

Alkanes and Cycloalkanes

The burners of gas grills are fueled by liquefied petroleum gas (LPG). LPG contains mostly propane, which is how their containers became known as "propane tanks," but LPG also contains small amounts of ethane, propene, and butane. Inset: A model of propane. (© Lauri Patterson/iStockphoto)

KEY QUESTIONS

- 3.1 What Are Alkanes?
- 3.2 What Is Constitutional Isomerism in Alkanes?
- 3.3 How Do We Name Alkanes?
- 3.4 What Are Cycloalkanes?
- 3.5 What Is the IUPAC System of Nomenclature?
- 3.6 What Are the Conformations of Alkanes and Cycloalkanes?
- 3.7 What Is Cis–Trans Isomerism in Cycloalkanes?
- 3.8 What Are the Physical Properties of Alkanes and Cycloalkanes?
- 3.9 What Are the Characteristic Reactions of Alkanes?

3.10 What Are the Sources of Alkanes?

ноw то

- 3.1 How to Interpret Line-Angle Formulas
- 3.2 How to Visualize and Draw a Newman Projection
- 3.3 How to Draw Alternative Chair Conformations of Cyclohexane

CHEMICAL CONNECTIONS

- **3A** The Poisonous Puffer Fish
- 3B Octane Rating: What Those Numbers at the Pump Mean

IN THIS CHAPTER, we begin our study of organic compounds with the physical and chemical properties of alkanes, the simplest types of organic compounds. Actually, alkanes are members of a larger class of organic compounds called **hydrocarbons**. A hydrocarbon is a compound composed of only carbon and hydrogen. Figure 3.1 shows the four classes of hydrocarbons, along with the characteristic type of bonding between carbon atoms in each.

Hydrocarbon A compound that contains only carbon atoms and hydrogen atoms.



Alkane A saturated hydrocarbon whose carbon atoms are arranged in an open chain.

Saturated hydrocarbon

FIGURE 3.1 The four classes of

hydrocarbons.

A hydrocarbon containing only carbon-carbon single bonds.

Aliphatic hydrocarbon An alternative term to describe an alkane.

Alkanes are saturated hydrocarbons; that is, they contain only carbon-carbon single bonds. In this context, "saturated" means that each carbon has the maximum number of hydrogens bonded to it. We often refer to alkanes as aliphatic hydrocarbons, because the physical properties of the higher members of this class resemble those of the long carbon-chain molecules we find in animal fats and plant oils (Greek: aleiphar, fat or oil).

A hydrocarbon that contains one or more carbon-carbon double bonds, triple bonds, or benzene rings is classified as an unsaturated hydrocarbon. We study alkanes (saturated hydrocarbons) in this chapter. We study alkenes and alkynes (both unsaturated hydrocarbons) in Chapters 4 and 5, and arenes (also unsaturated hydrocarbons) in Chapter 9.



Methane (CH_4) and ethane (C_2H_6) are the first two members of the alkane family. Figure 3.2 shows molecular formulas, Lewis structures, and ball-and-stick models for these molecules. The shape of methane is tetrahedral, and all H-C-H bond angles are 109.5°. Each carbon atom in ethane is also tetrahedral, and all bond angles are approximately 109.5°.

Although the three-dimensional shapes of larger alkanes are more complex than those of methane and ethane, the four bonds about each carbon atom are still arranged in a tetrahedral manner, and all bond angles are still approximately 109.5°.

The next members of the alkane family are propane, butane, and pentane. In the representations that follow, these hydrocarbons are drawn first as condensed structural formulas that show all carbons and hydrogens. They are then drawn in an even more



Butane is the fuel in this lighter. Butane molecules are present in the liquid and gaseous states in the lighter.

Charles D. Winters

FIGURE 3.2 Methane and ethane. abbreviated form called a **line-angle formula.** In this type of representation, a line represents a carbon–carbon bond, and an angle represents a carbon atom. A line ending represents a $-CH_3$ group. Although hydrogen atoms are not shown in line-angle formulas, they are assumed to be there in sufficient numbers to give each carbon four bonds.

Line-angle formula An abbreviated way to draw structural formulas in which each vertex and each line ending represents a carbon atom and a line represents a bond.



We can write structural formulas for alkanes in still another abbreviated form. The structural formula of pentane, for example, contains three CH_2 (methylene) groups in the middle of the chain. We can collect these groups together and write the structural formula as $CH_3(CH_2)_3CH_3$. Table 3.1 gives the names and molecular formulas of the first 20 alkanes. Note that the names of all these alkanes end in *-ane*. We will have more to say about naming alkanes in Section 3.3.





ledia Baker

A tank for propane fuel.

TABLE 3.1 Names, Molecular Formulas, and Condensed Structural Formulas for the First 20 Alkanes with Unbranched Chains

Name	Molecular Formula	Condensed Structural Formula	Name	Molecular Formula	Condensed Structural Formula
methane	CH_4	CH_4	undecane	$C_{11}H_{24}$	$\mathrm{CH}_3(\mathrm{CH}_2)_9\mathrm{CH}_3$
ethane	C_2H_6	CH_3CH_3	dodecane	$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$
propane	C_3H_8	$CH_3CH_2CH_3$	tridecane	$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	tetradecane	$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentadecane	$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptadecane	$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonadecane	$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$
decane	$C_{10}H_{22}$	$\mathrm{CH}_3(\mathrm{CH}_2)_8\mathrm{CH}_3$	eicosane	$C_{20}H_{42}$	$\mathrm{CH}_3(\mathrm{CH}_2)_{18}\mathrm{CH}_3$

Alkanes have the general molecular formula C_nH_{2n+2} . Thus, given the number of carbon atoms in an alkane, it is easy to determine the number of hydrogens in the molecule and also its molecular formula. For example, decane, with 10 carbon atoms, must have $(2 \times 10) + 2 = 22$ hydrogens and the molecular formula C₁₀H₂₂.

What Is Constitutional Isomerism in Alkanes? 3.2

Constitutional isomers are compounds that have the same molecular formula, but different structural formulas. By "different structural formulas," we mean that these compounds differ in the kinds of bonds they have (single, double, or triple) or in their connectivity (the order of attachment among their atoms).

For the molecular formulas CH₄, C₂H₆, and C₃H₈, only one order of attachment of atoms is possible. For the molecular formula C_4H_{10} , two orders of attachment of atoms are possible. In one of these, named butane, the four carbons are bonded in a chain; in the other, named 2-methylpropane, three carbons are bonded in a chain, with the fourth carbon as a branch on the middle carbon of the chain.



Butane and 2-methylpropane are constitutional isomers; they are different compounds and have different physical and chemical properties. Their boiling points, for example, differ by approximately 11°C. We will discuss how to name alkanes in the next section.

In Section 1.7, we encountered several examples of constitutional isomers, although we did not call them that at the time. We saw that there are two alcohols with the molecular formula C_3H_8O , two aldehydes with the molecular formula C_4H_8O , and two carboxylic acids with the molecular formula C₄H₈O₂.

Constitutional isomers Compounds with the

same molecular formula, but a different order of attachment of their atoms. To find out whether two or more structural formulas represent constitutional isomers, write the molecular formula of each and then compare them. All compounds that have the same molecular formula, but different structural formulas, are constitutional isomers.

EXAMPLE 3.1

Do the structural formulas in each pair represent the same compound or constitutional isomers?

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2CH_2$ (each is C_6H_{14}) $CH_3CH_2CH_2CH_3$ (b) CH_3CHCH_2CH and $CH_3CH_2CHCHCH_3$ (each is C_7H_{16}) CH_3 CH_3 CH_3

STRATEGY

To determine whether these structural formulas represent the same compound or constitutional isomers, first find the longest chain of carbon atoms in each. Note that it makes no difference whether the chain is drawn straight or bent. Second, number the longest chain from the end nearest the first branch. Third, compare the lengths of each chain and the sizes and locations of any branches. Structural formulas that have the same connectivity of atoms represent the same compound; those that have a different connectivity of atoms represent constitutional isomers.

SOLUTION

(a) Each structural formula has an unbranched chain of six carbons. The two structures are identical and represent the same compound:



(b) Each structural formula has a chain of five carbons with two CH₃ branches. Although the branches are identical, they are at different locations on the chains. Therefore, these structural formulas represent constitutional isomers:



$\mathbf{PROBLEM} \quad 3.1$

Do the structural formulas in each pair represent the same compound or constitutional isomers?



EXAMPLE 3.2

Draw structural formulas for the five constitutional isomers with the molecular formula C_6H_{14} .

STRATEGY

In solving problems of this type, you should devise a strategy and then follow it. Here is one such strategy: First, draw a line-angle formula for the constitutional isomer with all six carbons in an unbranched chain. Then, draw line-angle formulas for all constitutional isomers with five carbons in a chain and one carbon as a branch on the chain. Finally, draw line-angle formulas for all constitutional isomers with four carbons in a chain and two carbons as branches.

SOLUTION



Six carbons in an unbranched chain

Five carbons in a chain; one carbon as a branch

Four carbons in a chain; two carbons as branches

No constitutional isomers with only three carbons in the longest chain are possible for C_6H_{14} .

See problems 3.21, 3.23

$\mathbf{PROBLEM} \quad 3.2$

Draw structural formulas for the three constitutional isomers with molecular formula C_5H_{12} .

The ability of carbon atoms to form strong, stable bonds with other carbon atoms results in a staggering number of constitutional isomers. As the following table shows, there are 3 constitutional isomers with the molecular formula C_5H_{12} , 75 constitutional isomers with the molecular formula $C_{10}H_{22}$, and almost 37 million constitutional isomers with the molecular formula $C_{25}H_{52}$:

Carbon Atoms	Constitutional Isomers
1	0
5	3
10	75
15	4,347
25	36,797,588

Thus, for even a small number of carbon and hydrogen atoms, a very large number of constitutional isomers is possible. In fact, the potential for structural and functional group individuality among organic molecules made from just the basic building blocks of carbon, hydrogen, nitrogen, and oxygen is practically limitless.

.

3.3

How Do We Name Alkanes?

A. The IUPAC System

Ideally, every organic compound should have a name from which its structural formula can be drawn. For this purpose, chemists have adopted a set of rules established by an organization called the International Union of Pure and Applied Chemistry (IUPAC).

The IUPAC name of an alkane with an unbranched chain of carbon atoms consists of two parts: (1) a prefix that indicates the number of carbon atoms in the chain and (2) the ending **-ane** to show that the compound is a saturated hydrocarbon. Table 3.2 gives the prefixes used to show the presence of 1 to 20 carbon atoms.

The first four prefixes listed in Table 3.2 were chosen by the IUPAC because they were well established in the language of organic chemistry. In fact, they were well established even before there were hints of the structural theory underlying the discipline. For example, the prefix *but*- appears in the name *butyric acid*, a compound of four carbon atoms formed by the air oxidation of butter fat (Latin: *butyrum*, butter). Prefixes to show five or more carbons are derived from Greek or Latin numbers. (See Table 3.1 for the names, molecular formulas, and condensed structural formulas for the first 20 alkanes with unbranched chains.)

The IUPAC name of an alkane with a branched chain consists of a **parent name** that indicates the longest chain of carbon atoms in the compound and substituent names that indicate the groups bonded to the parent chain.



