessing one more neutron than hydrogen. Recall from Chapter 1 that the size of an atom is dictated by the size of its electron cloud.)



problem 4.10 For which compound—triiodomethylcyclohexane or trifluoromethylcyclohexane—would you expect to find a greater percentage of molecules that have the substituent in the axial position? Explain.

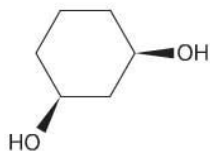


Triiodomethylcyclohexane

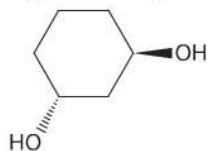


Trifluoromethylcyclohexane

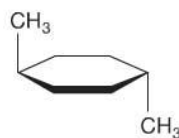
Draw each line structure as a Haworth projection and each Haworth projection as a line structure including dash-wedge notation.



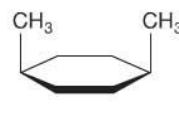
(a)



(b)



(c)



(d)

(a)

(b)

(c)

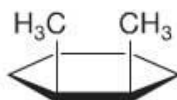
(d)

4.21 YOUR TURN

YOUR TURN 4.22

Use a molecular modeling kit to build a model of *trans*-1,3-dimethylcyclohexane so that it looks exactly like the chair conformation shown on the left in Figure 4-33b. Without flipping the chair, simply rotate the molecule again until it looks like the chair conformation on the right.

SOLVED problem 4.11 Draw the more stable chair conformation of *cis*-1,2-dimethylcyclohexane.



***cis*-1,2-Dimethylcyclohexane**

Think Which substituents require the most room? Which position, axial or equatorial, offers more room? Can both substituents achieve that position?

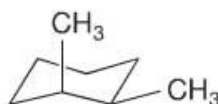
Solve The two methyl groups are the largest substituents on the ring and each is more stable in an equatorial position. To determine whether they can both occupy equatorial positions, begin by drawing a chair conformation with one equatorial methyl group.



For the two groups to be *cis*, the other methyl group must be in the less favorable axial position.



If we perform a chair flip, the equatorial methyl group becomes axial and vice versa, yielding the following conformation.



This chair has precisely the same stability as the first one, so both conformations are favored equally.

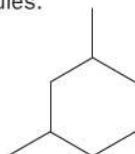
problem 4.12 Draw the most stable conformation of *trans*-1,2-dimethylcyclohexane.

problem 4.13 Draw the most stable conformation of the following molecule.



problem 4.14 Draw the most stable conformation of *cis*-1-methyl-4-trichloromethylcyclohexane.

Using the above method, show that the following molecule is not a constitutional isomer of the previous two molecules.



4.23 YOUR TURN

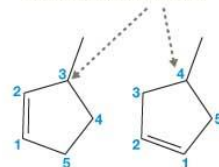
SOLVED problem 4.15 Are the two molecules at the right constitutional isomers of each other?

Think Do both compounds have the same molecular formula? Is the largest continuous chain or ring in each molecule the same? Are the C atoms that are involved in the double bonds assigned the same numbers in each molecule? In each molecule, is the C atom to which the methyl group is attached assigned the same number?

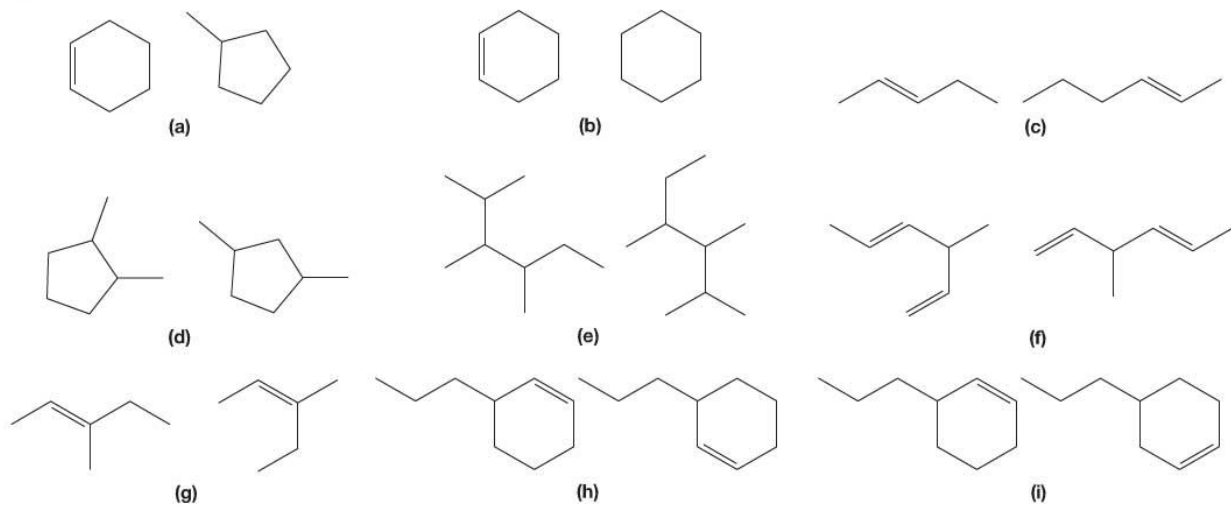
Solve Both compounds have a molecular formula of C_6H_{10} . In each molecule, the largest continuous ring has five C atoms. As shown at the right, the numbers assigned to the doubly bonded C atoms are the same in each molecule. However, the molecules differ in the number assigned to the C atom to which the methyl group is attached. In the first molecule, the methyl group is attached to C3, whereas in the second molecule, it is attached to C4. Thus, the molecules have different connectivity, making them constitutional isomers.



