




3

Organic Compounds: Alkanes and Their Stereochemistry

Organic KNOWLEDGE TOOLS

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 Online homework for this chapter may be assigned in Organic OWL.

According to *Chemical Abstracts*, the publication that abstracts and indexes the chemical literature, there are more than 30 million known organic compounds. Each of these compounds has its own physical properties, such as melting point and boiling point, and each has its own chemical reactivity.

Chemists have learned through many years of experience that organic compounds can be classified into families according to their structural features and that the members of a given family often have similar chemical behavior. Instead of 30 million compounds with random reactivity, there are a few dozen families of organic compounds whose chemistry is reasonably predictable. We'll study the chemistry of specific families throughout much of this book, beginning in this chapter with a look at the simplest family, the *alkanes*.

WHY THIS CHAPTER?

Alkanes are relatively unreactive, but they nevertheless provide a useful vehicle for introducing some important general ideas. In this chapter, we'll use alkanes for discussing the basic approach to naming organic compounds and for taking an initial look at some of the three-dimensional aspects of molecules, a topic of particular importance in understanding biological organic chemistry.

3.1 Functional Groups

ThomsonNOW Click *Organic Interactive* to learn how to **recognize functional groups in organic molecules**.

The structural features that make it possible to classify compounds into families are called *functional groups*. A **functional group** is a group of atoms that has a characteristic chemical behavior in every molecule where it occurs. For example, compare ethylene, a plant hormone that causes fruit to ripen, with menthene, a much more complicated molecule. Both substances contain a carbon-carbon double-bond functional group, and both therefore react with Br_2 in the same way to give products in which a Br atom has added to each of the double-bond carbons (Figure 3.1). This example is typical: *the chemistry of every organic molecule, regardless of size and complexity, is determined by the functional groups it contains.*

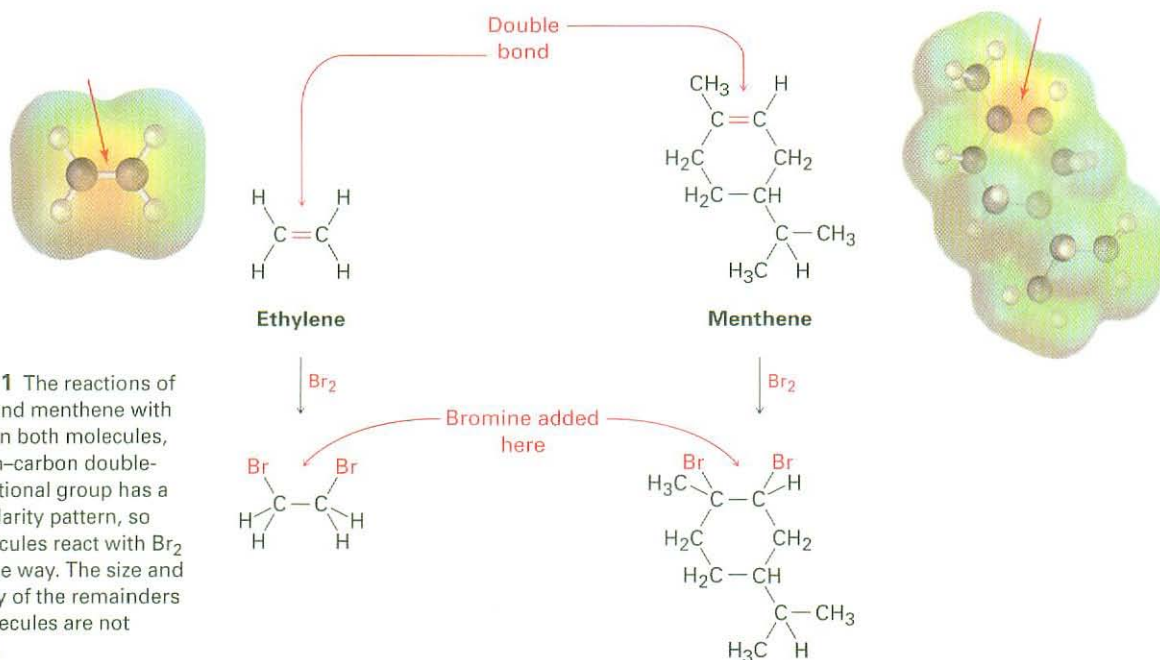
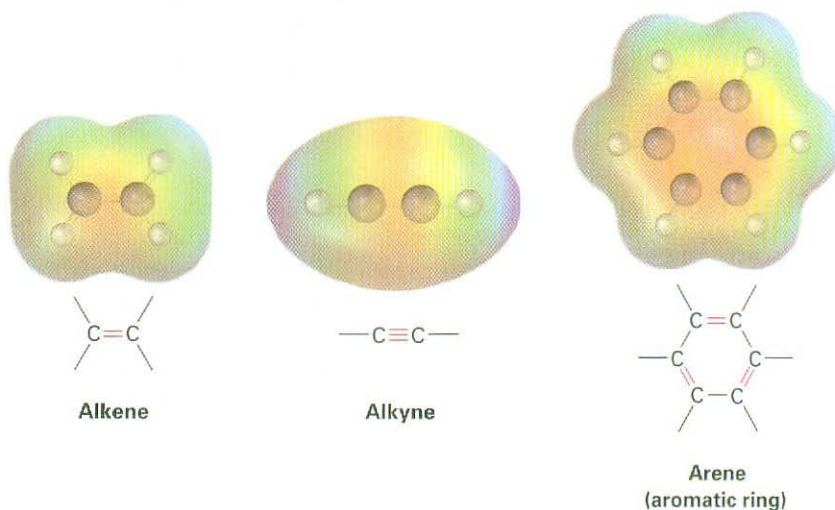


Figure 3.1 The reactions of ethylene and menthene with bromine. In both molecules, the carbon-carbon double-bond functional group has a similar polarity pattern, so both molecules react with Br_2 in the same way. The size and complexity of the remainders of the molecules are not important.

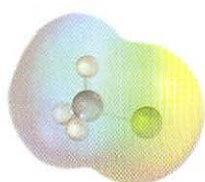
Look carefully at Table 3.1 on pages 76 and 77, which lists many of the common functional groups and gives simple examples of their occurrence. Some functional groups have only carbon-carbon double or triple bonds; others have halogen atoms; and still others contain oxygen, nitrogen, or sulfur. Much of the chemistry you'll be studying is the chemistry of these functional groups.

Functional Groups with Carbon-Carbon Multiple Bonds

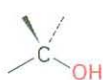
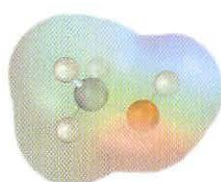
Alkenes, alkynes, and arenes (aromatic compounds) all contain carbon-carbon multiple bonds. *Alkenes* have a double bond, *alkynes* have a triple bond, and *arenes* have alternating double and single bonds in a six-membered ring of carbon atoms. Because of their structural similarities, these compounds also have chemical similarities.



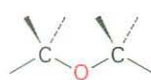
Functional Groups with Carbon Singly Bonded to an Electronegative Atom Alkyl halides (haloalkanes), alcohols, ethers, amines, thiols, sulfides, and disulfides all have a carbon atom singly bonded to an electronegative atom—halogen, oxygen, nitrogen, or sulfur. *Alkyl halides* have a carbon atom bonded to halogen ($-X$), *alcohols* have a carbon atom bonded to the oxygen of a hydroxyl group ($-OH$), *ethers* have two carbon atoms bonded to the same oxygen, *organophosphates* have a carbon atom bonded to the oxygen of a phosphate group ($-OPO_3^{2-}$), *amines* have a carbon atom bonded to a nitrogen, *thiols* have a carbon atom bonded to an $-SH$ group, *sulfides* have two carbon atoms bonded to the same sulfur, and *disulfides* have carbon atoms bonded to two sulfurs that are joined together. In all cases, the bonds are polar, with the carbon atom bearing a partial positive charge ($\delta+$) and the electronegative atom bearing a partial negative charge ($\delta-$).