A substituent group derived from an alkane by the removal of a hydrogen atom is called an **alkyl group** and is commonly represented by the symbol **R**-. We name alkyl groups by dropping the *-ane* from the name of the parent alkane and adding the suffix *-yl*. Table 3.3 gives the names and structural formulas for eight of the most common alkyl groups. The prefix *sec-* is an abbreviation for secondary, meaning a carbon bonded to two other carbons. The

Alkyl group A group derived by removing a hydrogen from an alkane; given the symbol R-.

R- A symbol used to represent an alkyl group.

TABLE 3.	TABLE 3.2 Prefixes Used in the IUPAC System to Show the Presence of 1 to 20 Carbons in an Unbranched Chain				
Prefix	Number of Carbon Atoms	Prefix	Number of Carbon Atoms		
meth-	1	undec-	11		
eth-	2	dodec-	12		
prop-	3	tridec-	13		
but-	4	tetradec-	14		
pent-	5	pentadec-	15		
hex-	6	hexadec-	16		
hept-	7	heptadec-	17		
oct-	8	octadec-	18		
non-	9	nonadec-	19		
dec-	10	eicos-	20		

TABLE 3.3	TABLE 3.3 Names of the Most Common Alkyl Groups			
Name	Condensed Structural Formula	Name	Condensed Structural Formula	
methyl	— CH ₃	isobutyl	$-CH_2CHCH_3$ CH_3	
ethyl	—СН ₂ СН ₃	sec-butyl abbreviation for "secondary"	-CHCH ₂ CH ₃ CH ₃	
propyl	-CH ₂ CH ₂ CH ₃	<i>tert</i> -butyl abbreviation for "tertiary"	$\begin{array}{c} \mathrm{CH}_3\\ \\ -\mathrm{CCH}_3\\ \\ \mathrm{CH}_3\end{array}$	
isopropyl	$- \underset{ \\ CH_3}{CH_3}$			
butyl	$-CH_2CH_2CH_2CH_3$			

prefix *tert-* is an abbreviation for tertiary, meaning a carbon bonded to three other carbons. Note that when these two prefixes are part of a name, they are always italicized.

The rules of the IUPAC system for naming alkanes are as follows:

- 1. The name for an alkane with an unbranched chain of carbon atoms consists of a prefix showing the number of carbon atoms in the chain and the ending *-ane*.
- 2. For branched-chain alkanes, take the longest chain of carbon atoms as the parent chain, and its name becomes the root name.
- **3.** Give each substituent on the parent chain a name and a number. The number shows the carbon atom of the parent chain to which the substituent is bonded. Use a hyphen to connect the number to the name:



2-Methylpropane

4. If there is one substituent, number the parent chain from the end that gives it the lower number:



2-Methylpentane (not 4-methylpentane)

5. If there are two or more identical substituents, number the parent chain from the end that gives the lower number to the substituent encountered first. The number of times the substituent occurs is indicated by the prefix *di-, tri-, tetra-, penta-, hexa-*, and so on. A comma is used to separate position numbers:

 $\begin{array}{c} CH_3 & CH_3 \\ | & | \\ CH_3CH_2CHCH_2CHCH_3 & 6 \end{array}$

2,4-Dimethylhexane

(not 3,5-dimethylhexane)

6. If there are two or more different substituents, list them in alphabetical order, and number the chain from the end that gives the lower number to the substituent encountered first. If there are different substituents in equivalent positions on opposite ends of the parent chain, the substituent of lower alphabetical order is given the lower number:



7. The prefixes *di*, *tri*, *tetra*, and so on are not included in alphabetizing. Neither are the hyphenated prefixes *sec*- and *tert*-. "Iso," as in isopropyl, is included in alphabetizing. Alphabetize the names of the substituents first, and then insert the prefix. In the following example, the alphabetizing parts are ethyl and methyl, not ethyl and dimethyl:

CH₃ CH₂CH₃ CH₃CCH₂CHCH₂CH₃ ĊH₂

4-Ethyl-2,2-dimethylhexane (not 2,2-dimethyl-4-ethylhexane)

EXAMPLE 3.3

Write IUPAC names for these alkanes: (a) (b) (c) (d) (d)

SOLUTION





2-Methylbutane

4-lsopropyl-2-methylheptane



5-Ethyl-3-methyloctane



5-lsopropyl-3,6,8-trimethyldecane (not 6-isopropyl-3,5,8-trimethyldecane)

STRATEGY

First determine the root name of the alkane. Then name the substituents and place them in alphabetical order. Number the parent chain so as to give the lower number to the substituents encountered first. If substituents have equivalent positions, the lower number is assigned to the substituents with the lower alphabetical order.

See problems 3.24, 3.25, 3.28

PROBLEM 3.3

Write IUPAC names for these alkanes:



B. Common Names

In the older system of common nomenclature, the total number of carbon atoms in an alkane, regardless of their arrangement, determines the name. The first three alkanes are methane, ethane, and propane. All alkanes with the molecular formula C_4H_{10} are called butanes, all those with the molecular formula C_5H_{12} are called pentanes, and all those with the molecular formula C_6H_{14} are called hexanes. For alkanes beyond propane, *iso* indicates that one end of an otherwise unbranched chain terminates in a $(CH_3)_2CH$ —group. Following are examples of common names:



This system of common names has no good way of handling other branching patterns, so, for more complex alkanes, it is necessary to use the more flexible IUPAC system of nomenclature.

In this text, we concentrate on IUPAC names. However, we also use common names, especially when the common name is used almost exclusively in the everyday discussions of chemists and biochemists. When both IUPAC and common names are given in the text, we always give the IUPAC name first, followed by the common name in parentheses. In this way, you should have no doubt about which name is which.

C. Classification of Carbon and Hydrogen Atoms

We classify a carbon atom as primary (1°) , secondary (2°) , tertiary (3°) , or quaternary (4°) , depending on the number of carbon atoms bonded to it. A carbon bonded to one carbon atom is a primary carbon; a carbon bonded to two carbon atoms is a secondary carbon, and so forth. For example, propane contains two primary carbons and one secondary carbon, 2-methylpropane contains three primary carbons and one tertiary carbon, and 2,2,4-trimethylpentane contains five primary carbons, one secondary carbon, one tertiary carbon, and one quaternary carbon:



Similarly, hydrogens are also classified as primary, secondary, or tertiary, depending on the type of carbon to which each is bonded. Those bonded to a primary carbon are classified as primary hydrogens, those on a secondary carbon are secondary hydrogens, and those on a tertiary carbon are tertiary hydrogens.

EXAMPLE 3.4

Classify each carbon atom in the following compounds as 1°, 2°, 3°, or 4°.



STRATEGY

3.4

To classify carbons, determine whether each is bonded to 1 carbon (1°), 2 carbons (2°), 3 carbons (3°), or 4 carbons (4°).

PROBLEM 3.4

Classify each hydrogen atom in the following compounds as 1°, 2°, or 3°.



What Are Cycloalkanes?



See problems 3.26, 3.27

A hydrocarbon that contains carbon atoms joined to form a ring is called a *cyclic hydrocar*bon. When all carbons of the ring are saturated, we call the hydrocarbon a cycloalkane. Cycloalkane A saturated Cycloalkanes of ring sizes ranging from 3 to over 30 abound in nature, and, in principle, there is no limit to ring size. Five-membered (cyclopentane) and six-membered (cyclohex-

hydrocarbon that contains carbon atoms joined to form a ring.

Figure 3.3 shows the structural formulas of cyclobutane, cyclopentane, and cyclohexane. When writing structural formulas for cycloalkanes, chemists rarely show all carbons and hydrogens. Rather, they use line-angle formulas to represent cycloalkane rings. Each ring is represented by a regular polygon having the same number of sides as there are carbon atoms in the ring. For example, chemists represent cyclobutane by a square, cyclopentane by a pentagon, and cyclohexane by a hexagon.

ane) rings are especially abundant in nature and have received special attention.

 $H_2C - CH_2$ | | or $H_2C - CH_2$ H_9 $H_{2}C$ H_2C Cyclobutane Cyclohexane Cyclopentane

FIGURE 3.3 Examples of cycloalkanes. Cycloalkanes contain two fewer hydrogen atoms than an alkane with the same number of carbon atoms. For instance, compare the molecular formulas of cyclohexane (C_6H_{12}) and hexane (C_6H_{14}). The general formula of a cycloalkane is C_nH_{2n} .

To name a cycloalkane, prefix the name of the corresponding open-chain hydrocarbon with *cyclo*-, and name each substituent on the ring. If there is only one substituent, there is no need to give it a number. If there are two substituents, number the ring by beginning with the substituent of lower alphabetical order. If there are three or more substituents, number the ring so as to give them the lowest set of numbers, and then list the substituents in alphabetical order.

EXAMPLE 3.5

Write the molecular formula and IUPAC name for each cycloalkane.



STRATEGY

First determine the root name of the cycloalkane. Then name the substituents and place them in alphabetical order. Number the parent chain so as to give the lower number to the substituent encountered first. If substituents have equivalent positions, the lower number is assigned to the substituent with the lower alphabetical order.

SOLUTION

- (a) The molecular formula of this cycloalkane is C_8H_{16} . Because there is only one substituent on the ring, there is no need to number the atoms of the ring. The IUPAC name of this compound is isopropylcyclopentane.
- (b) Number the atoms of the cyclohexane ring by beginning with *tert*-butyl, the substituent of lower alphabetical order. The compound's name is 1-*tert*-butyl-4-methylcyclohexane, and its molecular formula is $C_{11}H_{22}$.
- (c) The molecular formula of this cycloalkane is $C_{13}H_{26}$. The compound's name is 1-ethyl-2-isopropyl-4-methylcycloheptane. The ethyl group is numbered 1 because this allows the isopropyl group to be encountered sooner than if the methyl group were numbered 1.
- (d) The molecular formula of this cycloalkane is $C_{10}H_{20}$. The compound's name is 2-*sec*-butyl-1,1-dimethylcyclobutane. This example illustrates that "*sec*" and "di" are not used in alphabetizing for nomenclature.

recall that *tert* is not considered when alphabetizing substituents

recall that "iso" is considered when alphabetizing substituents. The numbering pattern 1,2,4 is preferred over 1,3,4 or 1,5,7

See problems 3.24, 3.25, 3.28

$\mathbf{PROBLEM} \quad 3.5$

Write the molecular formula and IUPAC name for each cycloalkane:



3.5 What Is the IUPAC System of Nomenclature?

The naming of alkanes and cycloalkanes in Sections 3.3 and 3.4 illustrates the application of the IUPAC system of nomenclature to these two specific classes of organic compounds. Now let us describe the general approach of the IUPAC system. The name we give to any compound with a chain of carbon atoms consists of three parts: a prefix, an infix (a modifying element inserted into a word), and a suffix. Each part provides specific information about the structural formula of the compound.