Methyl groups attached to different carbons

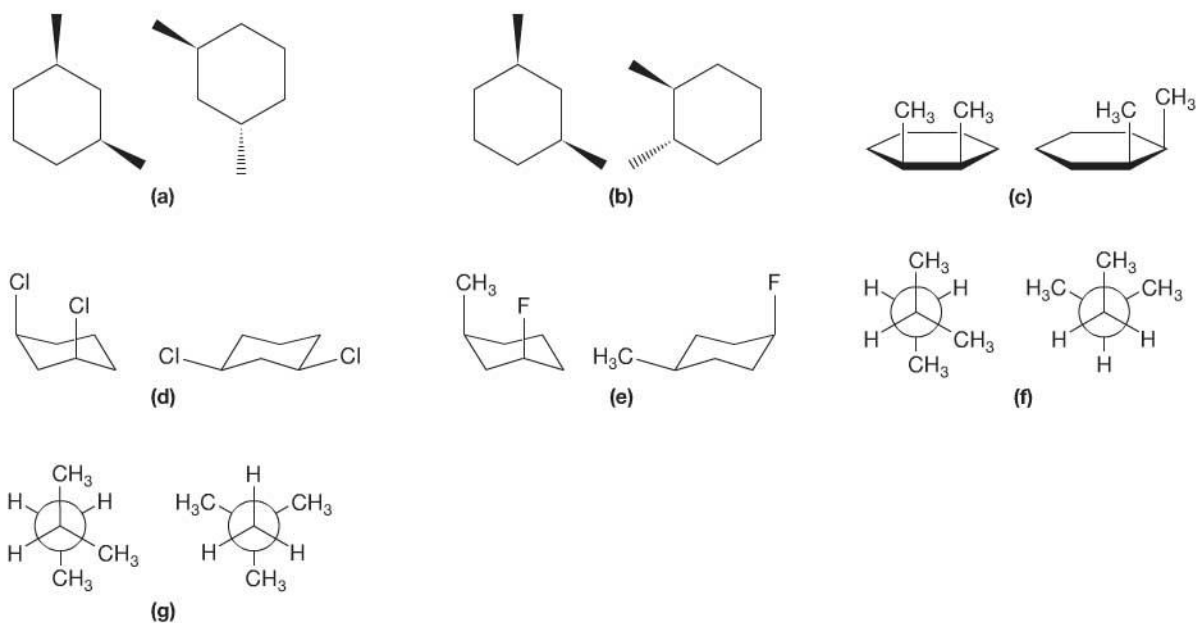


problem 4.16 For each pair of molecules, determine whether they are constitutional isomers.



- (a) (b)
 (c) (e)
 (f) (g)
 (h) (i)

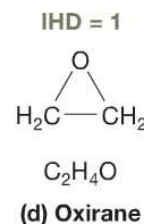
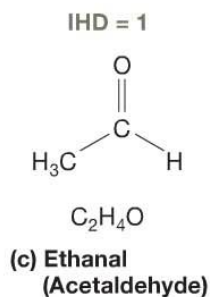
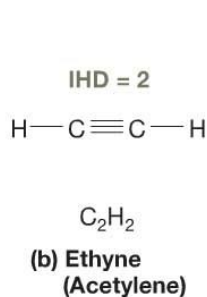
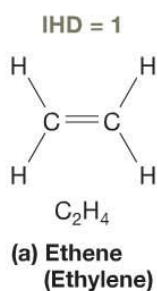
problem 4.17 For each pair of molecules, determine whether they are constitutional isomers.



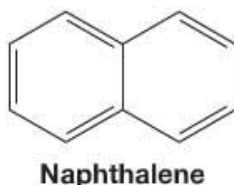
- (a) (b)
 (c) (e)
 (f) (g)

Draw the structure of a *saturated* molecule that corresponds to each of the unsaturated molecules in Figure 4-37.