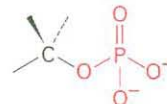
Alkyl halide
(haloalkane)



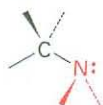
Alcohol



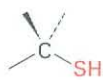
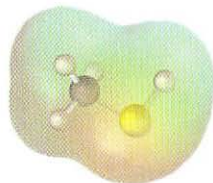
Ether



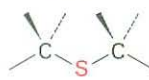
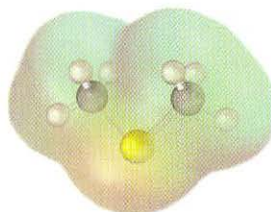
Phosphate



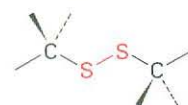
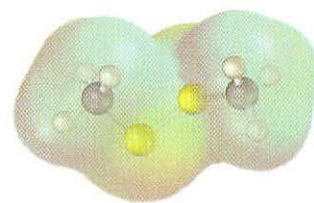
Amine



Thiol




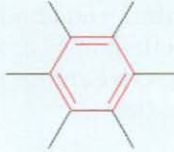



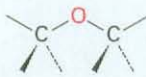
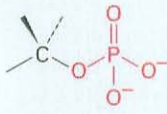

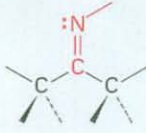
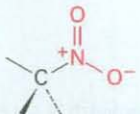

Sulfide



Disulfide

Functional Groups with a Carbon–Oxygen Double Bond (Carbonyl Groups) Note particularly the last seven entries in Table 3.1, which list different families of compounds that contain the *carbonyl group*, $C=O$ (pronounced car-bo-neel). Functional groups with a carbon–oxygen double bond are present in the great majority of organic compounds and in practically all biological molecules. These compounds behave similarly in many respects but differ depending on the identity of the atoms bonded to the carbonyl-group carbon. *Aldehydes* have at least one hydrogen bonded to the $C=O$, *ketones* have two carbons bonded to the $C=O$, *carboxylic acids* have an $-OH$ group bonded to the $C=O$, *esters* have an ether-like oxygen bonded to the $C=O$, *amides* have an amine-like nitrogen

Table 3.1 Structures of Some Common Functional Groups

Name	Structure*	Name ending	Example
Alkene (double bond)		-ene	$\text{H}_2\text{C}=\text{CH}_2$ Ethene
Alkyne (triple bond)	$-\text{C}\equiv\text{C}-$	-yne	$\text{HC}\equiv\text{CH}$ Ethyne
Arene (aromatic ring)		None	 Benzene
Halide	 (X = F, Cl, Br, I)	None	CH_3Cl Chloromethane
Alcohol		-ol	CH_3OH Methanol
Ether		ether	CH_3OCH_3 Dimethyl ether
Monophosphate		phosphate	$\text{CH}_3\text{OPO}_3^{2-}$ Methyl phosphate
Amine		-amine	CH_3NH_2 Methylamine
Imine (Schiff base)		None	$\text{CH}_3\text{C}(\text{NH})\text{CH}_3$ Acetone imine
Nitrile	$-\text{C}\equiv\text{N}$	-nitrile	$\text{CH}_3\text{C}\equiv\text{N}$ Ethanenitrile
Nitro		None	CH_3NO_2 Nitromethane
Thiol		-thiol	CH_3SH Methanethiol

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

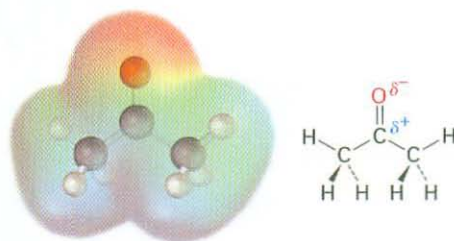
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Table 3.1 Structures of Some Common Functional Groups (continued)

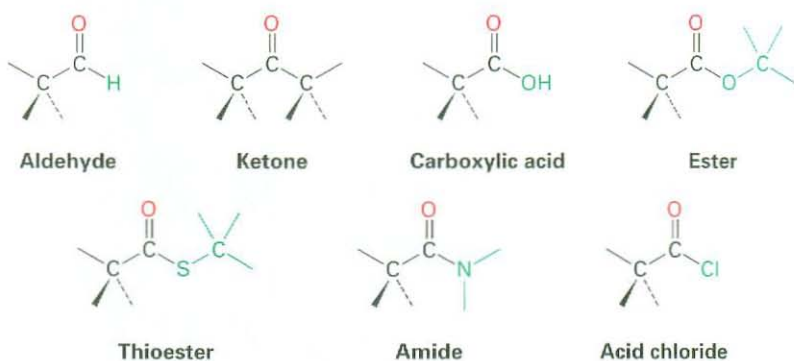
Name	Structure*	Name ending	Example
Sulfide		<i>sulfide</i>	CH_3SCH_3 Dimethyl sulfide
Disulfide		<i>disulfide</i>	CH_3SSCH_3 Dimethyl disulfide
Carbonyl			
Aldehyde		<i>-al</i>	CH_3CHO Ethanal
Ketone		<i>-one</i>	CH_3COCH_3 Propanone
Carboxylic acid		<i>-oic acid</i>	CH_3COOH Ethanoic acid
Ester		<i>-oate</i>	$\text{CH}_3\text{COOCH}_3$ Methyl ethanoate
Amide		<i>-amide</i>	CH_3CONH_2 Ethanamide
Carboxylic acid anhydride		<i>-oic anhydride</i>	$\text{CH}_3\text{COOCCOCH}_3$ Ethanoic anhydride
Carboxylic acid chloride		<i>-oyl chloride</i>	CH_3COCl Ethanoyl chloride

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

bonded to the C=O, *acid chlorides* have a chlorine bonded to the C=O, and so on. The carbonyl carbon atom bears a partial positive charge (δ^+), and the oxygen bears a partial negative charge (δ^-).

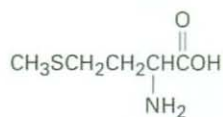


Acetone—a typical carbonyl compound

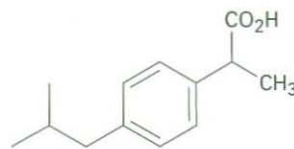


Problem 3.1 Identify the functional groups in each of the following molecules:

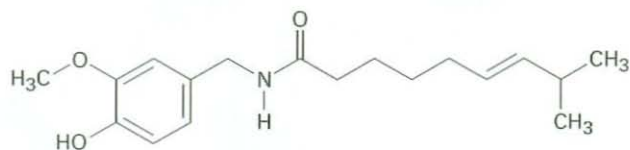
(a) Methionine, an amino acid:



(b) Ibuprofen, a pain reliever:



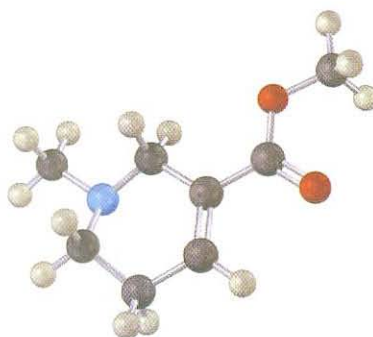
(c) Capsaicin, the pungent substance in chili peppers:



Problem 3.2 Propose structures for simple molecules that contain the following functional groups:

- (a) Alcohol (b) Aromatic ring (c) Carboxylic acid
 (d) Amine (e) Both ketone and amine (f) Two double bonds

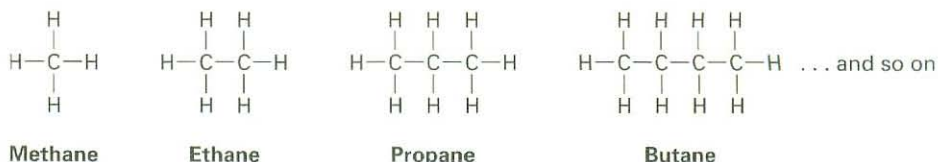
Problem 3.3 Identify the functional groups in the following model of arecoline, a veterinary drug used to control worms in animals. Convert the drawing into a line-bond structure and a molecular formula (red = O, blue = N).



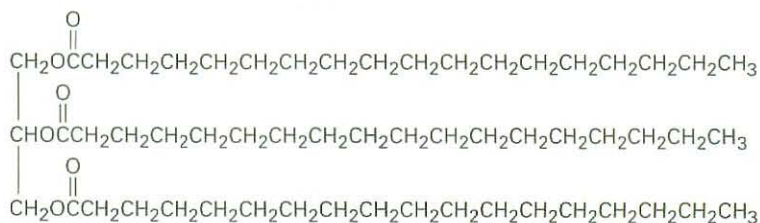
3.2 Alkanes and Alkane Isomers

ThomsonNOW Click *Organic Interactive* to learn to draw and recognize alkane isomers.

Before beginning a systematic study of the different functional groups, let's look first at the simplest family of molecules—the *alkanes*—to develop some general ideas that apply to all families. We saw in Section 1.7 that the carbon-carbon single bond in ethane results from σ (head-on) overlap of carbon sp^3 orbitals. If we imagine joining three, four, five, or even more carbon atoms by C–C single bonds, we can generate the large family of molecules called **alkanes**.