- 1. The prefix shows the number of carbon atoms in the parent chain. Prefixes that show the presence of 1 to 20 carbon atoms in a chain were given in Table 3.2.
- 2. The infix shows the nature of the carbon–carbon bonds in the parent chain:

Infix	Nature of Carbon–Carbon Bonds in the Parent Chain	
-an-	all single bonds	keep in mind that
-en-	one or more double bonds	the infix refers to the nature of the <i>C</i> – <i>C</i>
-yn-	one or more triple bonds	bonds in the parent chain

3. The suffix shows the class of compound to which the substance belongs:

Suffix	Class of Compound		
-е	hydrocarbon	\leq	we will learn suffixes for other classes of compounds
-ol	alcohol		in later chapters
-al	aldehyde		
-one	ketone		
-oic acid	carboxylic acid		

EXAMPLE 3.6

Following are IUPAC names and structural formulas for four compounds:

(a) CH ₂ =CHCH ₃	(b) CH ₃ CH ₂ OH	(c) CH ₃ CH ₂ CH ₂ CH ₂ COH	(d) HC≡CH
Propene	Ethanol	Pentanoic acid	Ethyne

Divide each name into a prefix, an infix, and a suffix, and specify the information about the structural formula that is contained in each part of the name.

STRATEGY

First look at the first few letters of the name (meth, eth, prop, but, etc.). This is the prefix that tells the number of carbons in the parent chain. Next look at "an," "en," or "yn." These infixes indicate the nature of the carbon–carbon bonds in the parent chain. The letters that follow the infix are part of the suffix, which determines the class of compound to which the molecule belongs.

SOLUTION

```
a carbon-carbon double bond

(a) propene

a hydrocarbon

three carbon atoms
only carbon-carbon single bonds

(b) ethanol

an alcohol

two carbon atoms
```



Combine the proper prefix, infix, and suffix, and write the IUPAC name for each compound:

(a) CH_3CCH_3 (b) $CH_3CH_2CH_2CH_2CH$ (c) (d)

3.6 What Are the Conformations of Alkanes and Cycloalkanes?

Even though structural formulas are useful for showing the order of attachment of atoms, they do not show three-dimensional shapes. As chemists try to understand more and more about the relationships between structure and the chemical and physical properties of molecules, it becomes increasingly important to know more about the three-dimensional shapes of molecules.

In this section, we concentrate on ways to visualize molecules as three-dimensional objects and to visualize not only bond angles within molecules, but also distances between various atoms and groups of atoms not bonded to each other. We also describe strain, which we divide into three types: torsional strain, angle strain, and steric strain. We urge you to build models and to study and manipulate them. Organic molecules are three-dimensional objects, and it is essential that you become comfortable in dealing with them as such.

A. Alkanes

Alkanes with two or more carbons can be twisted into a number of different three-dimensional arrangements of their atoms by rotating about one or more carbon–carbon bonds. Any three-dimensional arrangement of atoms that results from rotation about a single bond is called a **conformation**. Figure 3.4(a) shows a ball-and-stick model of a **staggered conformation**



FIGURE 3.4

A staggered conformation of ethane. (a) Ball-and-stick model and (b) Newman projection.

Conformation Any threedimensional arrangement of atoms in a molecule that results by rotation about a single bond.

Staggered conformation

A conformation about a carbon–carbon single bond in which the atoms on one carbon are as far apart as possible from the atoms on the adjacent carbon.

Newman projection A way to view a molecule by looking along a carbon–carbon bond.

of ethane. In this conformation, the three C—H bonds on one carbon are as far apart as possible from the three C—H bonds on the adjacent carbon. Figure 3.4(b), called a **Newman projection**, is a shorthand way of representing the staggered conformation of ethane. In a Newman projection, we view a molecule along the axis of a C—C bond. The three atoms or groups of atoms nearer your eye appear on lines extending from the center of the circle at angles of 120°. The three atoms or groups of atoms on the carbon farther from your eye appear on lines extending from the circumference of the circle at angles of 120°. Remember that bond angles about each carbon in ethane are approximately 109.5° and not 120°, as this Newman projection might suggest.

Visualize and Draw a Newman Projection

A Newman projection is a two-dimensional drawing of a three-dimensional molecule viewed down a carbon-carbon bond. Here are some steps you can apply when drawing Newman projections of molecules:

 Select the C-C bond you wish to look down. Using butane as an example, let's select the C₂-C₃ bond.



 Draw in the hydrogens using dashed wedges to show bonds going behind the plane of the paper and solid wedges to show bonds coming out of the plane of the paper. Hydrogens and groups that are not attached to the bond we are looking down can be shown as condensed formulas.



3. Decide which direction to view the bond from. Here we view the bond from right to left. The





4. Place the atoms and groups in your Newman projection. You can reference the groups to the eye that you drew. Here, the red hydrogen is to the left of the eye and pointing diagonally upward and thus ends up on the bond pointing left and diagonally upward in the Newman projection. The rightmost methyl group is pointing down relative to the eye that we drew and is therefore drawn on the vertical bond in the Newman projection. In this way, you can accurately draw in the remaining atoms and groups. This molecule turns out to be in a staggered conformation.

Figure 3.5 shows a ball-and-stick model and a Newman projection of an **eclipsed conformation** of ethane. In this conformation, the three C—H bonds on one carbon are as close as possible to the three C—H bonds on the adjacent carbon. In other words, hydrogen atoms on the back carbon are eclipsed by the hydrogen atoms on the front carbon.

For a long time, chemists believed that rotation about the C — C single bond in ethane was completely free. Studies of ethane and other molecules, however, have shown that a potential energy difference exists between its staggered and eclipsed conformations and that rotation

Eclipsed conformation

A conformation about a carbon–carbon single bond in which the atoms on one carbon are as close as possible to the atoms on the adjacent carbon.





An eclipsed conformation of ethane. (a, b) Ball-and-stick models and (c) Newman projection.

Torsional strain (also

called eclipsed interaction strain) Strain that arises when atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation. is not completely free. In ethane, the potential energy of the eclipsed conformation is a maximum and that of the staggered conformation is a minimum. The difference in potential energy between these two conformations is approximately 12.6 kJ/mol (3.0 kcal/mol).

The strain induced in the eclipsed conformation of ethane is an example of torsional strain. **Torsional strain** (also called eclipsed interaction strain) is strain that arises when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation.

EXAMPLE 3.7

Draw Newman projections for one staggered conformation and one eclipsed conformation of propane.

STRATEGY

Draw the line-angle formula of propane and choose a bond along which to view for the Newman projection. Keep track of the carbons in the line-angle formula and in the Newman projection (numbering them helps). Draw the staggered and eclipsed Newman projections and complete them by adding in the carbons and hydrogens.

SOLUTION

Following are Newman projections and ball-and-stick models of these conformations:



Draw Newman projections for two staggered and two eclipsed conformations of 1,2-dichloroethane.

B. Cycloalkanes

We limit our discussion to the conformations of cyclopentanes and cyclohexanes because these are the most common carbon rings in the molecules of nature.

Cyclopentane

We can draw cyclopentane [Figure 3.6(a)] as a planar conformation with all C-C-C bond angles equal to 108° [Figure 3.6(b)]. This angle differs only slightly from the tetrahedral

3.6 What Are the Conformations of Alkanes and Cycloalkanes?



Puckered envelope conformation

angle of 109.5°; consequently, there is little angle strain in the planar conformation of cyclopentane. Angle strain results when a bond angle in a molecule is either expanded or compressed compared with its optimal values. There are 10 fully eclipsed C—H bonds creating a torsional strain of approximately 42 kJ/mol (10 kcal/mol). To relieve at least a part of this strain, the atoms of the ring twist into the "envelope" conformation [Figure 3.6(c)]. In this conformation, four carbon atoms are in a plane, and the fifth is bent out of the plane, rather like an envelope with its flap bent upward.

In the envelope conformation, the number of eclipsed hydrogen interactions is reduced, thereby decreasing torsional strain. The C-C-C bond angles, however, are also reduced, which increases angle strain. The observed C-C-C bond angles in cyclopentane are 105°, indicating that, in its conformation of lowest energy, cyclopentane is slightly puckered. The strain energy in cyclopentane is approximately 23.4 kJ/mol (5.6 kcal/mol).

Cyclohexane

Cyclohexane adopts a number of puckered conformations, the most stable of which is a chair conformation. In this conformation (Figure 3.7), all C-C-C bond angles are 109.5° (minimizing angle strain), and hydrogens on adjacent carbons are staggered with respect to one another (minimizing torsional strain). Thus, there is very little strain in a chair conformation of cyclohexane.

In a chair conformation, the C—H bonds are arranged in two different orientations. Six C—H bonds are called **equatorial bonds**, and the other six are called **axial bonds**. One way to visualize the difference between these two types of bonds is to imagine an axis through the center of the chair, perpendicular to the floor [Figure 3.8(a)]. Equatorial bonds are approximately perpendicular to our imaginary axis and alternate first slightly up and then slightly down as you move from one carbon of the ring to the next. Axial bonds are parallel to the imaginary axis. Three axial bonds point up; the other three point down. Notice that axial bonds alternate also, first up and then down as you move from one carbon of the ring to the next. Notice further that if the axial bond on a carbon points upward, then the equatorial bond on that carbon points slightly downward. Conversely, if the axial bond on a particular carbon points downward, then the equatorial bond on that carbon points slightly upward.



FIGURE 3.6

Cyclopentane. (a) Structural formula. (b) In the planar conformation, there are 10 pairs of eclipsed C-H interactions. (c) The most stable conformation is a puckered "envelope" conformation.

Angle strain The strain that arises when a bond angle is either compressed or expanded compared with its optimal value.

Chair conformation The most stable puckered conformation of a cyclohexane ring; all bond angles are approximately 109.5°, and bonds to all adjacent carbons are staggered.

Equatorial bond A bond on a chair conformation of a cyclohexane ring that extends from the ring roughly perpendicular to the imaginary axis of the ring.

Axial bond A bond on a chair conformation of a cyclohexane ring that extends from the ring parallel to the imaginary axis of the ring.

FIGURE 3.7 Cyclohexane. The most stable conformation is the puckered "chair" conformation.

Skeletal model

Η

Ball-and-stick model viewed from the side

Ball-and-stick model viewed from above



Axis through the

(a) Ball-and-stick model showing all 12 hydrogens (b) The six equatorial C—H bonds shown in red



(c) The six axial C—H bonds shown in blue

FIGURE 3.8

Chair conformation of cyclohexane, showing axial and equatorial C-H bonds.

Н





There are many other nonplanar conformations of cyclohexane, one of which is the **boat conformation**. You can visualize the interconversion of a chair conformation to a boat conformation by twisting the ring as illustrated in Figure 3.9. A boat conformation is considerably less stable than a chair conformation. In a boat conformation, torsional strain is created by four sets of eclipsed hydrogen interactions, and steric strain is created by the one set of flagpole interactions. **Steric strain** (also called nonbonded interaction strain) results when nonbonded atoms separated by four or more bonds are forced abnormally close to each other—that is, when they are forced closer than their atomic (contact) radii allow. The difference in potential energy between chair and boat conformations is approximately 27 kJ/mol (6.5 kcal/mol), which means that, at room temperature, approximately 99.99% of all cyclohexane molecules are in the chair conformation.

FIGURE 3.9

Conversion of (a) a chair conformation to (b) a boat conformation. In the boat conformation, there is torsional strain due to the four sets of eclipsed hydrogen interactions and steric strain due to the one set of flagpole interactions. A chair conformation is more stable than a boat conformation.

Boat conformation A

puckered conformation of a cyclohexane ring in which carbons 1 and 4 of the ring are bent toward each other.

Steric strain The strain that arises when atoms separated by four or more bonds are forced abnormally close to one another.

EXAMPLE 3.8

Following is a chair conformation of cyclohexane showing a methyl group and one hydrogen:



- (a) Indicate by a label whether each group is equatorial or axial.
- (b) Draw the other chair conformation, and again label each group as equatorial or axial.