4.24 YOUR TURN



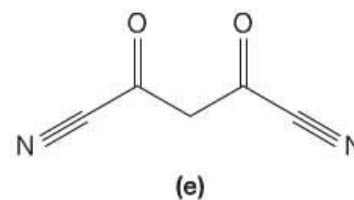
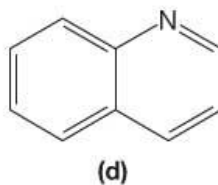
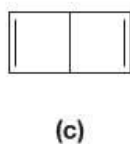
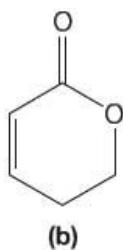
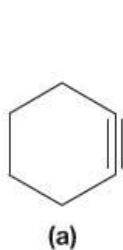
SOLVED problem 4.18 What is the IHD of naphthalene?



Think How many double bonds are there? How many triple bonds are there? How many rings are there? How much does each contribute to the overall IHD?

Solve There are five double bonds, each contributing 1 to the IHD, and there are two rings, each contributing 1 to the IHD. There are no triple bonds. The total IHD, therefore, is $5(1) + 2(1) = 7$.

problem 4.19 Determine the IHD for each of the following molecules.



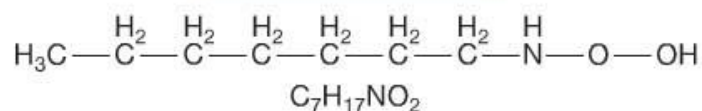
problem 4.20 Identify all of the functional groups listed in Table 1-6 that contribute **(a)** an IHD of 1, **(b)** an IHD of 2, **(c)** an IHD of 3, and **(d)** an IHD of 4.

SOLVED problem 4.21 Determine the IHD for a compound whose molecular formula is C₇H₇NO₂.

Think What is the formula for an analogous saturated compound? How many hydrogen atoms are missing from the formula we are given?

Solve We can construct a saturated compound containing seven carbon atoms, one nitrogen atom, and two oxygen atoms simply by connecting all of these atoms in a row using single bonds only.

A saturated compound



It takes 17 hydrogen atoms in total to saturate each carbon, nitrogen, and oxygen in this compound. Thus, the formula we were given is missing 10 H atoms, for an IHD of 5.

problem 4.22 Compute the IHD for a compound whose molecular formula is C₄N₂O₇F.

problem 4.23 If a saturated compound contains four carbon atoms as the only nonhydrogen atoms, how many hydrogen atoms does it contain? How many hydrogen atoms are in a saturated compound containing four carbon atoms and one oxygen atom? How many hydrogen atoms are in a saturated compound containing four carbon atoms and two oxygen atoms? What can you conclude about the effect that each oxygen atom has on the formula for a completely saturated molecule?

problem 4.24 (a) Repeat Problem 4.23, adding nitrogen atoms instead of oxygen atoms. (b) Repeat it once again, adding fluorine atoms instead of oxygen atoms.

YOUR TURN 4.25

Identify the functional groups present in *each* molecule in Figure 4-45.

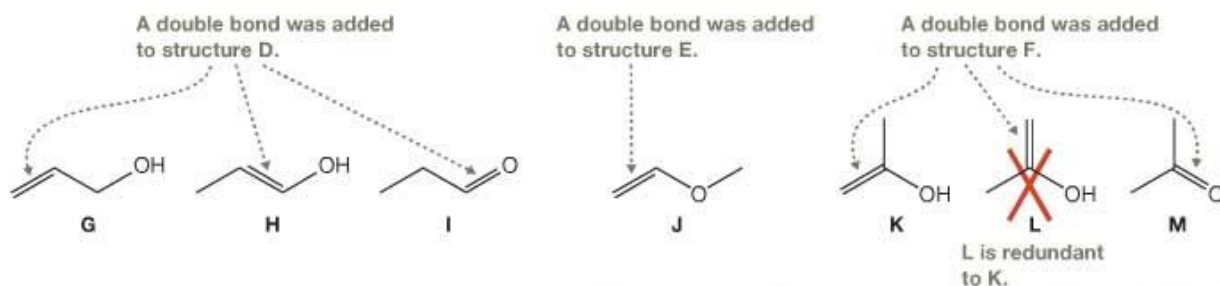


FIGURE 4-45 Isomers resulting from the addition of a double bond to Structures D–F (Step 3) Structures G–I were produced by adding a double bond to various locations in Structure D. Structure J was produced by adding a double bond to Structure E. Structures K–M were produced by adding a double bond to various locations in Structure F. Structure L is redundant to K.