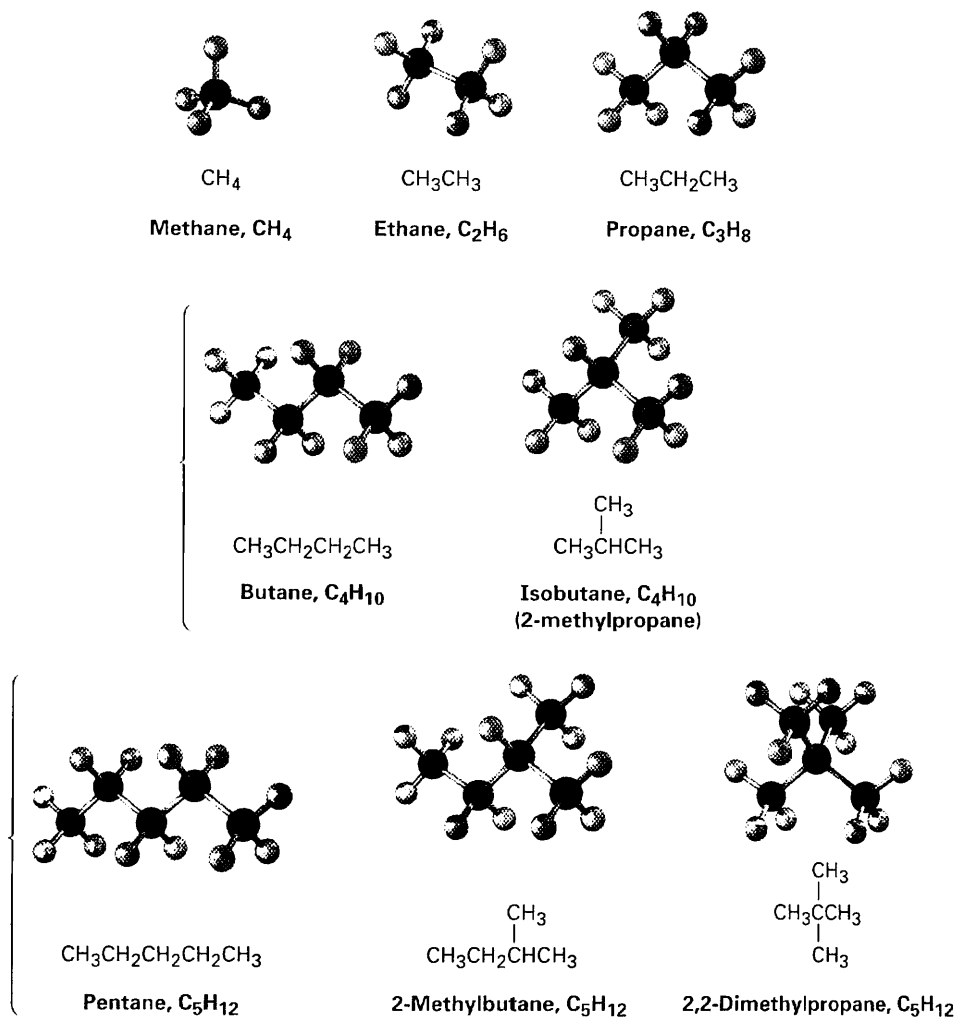


Alkanes are often described as *saturated hydrocarbons*—**hydrocarbons** because they contain only carbon and hydrogen; **saturated** because they have only C–C and C–H single bonds and thus contain the maximum possible number of hydrogens per carbon. They have the general formula C_nH_{2n+2} , where n is an integer. Alkanes are also occasionally referred to as **aliphatic** compounds, a name derived from the Greek *aleiphas*, meaning “fat.” We’ll see in Section 27.1 that many animal fats contain long carbon chains similar to alkanes.



A typical animal fat

Think about the ways that carbon and hydrogen might combine to make alkanes. With one carbon and four hydrogens, only one structure is possible: methane, CH_4 . Similarly, there is only one combination of two carbons with six hydrogens (ethane, CH_3CH_3) and only one combination of three carbons with eight hydrogens (propane, $\text{CH}_3\text{CH}_2\text{CH}_3$). If larger numbers of carbons and hydrogens combine, however, more than one structure is possible. For example, there are *two* substances with the formula C_4H_{10} : the four carbons can all be in a row (butane), or they can branch (isobutane). Similarly, there are three C_5H_{12} molecules, and so on for larger alkanes.



Compounds like butane and pentane, whose carbons are all connected in a row, are called **straight-chain alkanes**, or *normal alkanes*. Compounds like 2-methylpropane (isobutane), 2-methylbutane, and 2,2-dimethylpropane, whose carbon chains branch, are called **branched-chain alkanes**. The difference between the two is that you can draw a line connecting all the carbons of a straight-chain alkane without retracing your path or lifting your pencil from

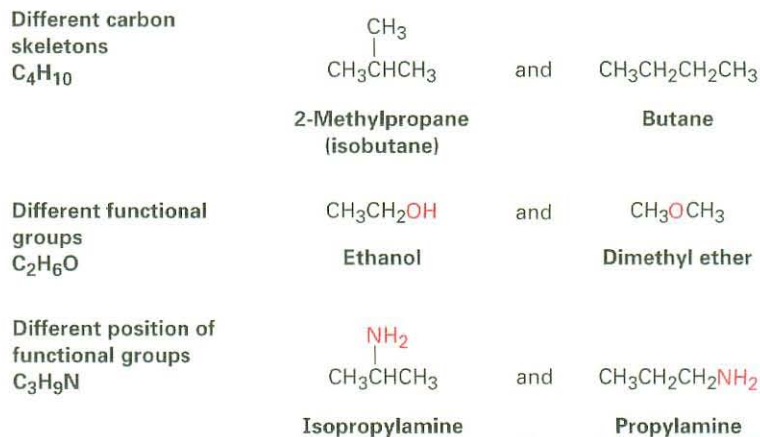
Table 3.2 Number of Alkane Isomers

Formula	Number of isomers
C ₆ H ₁₄	5
C ₇ H ₁₆	9
C ₈ H ₁₈	18
C ₉ H ₂₀	35
C ₁₀ H ₂₂	75
C ₁₅ H ₃₂	4,347
C ₂₀ H ₄₂	366,319
C ₃₀ H ₆₂	4,111,846,763

the paper. For a branched-chain alkane, however, you either have to retrace your path or lift your pencil from the paper to draw a line connecting all the carbons.

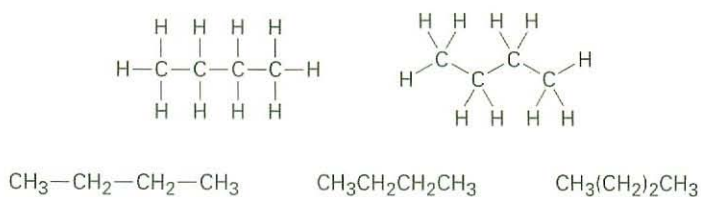
Compounds like the two C₄H₁₀ molecules and the three C₅H₁₂ molecules, which have the same formula but different structures, are called *isomers*, from the Greek *isos* + *meros*, meaning “made of the same parts.” **Isomers** are compounds that have the same numbers and kinds of atoms but differ in the way the atoms are arranged. Compounds like butane and isobutane, whose atoms are connected differently, are called **constitutional isomers**. We’ll see shortly that other kinds of isomers are also possible, even among compounds whose atoms are connected in the same order. As Table 3.2 shows, the number of possible alkane isomers increases dramatically as the number of carbon atoms increases.

Constitutional isomerism is not limited to alkanes—it occurs widely throughout organic chemistry. Constitutional isomers may have different carbon skeletons (as in isobutane and butane), different functional groups (as in ethanol and dimethyl ether), or different locations of a functional group along the chain (as in isopropylamine and propylamine). Regardless of the reason for the isomerism, constitutional isomers are always different compounds with different properties, but with the same formula.



A given alkane can be drawn arbitrarily in many ways. For example, the straight-chain, four-carbon alkane called butane can be represented by any of the structures shown in Figure 3.2. These structures don’t imply any particular three-dimensional geometry for butane; they indicate only the connections among atoms. In practice, as noted in Section 1.12, chemists rarely draw all the bonds in a molecule and usually refer to butane by the condensed structure, CH₃CH₂CH₂CH₃ or CH₃(CH₂)₂CH₃. Still more simply, butane can even be represented as *n*-C₄H₁₀, where *n* denotes *normal* (straight-chain) butane.