STRATEGY

A chair-to-chair interconversion is most often done by changing the orientation of the rightmost and leftmost carbons in

PROBLEM 3.8

Following is a chair conformation of cyclohexane with carbon atoms numbered 1 through 6:



the chair conformation of cyclohexane. Remember that after such an interconversion, all prior axial substituents become equatorial and all prior equatorial substituents become axial.

SOLUTION



- (a) Draw hydrogen atoms that are above the plane of the ring on carbons 1 and 2 and below the plane of the ring on carbon 4.
- (b) Which of these hydrogens are equatorial? Which are axial?
- (c) Draw the other chair conformation. Now which hydrogens are equatorial? Which are axial? Which are above the plane of the ring, and which are below it?



FIGURE 3.10

Interconversion of chair cyclohexanes. All C-H bonds that are equatorial in one chair are axial in the alternative chair, and vice versa.

For cyclohexane, the two equivalent chair conformations can interconvert by one chair twisting first into a boat and then into the other chair. When one chair is converted to the other, a change occurs in the relative orientations in space of the hydrogen atoms bonded to each carbon: All hydrogen atoms equatorial in one chair become axial in the other, and vice versa (Figure 3.10). The interconversion of one chair conformation of cyclohexane to the other occurs rapidly at room temperature.

If we replace a hydrogen atom of cyclohexane by an alkyl group, the group occupies an equatorial position in one chair and an axial position in the other chair. This means that the two chairs are no longer equivalent and no longer of equal stability.

A convenient way to describe the relative stabilities of chair conformations with equatorial or axial substituents is in terms of a type of steric strain called **axial-axial (diaxial)** interaction. *Axial-axial interaction* refers to the steric strain existing between an axial substituent and an axial hydrogen (or other group) on the same side of the ring. Consider methylcyclohexane (Figure 3.11). When the $-CH_3$ is equatorial, it is staggered with respect to all other groups on its adjacent carbon atoms. When the $-CH_3$ is axial, it is parallel to the axial C—H bonds on carbons 3 and 5. Thus, for axial methylcyclohexane, there are two unfavorable methyl-hydrogen axial-axial interactions. For methylcyclohexane, the equatorial methyl conformation is favored over the axial methyl conformation by approximately 7.28 kJ/mol (1.74 kcal/mol). At equilibrium at room temperature, approximately 95% of all methylcyclohexane molecules have their methyl group equatorial, and less than 5% have their methyl group axial.



Diaxial interactions

Interactions between groups in parallel axial positions on the same side of a chair conformation of a cyclohexane ring. As the size of the substituent increases, the relative amount of the conformation with the group equatorial increases. When the group is as large as *tert*-butyl, the equatorial conformation is approximately 4,000 times more abundant at room temperature than the axial conformation, and, in effect, the ring is "locked" into a chair conformation with the *tert*-butyl group equatorial.

EXAMPLE 3.9

Label all axial-axial interactions in the following chair conformation:



STRATEGY

Find each axial group. Those on the same side of the chair conformation (either above or below the ring) will participate in axial-axial interactions. Remember that the equatorial substituents do not participate in axial-axial interactions.

SOLUTION

There are four axial-axial interactions: Each axial methyl group has two sets of axial-axial interactions with parallel hydrogen atoms on the same side of the ring. The equatorial methyl group has no axial-axial interactions.



PROBLEM 3.9

The conformational equilibria for methyl-, ethyl-, and isopropylcyclohexane are all about 95% in favor of the equatorial conformation, but the conformational equilibrium for *tert*-butylcyclohexane is almost completely on the equatorial side. Explain why the conformational equilibria for the first three compounds are comparable, but that for *tert*-butylcyclohexane lies considerably farther toward the equatorial conformation.



What Is Cis-Trans Isomerism in Cycloalkanes?

Cycloalkanes with substituents on two or more carbons of the ring show a type of isomerism called *cis-trans* isomerism. *Cis-trans* isomers have (1) the same molecular formula, (2) the same order of attachment of atoms, and (3) an arrangement of atoms that cannot be interchanged by rotation about sigma bonds under ordinary conditions. By way of comparison,

Cis-trans isomers Isomers that have the same order of attachment of their atoms, but a different arrangement of their atoms in space, due to the presence of either a ring or a carbon-carbon double bond.

hemical Connections 3A

THE POISONOUS PUFFER FISH

Nature is by no means limited to carbon in sixmembered rings. Tetrodotoxin, one of the most potent toxins known, is composed of a set of interconnected six-membered rings, each in a chair conformation. All but one of these rings have atoms other than carbon in them. Tetrodotoxin is produced in the liver and





A puffer fish inflated.

ovaries of many species of *Tetraodontidae*, especially the puffer fish, so called because it inflates itself to an almost spherical spiny ball when alarmed. The puffer is evidently a species that is highly preoccupied with defense, but the Japanese are not put off. They regard the puffer, called *fugu* in Japanese, as a delicacy. To serve it in a public restaurant, a chef must be registered as sufficiently skilled in removing the toxic organs so as to make the flesh safe to eat.

Symptoms of tetrodotoxin poisoning begin with attacks of severe weakness, progressing to complete paralysis and eventual death. Tetrodotoxin exerts its severe poisonous effect by blocking Na⁺ ion channels in excitable membranes. The =NH₂⁺ end of tetrodotoxin lodges in the mouth of a Na⁺ ion channel, thus blocking further transport of Na⁺ ions through the channel.

Questions

How many chair conformations are present in tetrodotoxin? Which substituents in tetrodotoxin are involved in axial-axial interactions?



Cis A prefix meaning "on the same side."

Trans A prefix meaning "across from."

the potential energy difference between conformations is so small that they can be interconverted easily at or near room temperature by rotation about single bonds, while *cis*-*trans* isomers can only be interconverted at extremely high temperatures or not at all.

We can illustrate *cis–trans* isomerism in cycloalkanes using 1,2-dimethylcyclopentane as an example. In the following structural formula, the cyclopentane ring is drawn as a planar pentagon viewed edge on (in determining the number of *cis–trans* isomers in a substituted cycloalkane, it is adequate to draw the cycloalkane ring as a planar polygon):



Carbon–carbon bonds of the ring that project forward are shown as heavy lines. When viewed from this perspective, substituents bonded to the cyclopentane ring project above and below the plane of the ring. In one isomer of 1,2-dimethylcyclopentane, the methyl groups are on the same side of the ring (either both above or both below the plane of the ring); in the other isomer, they are on opposite sides of the ring (one above and one below the plane of the ring).

Alternatively, the cyclopentane ring can be viewed from above, with the ring in the plane of the paper. Substituents on the ring then either project toward you (that is, they project up above the page) and are shown by solid wedges, or they project away from you (they project down below the page) and are shown by broken wedges. In the following structural formulas, only the two methyl groups are shown (hydrogen atoms of the ring are not shown):



EXAMPLE 3.10

Which cycloalkanes show *cis-trans* isomerism? For each that does, draw both isomers.(a) Methylcyclopentane(b) 1,1-Dimethylcyclobutane(c) 1,3-Dimethylcyclobutane

STRATEGY

In order to exhibit *cis-trans* isomerism, a cyclic compound must have at least two substituents on the ring and there must be two possible arrangements (*cis* and *trans*) for any pair of substituents.

SOLUTION

- (a) Methylcyclopentane does not show *cis-trans* isomerism: It has only one substituent on the ring.
- (b) 1,1-Dimethylcyclobutane does not show *cis-trans* isomerism: Only one arrangement is possible for the two methyl groups on the ring, and they must be *trans*.
- (c) 1,3-Dimethylcyclobutane shows *cis-trans* isomerism. Note that, in these structural formulas, we show only the hydrogens on carbons bearing the methyl groups.



Which cycloalkanes show *cis-trans* isomerism? For each that does, draw both isomers.

(a) 1,3-Dimethylcyclopentane (b) Ethylcyclopentane (c) 1-Ethyl-2-methylcyclobutane

Two *cis–trans* isomers exist for 1,4-dimethylcyclohexane. For the purposes of determining the number of *cis–trans* isomers in substituted cycloalkanes, it is adequate to draw the cycloalkane ring as a planar polygon, as is done in the following disubstituted cyclohexanes:



We can also draw the *cis* and *trans* isomers of 1,4-dimethylcyclohexane as nonplanar chair conformations. In working with alternative chair conformations, it is helpful to remember that all groups axial on one chair are equatorial in the alternative chair, and vice versa. In one chair conformation of *trans*-1,4-dimethylcyclohexane, the two methyl groups are axial; in the alternative chair conformation, they are equatorial. Of these chair conformations, the one with both methyls equatorial is considerably more stable.



The alternative chair conformations of *cis*-1,4-dimethylcyclohexane are of equal energy. In each chair conformation, one methyl group is equatorial and the other is axial.



EXAMPLE 3.11

Following is a chair conformation of 1,3-dimethylcyclohexane:



- (a) Is this a chair conformation of cis-1,3-dimethylcyclohexane or of trans-1,3-dimethylcyclohexane?
- (b) Draw the alternative chair conformation. Of the two chair conformations, which is the more stable?
- (c) Draw a planar hexagon representation of the isomer shown in this example.

STRATEGY

Determine whether substituents are on the same or different sides of the ring to determine *cis* or *trans*. To perform a chairto-chair interconversion, change the orientation of the rightmost and leftmost carbons in the chair conformation of cyclohexane. Remember that after such an interconversion, all prior axial substituents become equatorial and all prior equatorial substituents become axial. When converting to planar representations of cyclohexane, show substituents above the ring as coming out of the page (wedges) and those below the ring as going behind the page (dashes).

SOLUTION

(a) The isomer shown is *cis*-1,3-dimethylcyclohexane; the two methyl groups are on the same side of the ring.



Following is a planar hexagon representation of one isomer of 1,2,4-trimethylcyclohexane. Draw the alternative chair conformations of this compound, and state which is the more stable.



3.8 What Are the Physical Properties of Alkanes and Cycloalkanes?

The most important property of alkanes and cycloalkanes is their almost complete lack of polarity. As we saw in Section 1.2C, the difference in electronegativity between carbon and hydrogen is 2.5 - 2.1 = 0.4 on the Pauling scale, and given this small difference, we classify a C—H bond as nonpolar covalent. Therefore, alkanes are nonpolar compounds, and there are only weak interactions between their molecules.



Pentane and cyclohexane. The electron density models show no evidence of any polarity in alkanes and cycloalkanes.

A. Boiling Points

The boiling points of alkanes are lower than those of almost any other type of compound with the same molecular weight. In general, both boiling and melting points of alkanes increase with increasing molecular weight (Table 3.4).

Alkanes containing 1 to 4 carbons are gases at room temperature, and those containing 5 to 17 carbons are colorless liquids. High-molecular-weight alkanes (those with 18 or more carbons) are white, waxy solids. Several plant waxes are high-molecular-weight alkanes. The wax found in apple skins, for example, is an unbranched alkane with the molecular formula $C_{27}H_{56}$. Paraffin wax, a mixture of high-molecular-weight alkanes, is used for wax candles, in lubricants, and to seal home-canned jams, jellies, and other preserves. Petrolatum, so named because it is derived from petroleum refining, is a liquid mixture of high-molecular-weight alkanes. Sold as mineral oil and Vaseline, petrolatum is used as an ointment base in pharmaceuticals and cosmetics and as a lubricant and rust preventative.

B. Dispersion Forces and Interactions between Alkane Molecules

Methane is a gas at room temperature and atmospheric pressure. It can be converted to a liquid if cooled to -164 °C and to a solid if further cooled to -182 °C. The fact that methane (or any other compound, for that matter) can exist as a liquid or a solid depends on the existence of forces of attraction between particles of the pure compound. Although the

TABLE 3.4 Physical Properties of Some Unbranched Alkanes				
Name	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)	*Density of Liquid (g/mL at 0 °C)
methane	CH_4	-182	-164	(a gas)
ethane	CH_3CH_3	-183	-88	(a gas)
propane	$CH_3CH_2CH_3$	-190	-42	(a gas)
butane	$CH_3(CH_2)_2CH_3$	-138	0	(a gas)
pentane	$CH_3(CH_2)_3CH_3$	-130	36	0.626
hexane	$CH_3(CH_2)_4CH_3$	-95	69	0.659
heptane	$CH_3(CH_2)_5CH_3$	-90	98	0.684
octane	$CH_3(CH_2)_6CH_3$	-57	126	0.703
nonane	$CH_3(CH_2)_7CH_3$	-51	151	0.718
decane	$CH_3(CH_2)_8CH_3$	-30	174	0.730
*For compariso	n, the density of H_2O is 1 g/	mL at 4 °C.	·	





Dispersion forces. (a) The average distribution of electron density in a methane molecule is symmetrical, and there is no polarity. (b) Temporary polarization of one molecule induces temporary polarization in an adjacent molecule. Electrostatic attractions between temporary partial positive and partial negative charges are called *dispersion forces*.

forces of attraction between particles are all electrostatic in nature, they vary widely in their relative strengths. The strongest attractive forces are between ions—for example, between Na⁺ and Cl⁻ in NaCl (787 kJ/mol, 188 kcal/mol). Hydrogen bonding is a weaker attractive force (8–42 kJ/mol, 2–10 kcal/mol). We will have more to say about hydrogen bonding in Chapter 8 when we discuss the physical properties of alcohols—compounds containing polar O—H groups.

Dispersion forces (0.08-8 kJ/mol, 0.02-2 kcal/mol) are the weakest intermolecular attractive forces. It is the existence of dispersion forces that accounts for the fact that low-molecular-weight, nonpolar substances such as methane can be liquefied. When we convert methane from a liquid to a gas at -164 °C, for example, the process of separating its molecules requires only enough energy to overcome the very weak dispersion forces.

To visualize the origin of dispersion forces, it is necessary to think in terms of instantaneous distributions of electron density rather than average distributions. Over time, the distribution of electron density in a methane molecule is symmetrical [Figure 3.12(a)], and there is no separation of charge. However, at any instant, there is a nonzero probability that the electron density is polarized (shifted) more toward one part of a methane molecule than toward another. This temporary polarization creates temporary partial positive and partial negative charges, which in turn induce temporary partial positive and negative charges in adjacent methane molecules [Figure 3.12(b)]. **Dispersion forces** are weak electrostatic attractive forces that occur between temporary partial positive and partial negative charges in adjacent atoms or molecules.

Because interactions between alkane molecules consist only of these very weak dispersion forces, the boiling points of alkanes are lower than those of almost any other type of compound with the same molecular weight. As the number of atoms and the molecular weight of an alkane increase, the strength of the dispersion forces among alkane molecules increases, and consequently, boiling points increase.

C. Melting Point and Density

The melting points of alkanes increase with increasing molecular weight. The increase, however, is not as regular as that observed for boiling points, because the ability of molecules to pack into ordered patterns of solids changes as the molecular size and shape change.

The average density of the alkanes listed in Table 3.4 is about 0.7 g/mL; that of highermolecular-weight alkanes is about 0.8 g/mL. All liquid and solid alkanes are less dense than water (1.0 g/mL); therefore, they float on water.

D. Constitutional Isomers Have Different Physical Properties

Alkanes that are constitutional isomers are different compounds and have different physical properties. Table 3.5 lists the boiling points, melting points, and densities of the five constitutional isomers with the molecular formula C_6H_{14} . The boiling point of

Dispersion forces Very weak intermolecular forces of attraction resulting from the interaction of temporary induced dipoles.





TABLE 3.5 Physical Properties of the Isomeric Alkanes with the Molecular Formula C₆H₁₄

Name	Melting Point (°C)	Boiling Point (°C)	Density (g/mL)
hexane	-95	69	0.659
3-methylpentane	-118	64	0.664
2-methylpentane	-154	62	0.653
2,3-dimethylbutane	-129	58	0.662
2,2-dimethylbutane	-100	50	0.649

2,2-Dimethylbutane

each of its branched-chain isomers is lower than that of hexane itself, and the more branching there is, the lower is the boiling point. These differences in boiling points are related to molecular shape in the following way: The only forces of attraction between alkane molecules are dispersion forces. As branching increases, the shape of an alkane molecule becomes more compact, and its surface area decreases. As the surface area decreases, the strength of the dispersion forces decreases, and boiling points decrease. Thus, for any group of alkane constitutional isomers, it is usually observed that the least-branched isomer has the highest boiling point and the most-branched isomer has the lowest boiling point. The trend in melting points is less obvious, but as previously mentioned, it correlates with a molecule's ability to pack into ordered patterns of solids.

EXAMPLE 3.12

Arrange the alkanes in each set in order of increasing boiling point:(a) Butane, decane, and hexane(b) 2-Methylheptane, octane, and 2,2,4-trimethylpentane

STRATEGY

When determining relative boiling points, remember that as the number of carbon atoms in the chain increases, the dispersion forces among molecules increase and the boiling points increase. Boiling point is also dependent on the degree of branching. For constitutional isomers, the most highly branched isomer has the smallest surface area and the lowest boiling point.

SOLUTION

(a) All of the compounds are unbranched alkanes. As the number of carbon atoms in the chain increases, the dispersion forces among molecules increase, and the boiling points increase. Decane has the highest boiling point, butane the lowest:



in unbranched hydrocarbons, the longer the chain length, the higher is the surface area. This results in an increase in the dispersion forces and an increase in boiling point

(b) These three alkanes are constitutional isomers with the molecular formula C₈H₁₈. Their relative boiling points depend on the degree of branching. 2,2,4-Trimethylpentane, the most highly branched isomer, has the smallest surface area and the lowest boiling point. Octane, the unbranched isomer, has the largest surface area and the highest boiling point.



(a) 2-Methylbutane, 2,2-dimethylpropane, and pentane

(b) 3,3-Dimethylheptane, 2,2,4-trimethylhexane, and nonane

3.9 What Are the Characteristic Reactions of Alkanes?

The most important chemical property of alkanes and cycloalkanes is their inertness. They are quite unreactive toward most reagents, a behavior consistent with the fact that they are nonpolar compounds containing only strong sigma bonds. Under certain conditions, however, alkanes and cycloalkanes do react, with oxygen, O_2 . By far their most important reaction with oxygen is oxidation (combustion) to form carbon dioxide and water. The oxidation of saturated hydrocarbons is the basis for their use as energy sources for heat [natural gas, liquefied petroleum gas (LPG), and fuel oil] and power (gasoline, diesel fuel, and aviation fuel). Following are balanced equations for the complete combustion of methane, the major component of natural gas, and for propane, the major component of LPG:

when balancing equations for combustion reactions of hydrocarbons, first balance the number of carbons, next balance the number of hydrogens, then balance the number of oxygens. If the equation is still not balanced, consider doubling all coefficients on each side of the equation arrow

 $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $\Delta H^\circ = -886 \text{ kJ/mol}(-212 \text{ kcal/mol})$ Methane

 $CH_3CH_2CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O \quad \Delta H^\circ = -2,220 \text{ kJ/mol}(-530 \text{ kcal/mol})$ Propane

3.10 What Are the Sources of Alkanes?

The three major sources of alkanes throughout the world are the fossil fuels: natural gas, petroleum, and coal. Fossil fuels account for approximately 90% of the total energy consumed in the United States. Nuclear electric power and hydroelectric power make up most of the remaining 10%. In addition, fossil fuels provide the bulk of the raw material for the organic chemicals consumed worldwide.

A. Natural Gas

Natural gas consists of approximately 90–95% methane, 5–10% ethane, and a mixture of other relatively low-boiling alkanes—chiefly propane, butane, and 2-methylpropane. The current widespread use of ethylene as the organic chemical industry's most important building block is largely the result of the ease with which ethane can be separated from natural gas and cracked into ethylene. Cracking is a process whereby a saturated hydrocarbon is converted into an unsaturated hydrocarbon plus H_2 . Heating it in a furnace at 800 to 900 °C for a fraction of a second cracks ethane. The global production of ethylene in 2010 was 123 billion kg (271 billion pounds), making it the number-one organic compound produced, on a weight basis. The bulk of the ethylene produced is used to create organic polymers, as described in Chapter 16.

$$CH_3CH_3 \xrightarrow{800-900\,^{\circ}C} CH_2 = CH_2 + H_2$$

Ethane Ethylene

B. Petroleum

Petroleum is a thick, viscous liquid mixture of literally thousands of compounds, most of them hydrocarbons, formed from the decomposition of marine plants and animals. Petroleum and petroleum-derived products fuel automobiles, aircraft, and trains. They provide most of the greases and lubricants required for the machinery of our highly industrialized society. Furthermore, petroleum, along with natural gas, provides close to 90% of the organic raw materials used in the synthesis and manufacture of synthetic fibers, plastics, detergents, drugs, dyes, and a multitude of other products.

It is the task of a petroleum refinery to produce usable products, with a minimum of waste, from the thousands of different hydrocarbons in this liquid mixture. The various physical and chemical processes for this purpose fall into two broad categories: separation processes, which separate the complex mixture into various fractions, and re-forming processes, which alter the molecular structure of the hydrocarbon components themselves.

The fundamental separation process utilized in refining petroleum is fractional distillation (Figure 3.13). Practically all crude oil that enters a refinery goes to distillation units,





A petroleum refinery.

Fractional distillation of petroleum. The lighter, more volatile fractions are removed from higher up the column and the heavier, less volatile fractions from lower down. where it is heated to temperatures as high as 370 to 425 °C and separated into fractions. Each fraction contains a mixture of hydrocarbons that boils within a particular range:

- Gases boiling below 20 °C are taken off at the top of the distillation column. This fraction is a mixture of low-molecular-weight hydrocarbons, predominantly propane, butane, and 2-methylpropane, substances that can be liquefied under pressure at room temperature. The liquefied mixture, known as liquefied petroleum gas (LPG), can be stored and shipped in metal tanks and is a convenient source of gaseous fuel for home heating and cooking.
- 2. Naphthas, bp 20 to 200 °C, are a mixture of C_5 to C_{12} alkanes and cycloalkanes. Naphthas also contain small amounts of benzene, toluene, xylene, and other aromatic hydrocarbons (Chapter 9). The light naphtha fraction, bp 20 to 150 °C, is the source of straight-run gasoline and averages approximately 25% of crude petroleum. In a sense, naphthas are the most valuable distillation fractions, because they are useful not only as fuel, but also as sources of raw materials for the organic chemical industry.
- **3.** Kerosene, bp 175 to 275 °C, is a mixture of C_9 to C_{15} hydrocarbons.
- 4. Fuel oil, bp 250 to 400 °C, is a mixture of C_{15} to C_{18} hydrocarbons. Diesel fuel is obtained from this fraction.
- 5. Lubricating oil and heavy fuel oil distill from the column at temperatures above 350 °C.
- **6.** Asphalt is the black, tarry residue remaining after the removal of the other volatile fractions.