Figure 3.2 Some representations of butane, C₄H₁₀. The molecule is the same regardless of how it’s drawn. These structures imply only that butane has a continuous chain of four carbon atoms; they do not imply any specific geometry.



Straight-chain alkanes are named according to the number of carbon atoms they contain, as shown in Table 3.3. With the exception of the first four compounds—methane, ethane, propane, and butane—whose names have historical roots, the alkanes are named based on Greek numbers. The suffix *-ane* is added to the end of each name to indicate that the molecule identified is an alkane. Thus, *pentane* is the five-carbon alkane, *hexane* is the six-carbon alkane, and so on. We'll soon see that these alkane names form the basis for naming all other organic compounds, so at least the first ten should be memorized.

Table 3.3 Names of Straight-Chain Alkanes

Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH ₄
2	Ethane	C ₂ H ₆
3	Propane	C ₃ H ₈
4	Butane	C ₄ H ₁₀
5	Pentane	C ₅ H ₁₂
6	Hexane	C ₆ H ₁₄
7	Heptane	C ₇ H ₁₆
8	Octane	C ₈ H ₁₈
9	Nonane	C ₉ H ₂₀
10	Decane	C ₁₀ H ₂₂
11	Undecane	C ₁₁ H ₂₄
12	Dodecane	C ₁₂ H ₂₆
13	Tridecane	C ₁₃ H ₂₈
20	Icosane	C ₂₀ H ₄₂
30	Triacontane	C ₃₀ H ₆₂

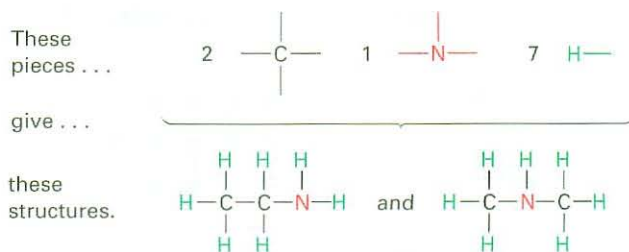
WORKED EXAMPLE 3.1

Drawing the Structures of Isomers

Propose structures for two isomers with the formula C₂H₇N.

Strategy We know that carbon forms four bonds, nitrogen forms three, and hydrogen forms one. Write down the carbon atoms first, and then use a combination of trial and error plus intuition to put the pieces together.

Solution There are two isomeric structures. One has the connection C–C–N, and the other has the connection C–N–C.



- Problem 3.4** Draw structures of the five isomers of C_6H_{14} .
- Problem 3.5** Propose structures that meet the following descriptions:
- Two isomeric esters with the formula $C_5H_{10}O_2$
 - Two isomeric nitriles with the formula C_4H_7N
 - Two isomeric disulfides with the formula $C_4H_{10}S_2$
- Problem 3.6** How many isomers are there with the following descriptions?
- Alcohols with the formula C_3H_8O
 - Bromoalkanes with the formula C_4H_9Br

3.3 Alkyl Groups

If you imagine removing a hydrogen atom from an alkane, the partial structure that remains is called an **alkyl group**. Alkyl groups are not stable compounds themselves, they are simply parts of larger compounds. Alkyl groups are named by replacing the *-ane* ending of the parent alkane with an *-yl* ending. For example, removal of a hydrogen from methane, CH_4 , generates a *methyl* group, $-CH_3$, and removal of a hydrogen from ethane, CH_3CH_3 , generates an *ethyl* group, $-CH_2CH_3$. Similarly, removal of a hydrogen atom from the end carbon of any straight-chain alkane gives the series of straight-chain alkyl groups shown in Table 3.4. Combining an alkyl group with any of the functional groups listed earlier makes it possible to generate and name many thousands of compounds. For example:

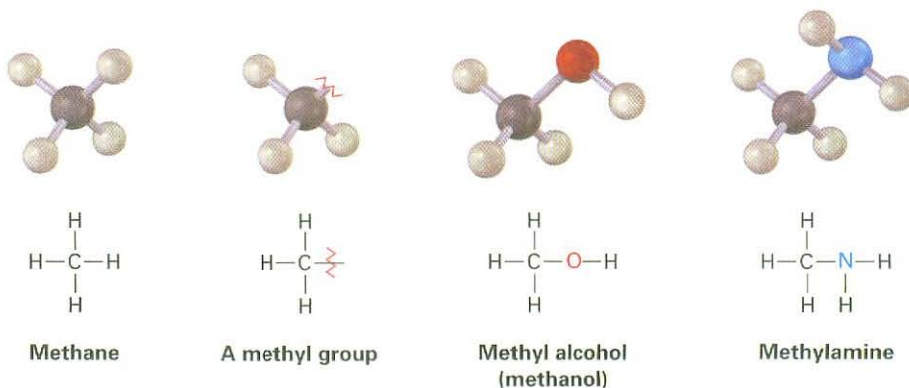
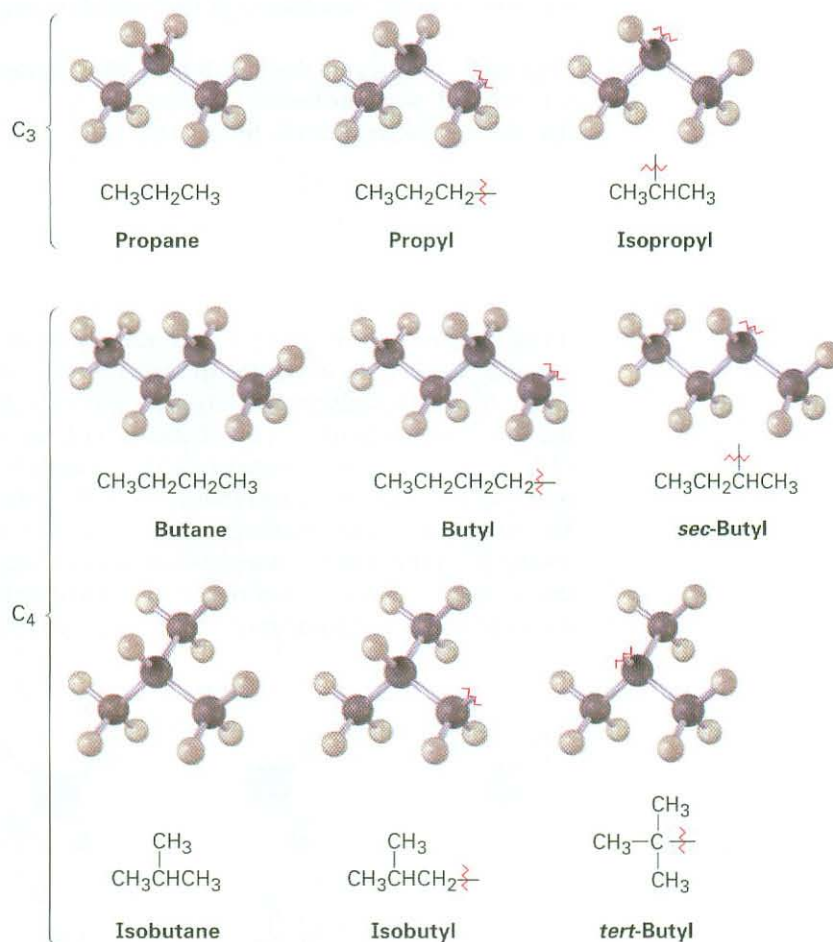


Table 3.4 Some Straight-Chain Alkyl Groups

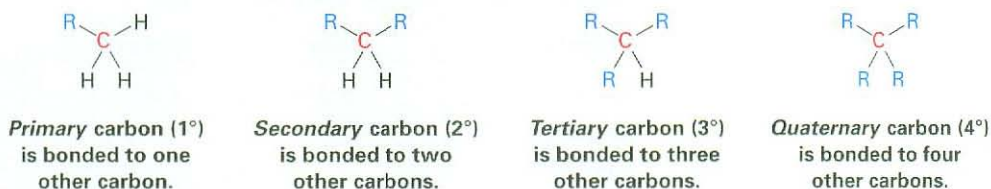
Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl

Just as straight-chain alkyl groups are generated by removing a hydrogen from an *end* carbon, branched alkyl groups are generated by removing a hydrogen atom from an *internal* carbon. Two 3-carbon alkyl groups and four 4-carbon alkyl groups are possible (Figure 3.3).

Figure 3.3 Alkyl groups generated from straight-chain alkanes.