The two most common re-forming processes are cracking, illustrated by the thermal conversion of ethane to ethylene (Section 3.10A), and catalytic re-forming, illustrated by the conversion of hexane first to cyclohexane and then to benzene:



C. Coal

To understand how coal can be used as a raw material for the production of organic compounds, it is necessary to discuss synthesis gas. Synthesis gas is a mixture of carbon monoxide and hydrogen in varying proportions, depending on the means by which it is manufactured. Synthesis gas is prepared by passing steam over coal. It is also prepared by the partial oxidation of methane by oxygen.

$$C + H_2O \xrightarrow{heat} CO + H_2$$
Coal
$$CH_4 + \frac{1}{2}O_2 \xrightarrow{catalyst} CO + 2H_2$$
Methane

Two important organic compounds produced today almost exclusively from carbon monoxide and hydrogen are methanol and acetic acid. In the production of methanol, the ratio of carbon monoxide to hydrogen is adjusted to 1:2, and the mixture is passed over a catalyst at elevated temperature and pressure:

$$CO + 2H_2 \xrightarrow{\text{catalyst}} CH_3OH$$

Methanol

The treatment of methanol, in turn, with carbon monoxide over a different catalyst gives acetic acid:

$$\begin{array}{c} & & & \\ & & & \\ &$$

Because the processes for making methanol and acetic acid directly from carbon monoxide are commercially proven, it is likely that the decades ahead will see the development of routes to other organic chemicals from coal via methanol.

Chemical Connections 3B

OCTANE RATING: WHAT THOSE NUMBERS AT THE PUMP MEAN

Gasoline is a complex mixture of C_6 to C_{12} hydrocarbons. The quality of gasoline as a fuel for internal combustion engines is expressed in terms of an *octane rating*. Engine knocking occurs when a portion of the air-fuel mixture explodes prematurely (usually as a result of heat developed during compression) and independently of ignition by the spark plug. Two compounds were selected as reference fuels. One of these, 2,2,4-trimethylpentane (isooctane), has very good antiknock properties (the fuel-air mixture burns smoothly in the combustion chamber) and was assigned an octane rating of 100. (The name *isooctane* is a trivial name; its only relation to the name



Typical octane ratings of commonly available gasolines.

2,2,4-trimethylpentane is that both names show eight carbon atoms.) Heptane, the other reference compound, has poor antiknock properties and was assigned an octane rating of 0.



2,2,4-Trimethylpentane (octane rating 100)

Heptane (octane rating 0)

The octane rating of a particular gasoline is that percentage of isooctane in a mixture of isooctane and heptane that has antiknock properties equivalent to those of the gasoline. For example, the antiknock properties of 2-methylhexane are the same as those of a mixture of 42% isooctane and 58% heptane; therefore, the octane rating of 2-methylhexane is 42. Octane itself has an octane rating of -20, which means that it produces even more engine knocking than heptane. Ethanol, the additive to gasohol, has an octane rating of 105. Benzene and toluene have octane ratings of 106 and 120, respectively.

Question

Which would you expect to have a higher boiling point, octane or isooctane (2,2,4-trimethylpentane)?

SUMMARY OF KEY QUESTIONS

3.1 What Are Alkanes?

• A hydrocarbon is a compound that contains only carbon and hydrogen. An alkane is a saturated hydrocarbon and

contains only single bonds. Alkanes have the general formula $C_n H_{2n+2}$.

3.2 What Is Constitutional Isomerism in Alkanes?

• **Constitutional isomers** have the same molecular formula but a different connectivity (a different order of attachment) of their atoms.

3.3 How Do We Name Alkanes?

- Alkanes are named according to a set of rules developed by the International Union of Pure and Applied Chemistry (IUPAC).
- A carbon atom is classified as primary (1°), secondary (2°), tertiary (3°), or quaternary (4°), depending on the number of carbon atoms bonded to it.

3.4 What Are Cycloalkanes?

- A **cycloalkane** is an alkane that contains carbon atoms bonded to form a ring.
- To name a cycloalkane, prefix the name of the open-chain hydrocarbon with "cyclo."

3.5 What Is the IUPAC System of Nomenclature?

- The IUPAC system is a general system of nomenclature. The IUPAC name of a compound consists of three parts:
 - (1) A **prefix** that indicates the number of carbon atoms in the **parent chain**,
 - (2) An **infix** that indicates the nature of the carboncarbon bonds in the parent chain, and
 - (3) A **suffix** that indicates the class to which the compound belongs.

3.6 What Are the Conformations of Alkanes and Cycloalkanes?

- A conformation is any three-dimensional arrangement of the atoms of a molecule that results from rotation about a single bond.
- One convention for showing conformations is the Newman projection. Staggered conformations are lower in energy (more stable) than eclipsed conformations.
- There are three types of molecular strain:

Torsional strain (also called **eclipsed interaction strain**) that results when nonbonded atoms separated by three bonds are forced from a staggered conformation to an eclipsed conformation

Angle strain that results when a bond angle in a molecule is either expanded or compressed compared with its optimal values, and

Steric strain (also called nonbonded interaction strain) that results when nonbonded atoms separated

3.7 What Is *Cis–Trans* Isomerism in Cycloalkanes?

• *Cis-trans* isomers have the same molecular formula and the same order of attachment of atoms, but arrangements of atoms in space that cannot be interconverted by rotation about single bonds. *Cis* means that substituents are

- A hydrogen atom is classified as primary (1°), secondary (2°), or tertiary (3°), depending on the type of carbon to which it is bonded.
- Five-membered rings (cyclopentanes) and six-membered rings (cyclohexanes) are especially abundant in the biological world.
- **Substituents** derived from alkanes by the removal of a hydrogen atom are called **alkyl groups** and are given the symbol **R**. The name of an alkyl group is formed by dropping the suffix -ane from the name of the parent alkane and adding -yl in its place.

by four or more bonds are forced abnormally close to each other—that is, when they are forced closer than their **atomic (contact) radii** would otherwise allow.

 Cyclopentanes, cyclohexanes, and all larger cycloalkanes exist in dynamic equilibrium between a set of puckered conformations. The lowest energy conformation of cyclopentane is an envelope conformation. The lowest energy conformations of cyclohexane are two interconvertible chair conformations. In a chair conformation, six bonds are axial and six are equatorial. Bonds axial in one chair are equatorial in the alternative chair, and vice versa. A boat conformation is higher in energy than chair conformations. The more stable conformation of a substituted cyclohexane is the one that minimizes axial-axial interactions.

on the same side of the ring; *trans* means that they are on opposite sides of the ring. Most cycloalkanes with substituents on two or more carbons of the ring show *cis-trans* isomerism.

3.8 What Are the Physical Properties of Alkanes and Cycloalkanes?

- Alkanes are nonpolar compounds, and the only forces of attraction between their molecules are dispersion forces, which are weak electrostatic interactions between temporary partial positive and negative charges of atoms or molecules. Low-molecular-weight alkanes, such as methane, ethane, and propane, are gases at room temperature and atmospheric pressure.
- Higher-molecular-weight alkanes, such as those in gasoline and **kerosene**, are liquids.

3.9 What Are the Characteristic Reactions of Alkanes?

• The most important chemical property of alkanes and cycloalkanes is their inertness. Because they are nonpolar compounds containing only strong sigma bonds, they are quite unreactive toward most reagents.

3.10 What Are the Sources of Alkanes?

- Natural gas consists of 90–95% methane with lesser amounts of ethane and other lower-molecular-weight hydrocarbons.
- **Petroleum** is a liquid mixture of literally thousands of different hydrocarbons.

- Very high-molecular-weight alkanes, such as those in **paraffin wax**, are solids.
- Among a set of alkane constitutional isomers, the least branched isomer generally has the highest boiling point; the most branched isomer generally has the lowest boiling point.
- By far, their most important reaction is combustion to form carbon dioxide and water. The oxidation of saturated hydrocarbons is the basis for their use as energy sources for heat and power.
- Synthesis gas, a mixture of carbon monoxide and hydrogen, can be derived from natural gas and coal.

QUICK QUIZ

Answer true or false to the following questions to assess your general knowledge of the concepts in this chapter. If you have difficulty with any of them, you should review the appropriate section in the chapter (shown in parentheses) before attempting the more challenging end-of-chapter problems.

- 1. Combustion of alkanes is an endothermic process. (3.9)
- 2. All alkanes that are liquid at room temperature are more dense than water. (3.8)
- 3. The two main sources of alkanes the world over are petroleum and natural gas. (3.10)
- 4. There are four alkyl groups with the molecular formula C_4H_{9} . (3.3)
- 5. Sets of constitutional isomers have the same molecular formula and the same physical properties. (3.2)
- 6. A hydrocarbon is composed of only carbon and hydrogen. (3.1)
- 7. Cycloalkanes are saturated hydrocarbons. (3.4)
- 8. The products of complete combustion of an alkane are carbon dioxide and water. (3.9)
- 9. Alkanes and cycloalkanes show cis-trans isomerism. (3.6)
- 10. Alkenes and alkynes are unsaturated hydrocarbons. (3.1)
- 11. There are two constitutional isomers with the molecular formula C_4H_{10} . (3.2)
- Hexane and cyclohexane are constitutional isomers. (3.4)
- **13**. The propyl and isopropyl groups are constitutional isomers. (3.3)

- 14. There are five constitutional isomers with the molecular formula C_5H_{12} . (3.2)
- Boiling points among alkanes with unbranched carbon chains increase as the number of carbons in the chain increases. (3.8)
- 16. In a cyclohexane ring, if an axial bond is above the plane of the ring on a particular carbon atom, axial bonds on the two adjacent carbons are below the plane of the ring. (3.5)
- Fractional distillation of petroleum separates hydrocarbons based on their melting points (3.10)
- Among alkane constitutional isomers, the least branched isomer generally has the lowest boiling point. (3.8)
- 19. The parent name of a cycloalkane is the name of the unbranched alkane with the same number of carbon atoms as are in the cycloalkane ring. (3.4)
- **20.** Octane and 2,2,4-trimethylpentane are constitutional isomers and have the same octane number. (3.10)
- 21. Liquid alkanes and cycloalkanes are soluble in each other. (3.8)
- 22. Alkanes and cycloalkanes are insoluble in water. (3.8)
- The more stable chair conformation of a substituted cyclohexane has the greater number of substituents in equatorial positions. (3.5)

- 24. The parent name of an alkane is the name of the longest chain of carbon atoms. (3.3)
- 25. Alkanes are saturated hydrocarbons. (3.1)
- **26.** The general formula of an alkane is C_nH_{2n} , where *n* is the number of carbon atoms in the alkane. (3.1)
- **27.** The octane number of a particular gasoline is the number of grams of octane per liter. (3.10)
- Cis and trans isomers have the same molecular formula, the same connectivity, and the same physical properties. (3.8)
- **29.** A *cis* isomer of a disubstituted cycloalkane can be converted to a *trans* isomer by rotation about an appropriate carbon–carbon single bond. (3.6)
- **30**. All cycloalkanes with two substituents on the ring show *cis-trans* isomerism. (3.6)

- In all conformations of ethane, propane, butane, and higher alkanes, all C-C-C and C-C-H bond angles are approximately 109.5°. (3.5)
- Conformations have the same molecular formula and the same connectivity, but differ in the three-dimensional arrangement of their atoms in space. (3.5)
- Constitutional isomers have the same molecular formula and the same connectivity of their atoms. (3.2)

Detailed explanations for many of these answers can be tound in the accompanying Solutions Manual.