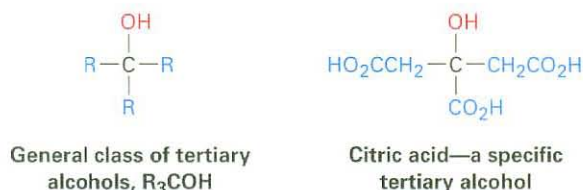
One further word about naming alkyl groups: the prefixes *sec-* (for secondary) and *tert-* (for tertiary) used for the C₄ alkyl groups in Figure 3.3 refer to *the number of other carbon atoms attached to the branching carbon atom*. There are four possibilities: primary (1°), secondary (2°), tertiary (3°), and quaternary (4°).



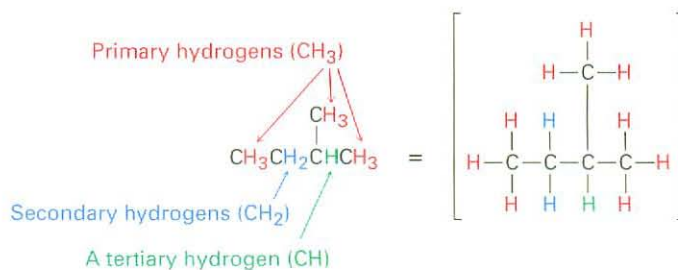
The symbol **R** is used in organic chemistry to represent a *generalized* organic group. The R group can be methyl, ethyl, propyl, or any of a multitude of others.

You might think of **R** as representing the **Rest** of the molecule, which we aren't bothering to specify.

The terms *primary*, *secondary*, *tertiary*, and *quaternary* are routinely used in organic chemistry, and their meanings need to become second nature. For example, if we were to say, "Citric acid is a tertiary alcohol," we would mean that it has an alcohol functional group ($-\text{OH}$) bonded to a carbon atom that is itself bonded to three other carbons. (These other carbons may in turn connect to other functional groups).

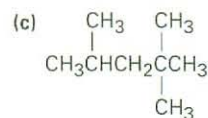
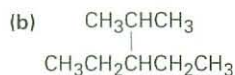
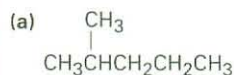


In addition, we also speak about hydrogen atoms as being primary, secondary, or tertiary. Primary hydrogen atoms are attached to primary carbons (RCH_3), secondary hydrogens are attached to secondary carbons (R_2CH_2), and tertiary hydrogens are attached to tertiary carbons (R_3CH). There is, of course, no such thing as a quaternary hydrogen. (Why?)



Problem 3.7 Draw the eight 5-carbon alkyl groups (pentyl isomers).

Problem 3.8 Identify the carbon atoms in the following molecules as primary, secondary, tertiary, or quaternary:



Problem 3.9 Identify the hydrogen atoms on the compounds shown in Problem 3.8 as primary, secondary, or tertiary.

Problem 3.10 Draw structures of alkanes that meet the following descriptions:

- An alkane with two tertiary carbons
- An alkane that contains an isopropyl group
- An alkane that has one quaternary and one secondary carbon

3.4 Naming Alkanes

ThomsonNOW Click *Organic Interactive* to learn to **write IUPAC names for simple alkanes.**

In earlier times, when relatively few pure organic chemicals were known, new compounds were named at the whim of their discoverer. Thus, urea ($\text{CH}_4\text{N}_2\text{O}$) is a crystalline substance isolated from urine; morphine ($\text{C}_{17}\text{H}_{19}\text{NO}_3$) is an analgesic (painkiller) named after Morpheus, the Greek god of dreams; and barbituric acid is a tranquilizing agent said to be named by its discoverer in honor of his friend Barbara.

As the science of organic chemistry slowly grew in the 19th century, so too did the number of known compounds and the need for a systematic method of naming them. The system of nomenclature we'll use in this book is that devised by the International Union of Pure and Applied Chemistry (IUPAC, usually spoken as eye-you-pac).

A chemical name typically has four parts in the IUPAC system of nomenclature: prefix, locant, parent, and suffix. The prefix specifies the location and identity of various **substituent** groups in the molecule, the locant gives the location of the primary functional group, the parent selects a main part of the molecule and tells how many carbon atoms are in that part, and the suffix identifies the primary functional group.

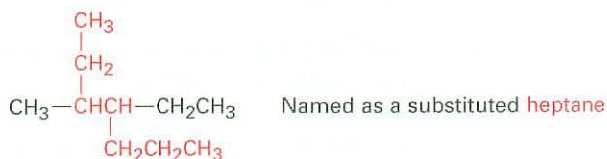


As we cover new functional groups in later chapters, the applicable IUPAC rules of nomenclature will be given. In addition, Appendix A at the back of this book gives an overall view of organic nomenclature and shows how compounds that contain more than one functional group are named. For the present, let's see how to name branched-chain alkanes and learn some general naming rules that are applicable to all compounds.

All but the most complex branched-chain alkanes can be named by following four steps. For a very few compounds, a fifth step is needed.

Step 1 Find the parent hydrocarbon.

- (a) Find the longest continuous chain of carbon atoms in the molecule, and use the name of that chain as the parent name. The longest chain may not always be apparent from the manner of writing; you may have to "turn corners."

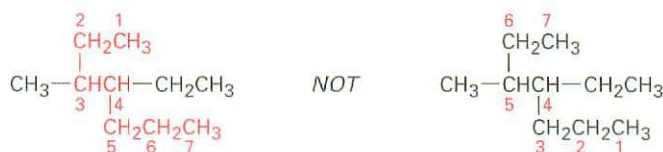


- (b) If two different chains of equal length are present, choose the one with the larger number of branch points as the parent.



Step 2 Number the atoms in the main chain.

- (a) Beginning at the end nearer the first branch point, number each carbon atom in the parent chain.



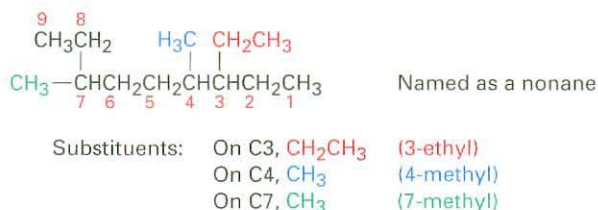
The first branch occurs at C3 in the proper system of numbering, not at C4.

- (b) If there is branching an equal distance away from both ends of the parent chain, begin numbering at the end nearer the second branch point.

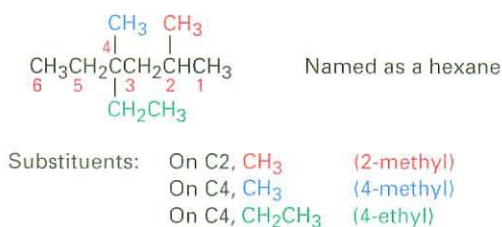


Step 3 Identify and number the substituents.

- (a) Assign a number, called a *locant*, to each substituent to locate its point of attachment to the parent chain.

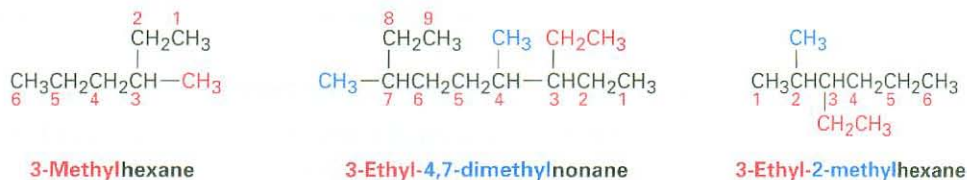


- (b) If there are two substituents on the same carbon, give both the same number. There must be as many numbers in the name as there are substituents.

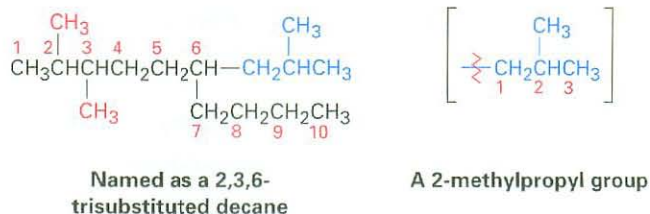


Step 4 Write the name as a single word.

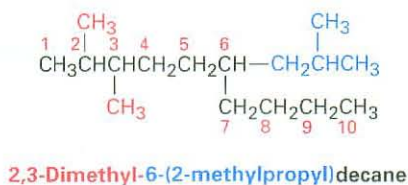
Use hyphens to separate the different prefixes, and use commas to separate numbers. If two or more different substituents are present, cite them in alphabetical order. If two or more identical substituents are present, use one of the multiplier prefixes *di-*, *tri-*, *tetra-*, and so forth, but don't use these prefixes for alphabetizing. Full names for some of the examples we have been using follow.