KEY REACTIONS

1. Oxidation of Alkanes (Section 3.9)

The oxidation of alkanes to carbon dioxide and water is the basis for their use as energy sources of heat and power:

 $CH_{3}CH_{2}CH_{3} + 5O_{2} \longrightarrow 3CO_{2} + 4H_{2}O + energy$

PROBLEMS

A problem marked with an asterisk indicates an applied "real-world" problem. Answers to problems whose numbers are printed in blue are given in Appendix D.

Section 3.1 Structure of Alkanes

3.13 For each condensed structural formula, write a lineangle formula:

(a)
$$CH_2CH_3 CH_3$$

 $| | |$
 $CH_3CH_2CHCHCH_2CHCH_3$
 $| |$
 $CH(CH_3)_2$

(h)

(c) $(CH_3)_2CHCH(CH_3)_2$

(d)
$$CH_3CH_2CCH_2CH_3$$

 $|$
 CH_2CH_3

(f) $CH_3(CH_2)_3CH(CH_3)_2$







3.15 For each of the following condensed structural formulas, provide an even more abbreviated formula, using parentheses and subscripts:

(a) $CH_3CH_2CH_2CH_2CH_2CHCH_3$

CH2CH2CH3

(b) $HCCH_2CH_2CH_3$ | $CH_2CH_3CH_3$

CH₂CH₂CH₃

(c) $CH_3CH_2CH_2CH_2CH_2CH_3$ | $CH_2CH_2CH_3$

Section 3.2 Constitutional Isomerism

- 3.16 Which statements are true about constitutional isomers?
 - (a) They have the same molecular formula.
 - (b) They have the same molecular weight.
 - (c) They have the same order of attachment of atoms.
 - (d) They have the same physical properties.
 - (e) Conformations are not constitutional isomers.
- **3.17** Each member of the following set of compounds is an alcohol; that is, each contains an —OH (hydroxyl group, Section 1.7A): (See Example 3.1)



Which structural formulas represent (1) the same compound, (2) different compounds that are constitutional isomers, or (3) different compounds that are not constitutional isomers?

3.18 Each member of the following set of compounds is an amine; that is, each contains a nitrogen atom bonded to one, two, or three carbon groups (Section 1.7B): (See Example 3.1)



Which structural formulas represent (1) the same compound, (2) different compounds that are constitutional isomers, or (3) different compounds that are not constitutional isomers?

3.19 Each member of the following set of compounds is either an aldehyde or a ketone (Section 1.7C): (See Example 3.1)



Which structural formulas represent (1) the same compound, (2) different compounds that are constitutional isomers, or (3) different compounds that are not constitutional isomers?

- 3.20 For each pair of compounds, tell whether the structural formulas shown represent (See Example 3.1)
 - (1) the same compound,
 - (2) different compounds that are constitutional isomers, or
 - (3) different compounds that are not constitutional isomers:



0



- 3.21 Name and draw line-angle formulas for the nine constitutional isomers with the molecular formula C₇H₁₆. (See Example 3.2)
- 3.22 Tell whether the compounds in each set are constitutional isomers: (See Example 3.1)



(d) $CH_3CHCH_2CH_3$ and $CH_3CCH_2CH_3$ (e) and $CH_3CH_2CH_2CH_2CH_3$ (f) and $CH_2=CHCH_2CH_2CH_3$

OH

3.23 Draw line-angle formulas for (See Example 3.2)

- (a) The four alcohols with the molecular formula $C_4H_{10}O$.
- (b) The two aldehydes with the molecular formula $C_4H_8O.$
- (c) The one ketone with the molecular formula $C_4 H_8 O. \label{eq:capacity}$
- (d) The three ketones with the molecular formula $C_5H_{10}O.$
- (e) The four carboxylic acids with the molecular formula $C_5 H_{10} O_2. \label{eq:carbox}$

Sections 3.3 – 3.5 Nomenclature of Alkanes and Cycloalkanes

3.24 Write IUPAC names for these alkanes and cycloal- *3.26 kanes: (See Examples 3.3, 3.5)



- 3.25 Write line-angle formulas for these alkanes: (See Examples 3.3, 3.5)
 - (a) 2,2,4-Trimethylhexane
 - (b) 2,2-Dimethylpropane
 - (c) 3-Ethyl-2,4,5-trimethyloctane
 - (d) 5-Butyl-2,2-dimethylnonane
 - (e) 4-lsopropyloctane
 - (f) 3,3-Dimethylpentane
 - (g) trans-1,3-Dimethylcyclopentane
 - (h) cis-1,2-Diethylcyclobutane

Following is the structure of limonene, the chemical component of oranges that is partly responsible for their citrus scent. Draw the hydrogens present in limonene and classify those bonded to sp^3 hybridized carbons as 1°, 2°, or 3°. (See Example 3.4)



Limonene

*3.27 Following is the structure of Germacrene A, a hydrocarbon synthesized in plants and studied for its insecticidal properties. Classify each of the *sp*³ hybridized carbons on Germacrene A as 1°, 2°, 3°, or 4°. (See Example 3.4)



Germacrene A

- 3.28 Explain why each of the following names is an incorrect IUPAC name and write the correct IUPAC name for the intended compound: (See Examples 3.3, 3.5)
 - (a) 1,3-Dimethylbutane
 - (b) 4-Methylpentane
 - (c) 2,2-Diethylbutane
 - (d) 2-Ethyl-3-methylpentane
 - (e) 2-Propylpentane
 - (f) 2,2-Diethylheptane
 - (g) 2,2-Dimethylcyclopropane
 - (h) 1-Ethyl-5-methylcyclohexane
- 3.29 Draw a structural formula for each compound: (See Example 3.6)

(a)	Ethanol	(b)	Ethanal
(c)	Ethanoic acid	(d)	Butanone

Section 3.6 Conformations of Alkanes and Cycloalkanes

- How many different staggered conformations are 3 31 there for 2-methylpropane? How many different eclipsed conformations are there?
- 3.32 Looking along the bond between carbons 2 and 3 of butane, there are two different staggered conformations and two different eclipsed conformations. Draw Newman projections of each, and arrange them in order from the most stable conformation to the least stable conformation. (See Example 3.7)
- 3.33 Explain why each of the following Newman projections might not represent the most stable conformation of that molecule:



3.34 Explain why the following are not different conformations of 3-hexene:



3.35 Which of the following two conformations is the more stable? (Hint: Use molecular models or draw Newman projections looking down the bond being

- (e) Butanal
- (g) Propanal
- (i) Cyclopentanol
- (k) Cyclopentanone
- (f) Butanoic acid
- (h) Cyclopropanol
- (j) Cyclopentene







3.36 Determine whether the following pairs of structures in each set represent the same molecule or constitutional isomers, and if they are the same molecule, determine whether they are in the same or different conformations:



3.37 Draw Newman projections for the most stable conformation of each of the following compounds looking down the indicated bond. (See Example 3.7)



Section 3.7 Cis-Trans Isomerism in Cycloalkanes

- **3.39** What structural feature of cycloalkanes makes *cis*-*trans* isomerism in them possible?
- 3.40 Is cis-trans isomerism possible in alkanes?
- 3.41 Name and draw structural formulas for the *cis* and *trans* isomers of 1,2 dimethylcyclopropane. (See Examples 3.10, 3.11)
- 3.42 Name and draw structural formulas for all cycloalkanes with the molecular formula C₅H₁₀. Be certain to include *cis-trans* isomers, as well as constitutional isomers. (See Examples 3.10, 3.11)
- 3.43 Using a planar pentagon representation for the cyclopentane ring, draw structural formulas for the *cis* and *trans* isomers of (See Examples 3.10, 3.11)
 - (a) 1,2-Dimethylcyclopentane
 - (b) 1,3-Dimethylcyclopentane
- 3.44 Draw the alternative chair conformations for the *cis* and *trans* isomers of 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, and 1,4-dimethylcyclohexane. (See Examples 3.10, 3.11)
 - (a) Indicate by a label whether each methyl group is axial or equatorial.
 - (b) For which isomer(s) are the alternative chair conformations of equal stability?
 - (c) For which isomer(s) is one chair conformation more stable than the other?
- **3.45** Use your answers from Problem 3.44 to complete the following table, showing correlations between *cis, trans* isomers and axial, equatorial positions for disubstituted derivatives of cyclohexane:

Position of Substitution	cis	trans
1,4-	a,e or e,a	e,e or a,a
1,3-	or	or
1,2-	or	or

3.38 Draw both chair forms of each of the following compounds and indicate the more stable conformation. (See Examples 3.8, 3.9)



*3.46 There are four *cis–trans* isomers of 2-isopropyl-5-methylcyclohexanol: (See Examples 3.10, 3.11)



2-Isopropyl-5-methylcyclohexanol

- (a) Using a planar hexagon representation for the cyclohexane ring, draw structural formulas for these four isomers.
- (b) Draw the more stable chair conformation for each of your answers in part (a).
- (c) Of the four *cis-trans* isomers, which is the most stable? If you answered this part correctly, you picked the isomer found in nature and given the name menthol.



Peppermint plant (*Mentha piperita*), a source of menthol, is a perennial herb with aromatic qualities used in candies, gums, hot and cold beverages, and garnish for punch and fruit.

3.47 Draw alternative chair conformations for each substituted cyclohexane, and state which chair is the more stable: (See Examples 3.8, 3.11)



3.48 How many six-membered rings exist in adamantane? What kinds of conformations do the six-membered rings exhibit in adamantane? (*Hint:* Build a molecular model of the compound.)



Section 3.8 Physical Properties of Alkanes and Cycloalkanes

- 3.49 In Problem 3.21, you drew structural formulas for all constitutional isomers with the molecular formula C₇H₁₆. Predict which isomer has the lowest boiling point and which has the highest. (See Example 3.12)
- 3.50 What generalizations can you make about the densities of alkanes relative to that of water?
- 3.51 What unbranched alkane has about the same boiling point as water? (See Table 3.4.) Calculate the molecular weight of this alkane, and compare it with that of water. Explain why water, which is lower in mass than the alkane, boils at the same temperature.
- 3.52 As you can see from Table 3.4, each CH₂ group added to the carbon chain of an alkane increases the boiling point of the alkane. The increase is greater going

Section 3.9 Reactions of Alkanes

- **3.55** Write balanced equations for the combustion of each hydrocarbon. Assume that each is converted completely to carbon dioxide and water.
 - (a) Hexane (b) Cyclohexane (c) 2-Methylpentane
- ***3.56** Following are heats of combustion of methane and propane:

Hydrocarbon	Component of	$\Delta H^{\circ} [kJ/mol (kcal/mol)]$
CH_4	natural gas	-886 (-212)
$\rm CH_3\rm CH_2\rm CH_3$	LPG	-2220 (-530)

from CH₄ to C₂H₆ and from C₂H₆ to C₃H₈ than it is from C₈H₁₈ to C₉H₂₀ or from C₉H₂₀ to C₁₀H₂₂. What do you think is the reason for this trend?

- **3.53** Dodecane, $C_{12}H_{26}$, is an unbranched alkane. Predict the following:
 - (a) Will it dissolve in water?
 - (b) Will it dissolve in hexane?
 - (c) Will it burn when ignited?
 - (d) Is it a liquid, solid, or gas at room temperature and atmospheric pressure?
 - (e) Is it more or less dense than water?
- *3.54 As stated in Section 3.8A, the wax found in apple skins is an unbranched alkane with the molecular formula $C_{27}H_{56}$. Explain how the presence of this alkane prevents the loss of moisture from within an apple.

On a gram-for-gram basis, which of these hydrocarbons is the better source of heat energy?

*3.57 When ethanol is added to gasoline to produce gasohol, the ethanol promotes more complete combustion of the gasoline and is an octane booster (Section 3.10 B). Compare the heats of combustion of 2,2,4-trimethylpentane 5460 kJ/mol (1304 kcal/mol) and ethanol 1369 kJ/mol (327 kcal/mol). Which has the higher heat of combustion in kJ/mol? in kJ/g?

LOOKING AHEAD

- 3.58 Explain why 1,2-dimethylcyclohexane can exist as *cis-trans* isomers, while 1,2-dimethylcyclododecane cannot.
- *3.59 Following is a representation of the glucose molecule (we discuss the structure and chemistry of glucose in Chapter 17):





- (a) Convert this representation to a planar hexagon representation.
- (b) Convert this representation to a chair conformation. Which substituent groups in the chair conformation are equatorial? Which are axial?
- *3.60 Following is the structural formula of cholic acid (Section 19.4A), a component of human bile whose function is to aid in the absorption and digestion of dietary fats:







- (a) What are the conformations of rings A, B, C, and D?
- (b) There are hydroxyl groups on rings A, B, and C. Tell whether each is axial or equatorial.
- (c) Is the methyl group at the junction of rings A and B axial or equatorial to ring A? Is it axial or equatorial to ring B?

- (d) Is the methyl group at the junction of rings C and D axial or equatorial to ring C?
- ***3.61** Following is the structural formula and ball-and-stick model of cholestanol:





The only difference between this compound and cholesterol (Section 19.4A) is that cholesterol has a carbon–carbon double bond in ring B.

- (a) Describe the conformation of rings A, B, C, and D in cholestanol.
- (b) Is the hydroxyl group on ring A axial or equatorial?
- (c) Consider the methyl group at the junction of rings A and B. Is it axial or equatorial to ring A? Is it axial or equatorial to ring B?
- (d) Is the methyl group at the junction of rings C and D axial or equatorial to ring C?
- **3.62** As we have seen in Section 3.4, the IUPAC system divides the name of a compound into a prefix (showing the number of carbon atoms), an infix (showing the presence of carbon-carbon single, double, or triple bonds), and a suffix (showing the presence of an alcohol, amine, aldehyde, ketone, or carboxylic acid). Assume for the purposes of this problem that, to be alcohol (-ol) or amine (-amine), the hydroxyl or amino group must be bonded to a tetrahedral (*sp*³ hybridized) carbon atom.



Given this information, write the structural formula of a compound with an unbranched chain of four carbon atoms that is an:

- (a) Alkane
- (b) Alkene (d) Alkanol
- (c) Alkyne (e) Alkenol
- (g) Alkanamine
- (f) Alkynol
- (h) Alkenamine
- (i) Alkynamine
- (k) Alkenal
- (j) Alkanal (I) Alkynal

- (m) Alkanone
- (o) Alkynone
- (n) Alkenone
- (q) Alkenoic acid
- (p) Alkanoic acid
- (r) Alkynoic acid

(Note: There is only one structural formula possible for some parts of this problem. For other parts, two or more structural formulas are possible. Where two or more are possible, we will deal with how the IUPAC system distinguishes among them when we come to the chapters on those particular functional groups.)

GROUP LEARNING ACTIVITIES

- ***3.63** Come up with reasons for the following phenomena. You may need to refer to concepts learned from previous chapters or from general chemistry.
 - (a) Gasoline is cool to the touch when spilled on bare skin.
 - (b) Water is more dense than methane.
 - (c) Butane is a more appropriate fuel for a disposable lighter than either propane or pentane.
- 3.64 See who can name the following stick figure molecules the fastest:



PUTTING IT TOGETHER

The following problems bring together concepts and material from Chapters 1-3.

Choose the best answer for each of the following questions.

- 1. Which of the following molecules has a net charge of +1?
 - (a) CH₂CHCH₃ (b) CH₃CHCH₃
 - (c) CHCCH₃ (d) $(CH_3)_3CH$
 - (e) CH₂CH₂
- 2. Which of the following statements is true concerning the following compound?

- (a) The central carbon is sp^2 hybridized, and the molecule is planar in geometry.
- (b) The central carbon is sp^2 hybridized, and the molecule is nonplanar in geometry.
- (c) The central carbon is sp hybridized, and the molecule is planar in geometry.
- (d) The central carbon is sp hybridized, and the molecule is nonplanar in geometry.
- (e) None of these statements is true.
- 3. Which of the following statements is false concerning p orbitals?
 - (a) They consist of two equivalent lobes.
 - (b) They are absent from the first shell of atomic orbitals.
 - (c) They can form π bonds.
 - (d) They only participate in bonding on carbon atoms.
 - (e) They can hold a maximum of two electrons.

4. Which base (A or B) is stronger and why?



- (a) A is stronger because it has fewer protons for the acid to compete with in acid-base reactions.
- (b) A is stronger because inductive effects increase the negative character of its oxygen.
- (c) **B** is stronger because inductive effects increase the negative character of its oxygen.
- (d) **B** is stronger because resonance effects can delocalize its negative charge throughout the molecule.
- (e) B is stronger because it has no resonance or inductive effects that can delocalize its negative charge throughout the molecule.
- 5. Which of the following is the initial product of the reaction between (CH₃)₃C⁺ and CH₃OH?

(a)
$$(CH_3)_3C - O:^+$$

H (b) $(CH_3)_3C - O:^+$
H H

(c)
$$(CH_3)_3C$$
— $\ddot{O}:$ + H₂ (d) $(CH_3)_3C$ — CH_2 + H₂ $\ddot{O}:$

(e)
$$(CH_3)_3C - H + CH_3 - O$$
:

6. Select the statement that is false concerning the following acid-base reaction.

$$\begin{array}{cccc} O & + & NaCl & \longrightarrow & O \\ \square & \square & -C & -OH & & CH_3 - C - ONa \end{array} + HCl$$

- (a) The equilibrium lies on the product side of the reaction.
- (b) The carboxylic acid does not possess a positive charge.
- (c) The chloride ion acts as a Lewis base.
- (d) The chloride ion acts as a Brønsted–Lowry base.
- (e) The carboxylic acid is a weaker acid than HCl.
- 7. Which of the following statements is false?
 - (a) Nonbonded interaction (steric) strain contributes to the energy of butane in the eclipsed conformation.
 - (b) All staggered conformations possess zero strain.
 - (c) A Newman projection is the picture of a molecule viewed down at least one of its bonds.
 - (d) Bonds represented by Newman projections do not freely rotate because they must overcome an energy barrier to rotation.
 - (e) Ring strain contributes to the instability of cyclopropane.
- 8. Which of the following statements is true concerning the isomers *cis*-1,2-dimethylcyclohexane and *cis*-1,3-dimethylcyclohexane?
 - (a) They are not constitutional isomers.
 - (b) They are conformers.
 - (c) The favored conformer of the 1,3-isomer is more stable than that of the 1,2-isomer.
 - (d) The favored conformer of the 1,3-isomer and that of the 1,2-isomer are equal in energy.
 - (e) The relative stability of the two molecules cannot be predicted.

 Select the correct order of stability (least stable → most stable) for the following conformations.



 Select the most stable conformation of those shown for 1-*tert*-butyl-3,5-dimethylcyclohexane.



Answer the questions that follow regarding the structure of paclitaxel (trade name Taxol®), a compound first isolated from the Pacific Yew tree, which is now used to treat ovarian, breast, and non-small cell lung cancer.
 (a) Identify all the hydroxy groups and classify them

as 1°, 2°, or 3°.



- (b) Identify all the carbonyl groups. Are any of them part of an aldehyde, a ketone, or a carboxylic acid?
- (c) What atomic or hybridized orbitals participate in the bond labeled A?
- (d) Are there any quaternary carbons in paclitaxel?
- (e) Explain why hydroxyl group B is more acidic than hydroxyl group C.
- (f) What is the angle of the bond containing atoms 1-2-3?
- 12. Draw Newman projections of the three most stable conformations of the following compound viewed down the indicated bond and in the indicated direction. Indicate the most favorable conformation. You should be able to briefly describe or illustrate why your choice is the most favorable conformation.



13. Provide IUPAC names for the following compounds.



- (c) $CH_3CH_2CH(CH_3)CH(CH_2CH_3)CH_2CH(CH_3)_2$
- 14. For each pair of molecules, select the one that best fits the accompanying description. Provide a concise but thorough rationale for each of your decisions using words and/or pictures.
 - (a) The higher boiling point?



(b) The more acidic hydrogen?



(c) The more basic atom?



(d) The more acidic set of protons?



(e) The stronger base?



(f) Possesses the least nonbonding interaction (steric) strain?



15. Glutamic acid is one of the common amino acids found in nature. Draw the predominant structure of glutamic acid when placed in a solution of pH = 3.2 and indicate its overall charge.



16. Use atomic and hybridized orbitals to illustrate (see example using H₂O) the location of bonding and nonbonding electrons in ethenimine. Do all of the atoms in ethenimine lie in the same plane?

Example orbital illustration for H₂O



17. The following values have been determined for the amount of energy it takes to place a substituent in the axial position. As shown in the table, going from H to CH₃ causes a drastic increase in free energy (7.28 kJ/mol). However, increasing the size of the R group results in only a minor change in ΔG even when the R group is isopropyl (this only increases ΔG by 1.72 kJ/mol over methyl). Using perspective (dashwedge) drawings, illustrate and explain why the increase in ΔG is only gradual up to isopropyl but increases drastically when the R group is *t*-butyl.



Н	0	
CH_3	7.28 (1.74)	
CH_2CH_3	7.32 (1.75)	
$CH(CH_3)_2$	9.00 (2.15)	
$C(CH_3)_3$	20.92 (5.00)	

18. (a) Draw the two possible products that can form from the Lewis acid-base reaction between methyl formate and BF₃. Indicate the major product and use curved arrow notation to illustrate its formation. Show all charges and nonbonded electrons *in your products*. (b) Use pictures and words to explain why the product you indicated is favored over the other product.



Methyl formate

- 19. Use resonance theory to predict whether [CNO]⁻ or [NCO]⁻ is the more stable ion. Use pictures and words to explain your decision.
- 20. Provide structures as indicated:
 - (a) All compounds with the molecular formula C_5H_{10} that exhibit *cis-trans* isomerism.
 - (b) Lewis structures and any resonance structures for the ion with formula CH₂NO₂. Show all formal charges and lone pairs of electrons.
 - (c) All compounds that upon combustion with 6 mol of O_2 would yield 4 mol of CO_2 and 4 mol of H_2O .