**Step 5** Name a complex substituent as though it were itself compound.

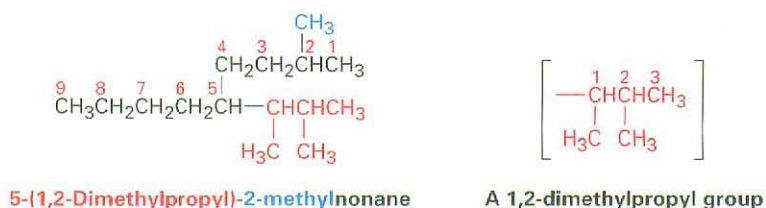
In some particularly complex cases, a fifth step is necessary. It occasionally happens that a substituent on the main chain has sub-branching. In the following case, for instance, the substituent at C6 is a three-carbon chain with a methyl sub-branch. To name the compound fully, the complex substituent must first be named.



Begin numbering the branched substituent at its point of its attachment to the main chain, and identify it as a 2-methylpropyl group. The substituent is alphabetized according to the first letter of its complete name, including any numerical prefix, and is set off in parentheses when naming the entire molecule.



As a further example:



For historical reasons, some of the simpler branched-chain alkyl groups also have nonsystematic, common names, as noted earlier.

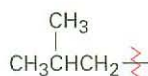
1. Three-carbon alkyl group:



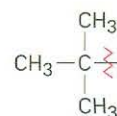
2. Four-carbon alkyl groups:



***sec*-Butyl
(*sec*-Bu)**

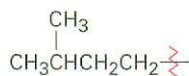


Isobutyl

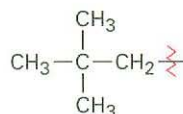


***tert*-Butyl
(*t*-butyl or *t*-Bu)**

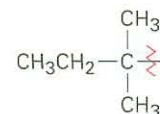
3. Five-carbon alkyl groups:



**Isopentyl, also called
isoamyl (*i*-amyl)**

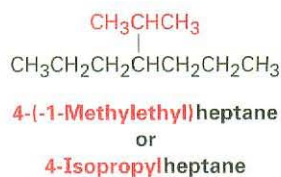


Neopentyl



***tert*-Pentyl, also called
tert-amyl (*t*-amyl)**

The common names of these simple alkyl groups are so well entrenched in the chemical literature that IUPAC rules make allowance for them. Thus, the following compound is properly named either 4-(1-methylethyl)heptane or 4-isopropylheptane. There is no choice but to memorize these common names; fortunately, there are only a few of them.



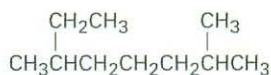
ThomsonNOW Click *Organic Interactive* to use an online palette to draw alkane structures based on IUPAC nomenclature.

When writing an alkane name, the nonhyphenated prefix *iso-* is considered part of the alkyl-group name for alphabetizing purposes, but the hyphenated and italicized prefixes *sec-* and *tert-* are not. Thus, isopropyl and isobutyl are listed alphabetically under *i*, but *sec*-butyl and *tert*-butyl are listed under *b*.

WORKED EXAMPLE 3.2

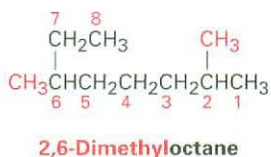
Practice in Naming Alkanes

What is the IUPAC name of the following alkane?



Strategy Find the longest continuous carbon chain in the molecule, and use that as the parent name. This molecule has a chain of eight carbons—octane—with two methyl substituents. (You have to turn corners to see it.) Numbering from the end nearer the first methyl substituent indicates that the methyls are at C2 and C6

Solution



WORKED EXAMPLE 3.3

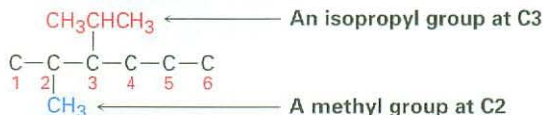
Converting a Chemical Name into a Structure

Draw the structure of 3-isopropyl-2-methylhexane.

Strategy This is the reverse of Worked Example 3.2 and uses a reverse strategy. Look at the parent name (hexane), and draw its carbon structure.

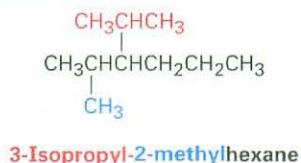


Next, find the substituents (3-isopropyl and 2-methyl), and place them on the proper carbons.



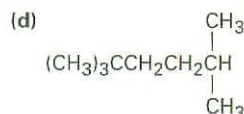
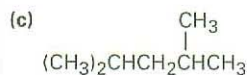
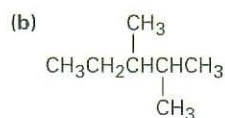
Finally, add hydrogens to complete the structure.

Solution



Problem 3.11 Give IUPAC names for the following compounds:

(a) The three isomers of C_5H_{12}

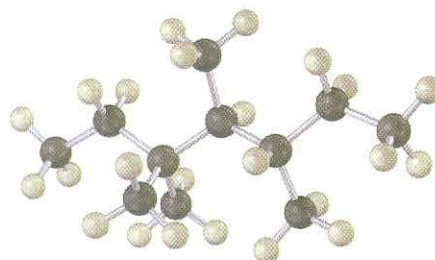


Problem 3.12 Draw structures corresponding to the following IUPAC names:

- (a) 3,4-Dimethylnonane (b) 3-Ethyl-4,4-dimethylheptane
 (c) 2,2-Dimethyl-4-propyloctane (d) 2,2,4-Trimethylpentane

Problem 3.13 Name the eight 5-carbon alkyl groups you drew in Problem 3.7.

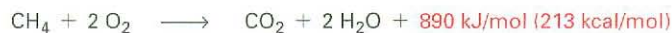
Problem 3.14 Give the IUPAC name for the following hydrocarbon, and convert the drawing into a skeletal structure.



3.5 Properties of Alkanes

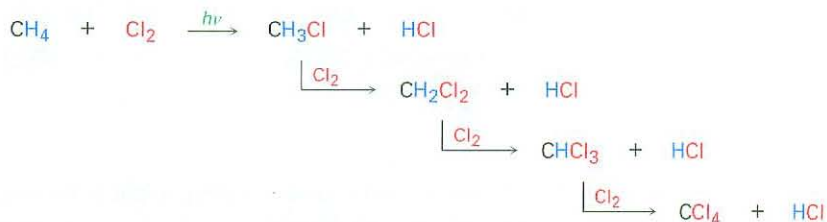
Alkanes are sometimes referred to as *paraffins*, a word derived from the Latin *parum affinis*, meaning “little affinity.” This term aptly describes their behavior, for alkanes show little chemical affinity for other substances and are chemically inert to most laboratory reagents. They are also relatively inert biologically and are not often involved in the chemistry of living organisms. Alkanes do, however, react with oxygen, halogens, and a few other substances under appropriate conditions.

Reaction with oxygen occurs during combustion in an engine or furnace when the alkane is used as a fuel. Carbon dioxide and water are formed as products, and a large amount of heat is released. For example, methane (natural gas) reacts with oxygen according to the equation



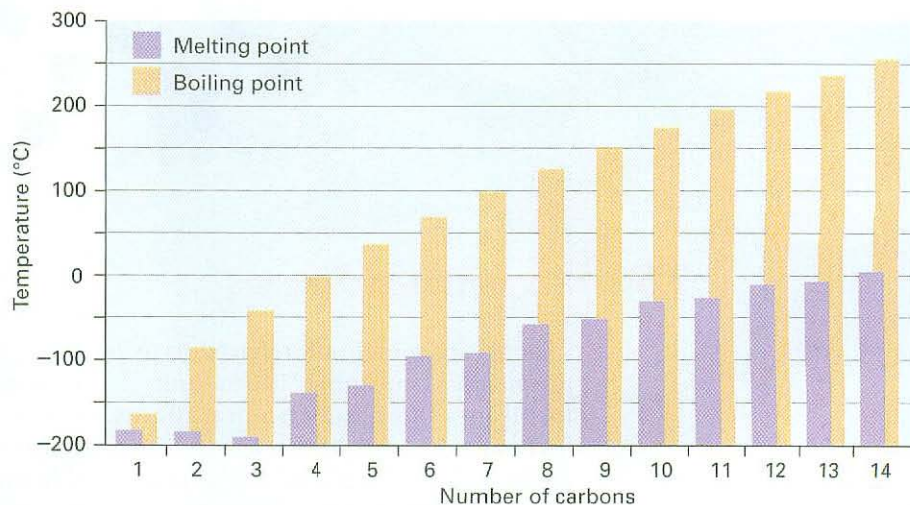
The reaction of an alkane with Cl_2 occurs when a mixture of the two is irradiated with ultraviolet light (denoted $h\nu$, where ν is the Greek letter nu).

Depending on the relative amounts of the two reactants and on the time allowed, a sequential substitution of the alkane hydrogen atoms by chlorine occurs, leading to a mixture of chlorinated products. Methane, for instance, reacts with Cl_2 to yield a mixture of CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 . We'll look at this reaction in more detail in Section 5.3.



Alkanes show regular increases in both boiling point and melting point as molecular weight increases (Figure 3.4), an effect due to the presence of weak dispersion forces between molecules (Section 2.13). Only when sufficient energy is applied to overcome these forces does the solid melt or liquid boil. As you might expect, dispersion forces increase as molecular size increases, accounting for the higher melting and boiling points of larger alkanes.

Active Figure 3.4 A plot of melting and boiling points versus number of carbon atoms for the C_1 - C_{14} alkanes. There is a regular increase with molecular size. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



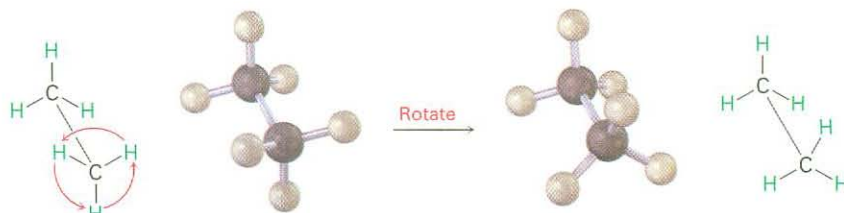
Another interesting effect seen in alkanes is that increased branching lowers an alkane's boiling point. Thus, pentane has no branches and boils at 36.1°C , isopentane (2-methylbutane) has one branch and boils at 27.85°C , and neopentane (2,2-dimethylpropane) has two branches and boils at 9.5°C . Similarly, octane boils at 125.7°C , whereas isooctane (2,2,4-trimethylpentane) boils at 99.3°C . Branched-chain alkanes are lower-boiling because they are more nearly spherical than straight-chain alkanes, have smaller surface areas, and consequently have smaller dispersion forces.

3.6 Conformations of Ethane

Up to this point, we've viewed molecules primarily in a two-dimensional way and have given little thought to any consequences that might arise from the spatial arrangement of atoms in molecules. Now it's time to add a third dimension to our study. **Stereochemistry** is the branch of chemistry concerned with the three-dimensional aspects of molecules. We'll see on many occasions in future chapters that the exact three-dimensional structure of a molecule is often crucial to determining its properties and biological behavior.

We know from Section 1.5 that σ bonds are cylindrically symmetrical. In other words, the intersection of a plane cutting through a carbon-carbon single-bond orbital looks like a circle. Because of this cylindrical symmetry, *rotation* is possible around carbon-carbon bonds in open-chain molecules. In ethane, for instance, rotation around the C-C bond occurs freely, constantly changing the spatial relationships between the hydrogens on one carbon and those on the other (Figure 3.5).

Active Figure 3.5 Rotation occurs around the carbon-carbon single bond in ethane because of σ bond cylindrical symmetry. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



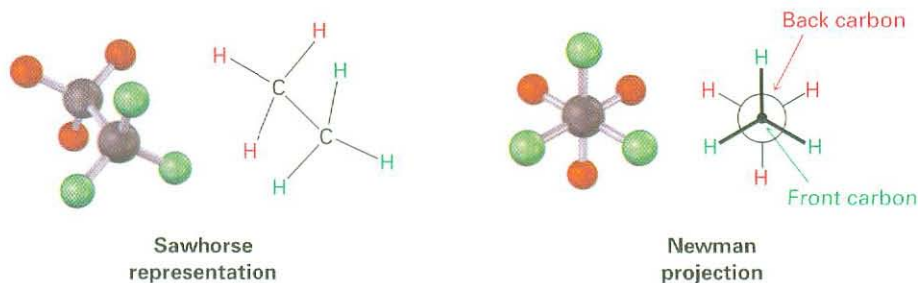
Melvin S. Newman

Melvin S. Newman (1908–1993) was born in New York and received his Ph.D. in 1932 from Yale University. He was professor of chemistry at the Ohio State University (1936–1973), where he was active in both research and chemical education.

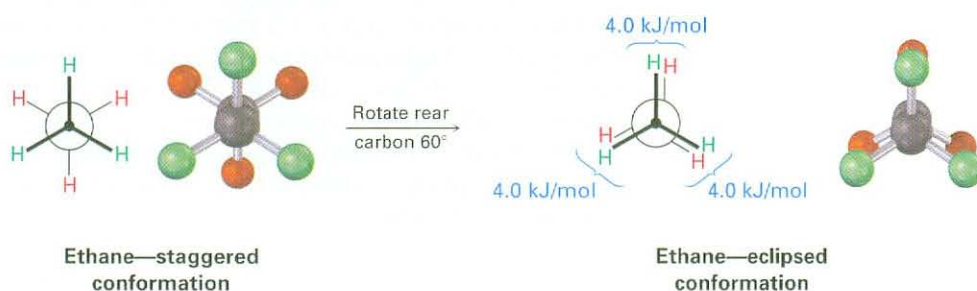
Figure 3.6 A sawhorse representation and a Newman projection of ethane. The sawhorse representation views the molecule from an oblique angle, while the Newman projection views the molecule end-on. Note that the molecular model of the Newman projection appears at first to have six atoms attached to a single carbon. Actually, the front carbon, with three attached green atoms, is directly in front of the rear carbon, with three attached red atoms.

The different arrangements of atoms that result from bond rotation are called **conformations**, and molecules that have different arrangements are called **conformational isomers**, or **conformers**. Unlike constitutional isomers, however, different conformers can't usually be isolated because they interconvert too rapidly.

Conformational isomers are represented in two ways, as shown in Figure 3.6. A *sawhorse representation* views the carbon-carbon bond from an oblique angle and indicates spatial orientation by showing all C-H bonds. A **Newman projection** views the carbon-carbon bond directly end-on and represents the two carbon atoms by a circle. Bonds attached to the front carbon are represented by lines to the center of the circle, and bonds attached to the rear carbon are represented by lines to the edge of the circle.

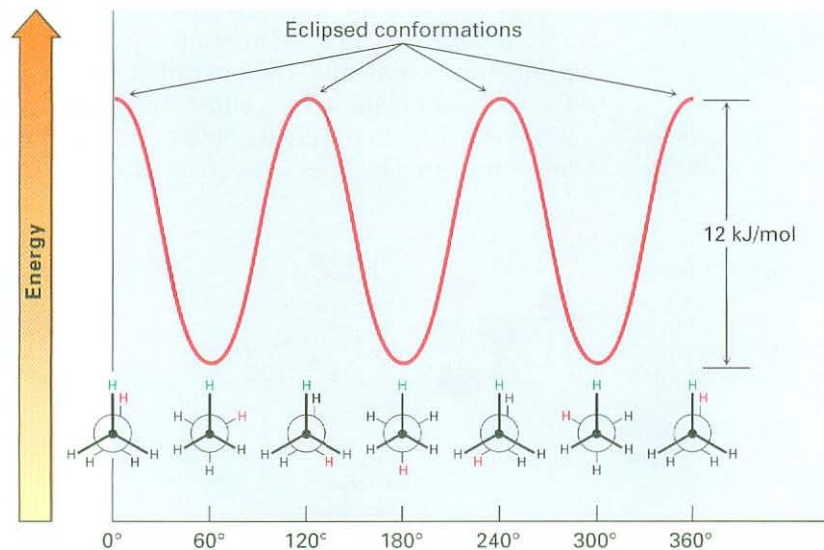


Despite what we've just said, we actually don't observe *perfectly* free rotation in ethane. Experiments show that there is a small (12 kJ/mol; 2.9 kcal/mol) barrier to rotation and that some conformers are more stable than others. The lowest-energy, most stable conformer is the one in which all six C–H bonds are as far away from one another as possible—**staggered** when viewed end-on in a Newman projection. The highest-energy, least stable conformer is the one in which the six C–H bonds are as close as possible—**eclipsed** in a Newman projection. At any given instant, about 99% of ethane molecules have an approximately staggered conformation and only about 1% are near the eclipsed conformation.



The extra 12 kJ/mol of energy present in the eclipsed conformer of ethane is called **torsional strain**. Its cause has been the subject of controversy, but the major factor is an interaction between C–H bonding orbitals on one carbon with antibonding orbitals on the adjacent carbon, which stabilizes the staggered conformer relative to the eclipsed conformer. Because the total strain of 12 kJ/mol arises from three equal hydrogen–hydrogen eclipsing interactions, we can assign a value of approximately 4.0 kJ/mol (1.0 kcal/mol) to each single interaction. The barrier to rotation that results can be represented on a graph of potential energy versus degree of rotation in which the angle between C–H bonds on front and back carbons as viewed end-on (the *dihedral angle*) goes full circle from 0° to 360°. Energy minima occur at staggered conformations, and energy maxima occur at eclipsed conformations, as shown in Figure 3.7.

Figure 3.7 A graph of potential energy versus bond rotation in ethane. The staggered conformers are 12 kJ/mol lower in energy than the eclipsed conformers.

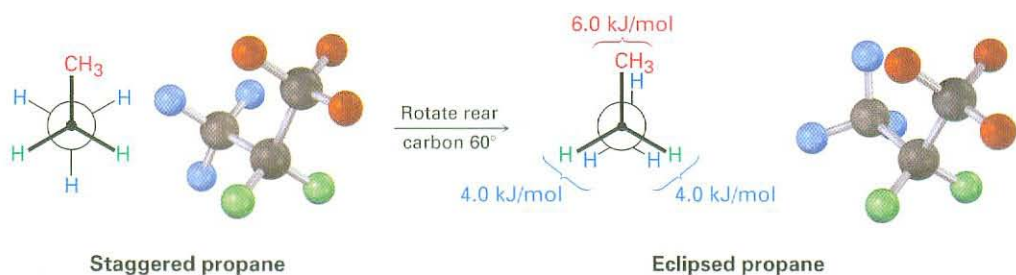


3.7 Conformations of Other Alkanes

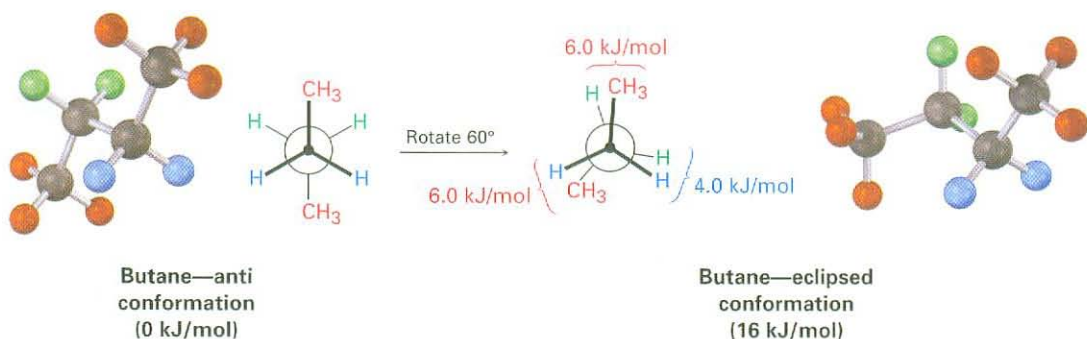
Propane, the next higher member in the alkane series, also has a torsional barrier that results in hindered rotation around the carbon–carbon bonds. The barrier is slightly higher in propane than in ethane—a total of 14 kJ/mol (3.4 kcal/mol) versus 12 kJ/mol.

The eclipsed conformer of propane has three interactions—two ethane-type hydrogen–hydrogen interactions and one additional hydrogen–methyl interaction. Since each eclipsing $\text{H} \leftrightarrow \text{H}$ interaction is the same as that in ethane and thus has an energy “cost” of 4.0 kJ/mol, we can assign a value of $14 - (2 \times 4.0) = 6.0$ kJ/mol (1.4 kcal/mol) to the eclipsing $\text{H} \leftrightarrow \text{CH}_3$ interaction (Figure 3.8).

Figure 3.8 Newman projections of propane showing staggered and eclipsed conformations. The staggered conformer is lower in energy by 14 kJ/mol.

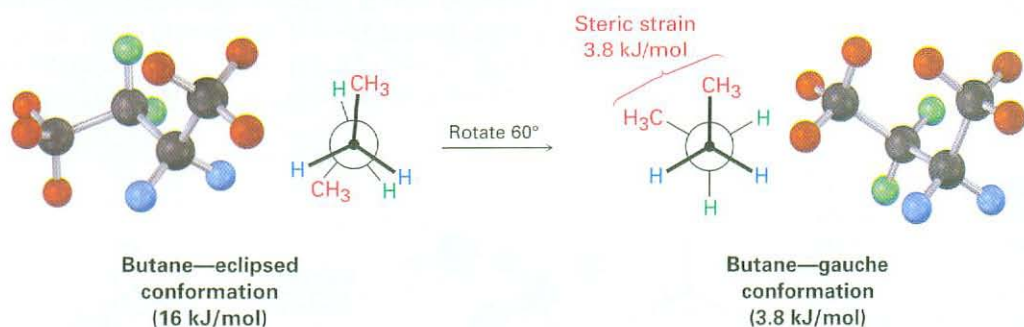


The conformational situation becomes more complex for larger alkanes because not all staggered conformations have the same energy and not all eclipsed conformations have the same energy. In butane, for instance, the lowest-energy arrangement, called the **anti conformation**, is the one in which the two methyl groups are as far apart as possible— 180° away from each other. As rotation around the $\text{C}2\text{--C}3$ bond occurs, an eclipsed conformation is reached in which there are two $\text{CH}_3 \leftrightarrow \text{H}$ interactions and one $\text{H} \leftrightarrow \text{H}$ interaction. Using the energy values derived previously from ethane and propane, this eclipsed conformation is more strained than the anti conformation by 2×6.0 kJ/mol + 4.0 kJ/mol (two $\text{CH}_3 \leftrightarrow \text{H}$ interactions plus one $\text{H} \leftrightarrow \text{H}$ interaction), for a total of 16 kJ/mol (3.8 kcal/mol).

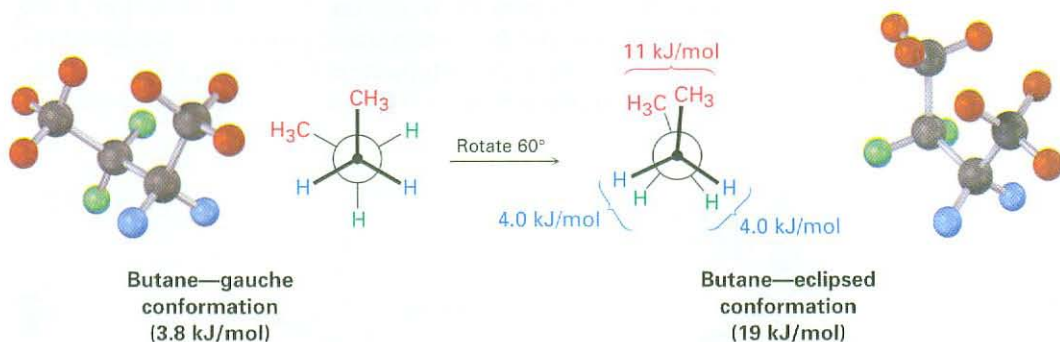


As bond rotation continues, an energy minimum is reached at the staggered conformation where the methyl groups are 60° apart. Called the **gauche**

conformation, it lies 3.8 kJ/mol (0.9 kcal/mol) higher in energy than the anti conformation *even though it has no eclipsing interactions*. This energy difference occurs because the hydrogen atoms of the methyl groups are near one another in the gauche conformation, resulting in what is called *steric strain*. **Steric strain** is the repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow. It's the result of trying to force two atoms to occupy the same space.



As the dihedral angle between the methyl groups approaches 0° , an energy maximum is reached at a second eclipsed conformation. Because the methyl groups are forced even closer together than in the gauche conformation, both torsional strain and steric strain are present. A total strain energy of 19 kJ/mol (4.5 kcal/mol) has been estimated for this conformation, making it possible to calculate a value of 11 kJ/mol (2.6 kcal/mol) for the $\text{CH}_3 \leftrightarrow \text{CH}_3$ eclipsing interaction: total strain of 19 kJ/mol less the strain of two $\text{H} \leftrightarrow \text{H}$ eclipsing interactions ($2 \times 4.0 \text{ kcal/mol}$) equals 11 kJ/mol.



After 0° , the rotation becomes a mirror image of what we've already seen: another gauche conformation is reached, another eclipsed conformation, and finally a return to the anti conformation. A plot of potential energy versus rotation about the C2–C3 bond is shown in Figure 3.9.

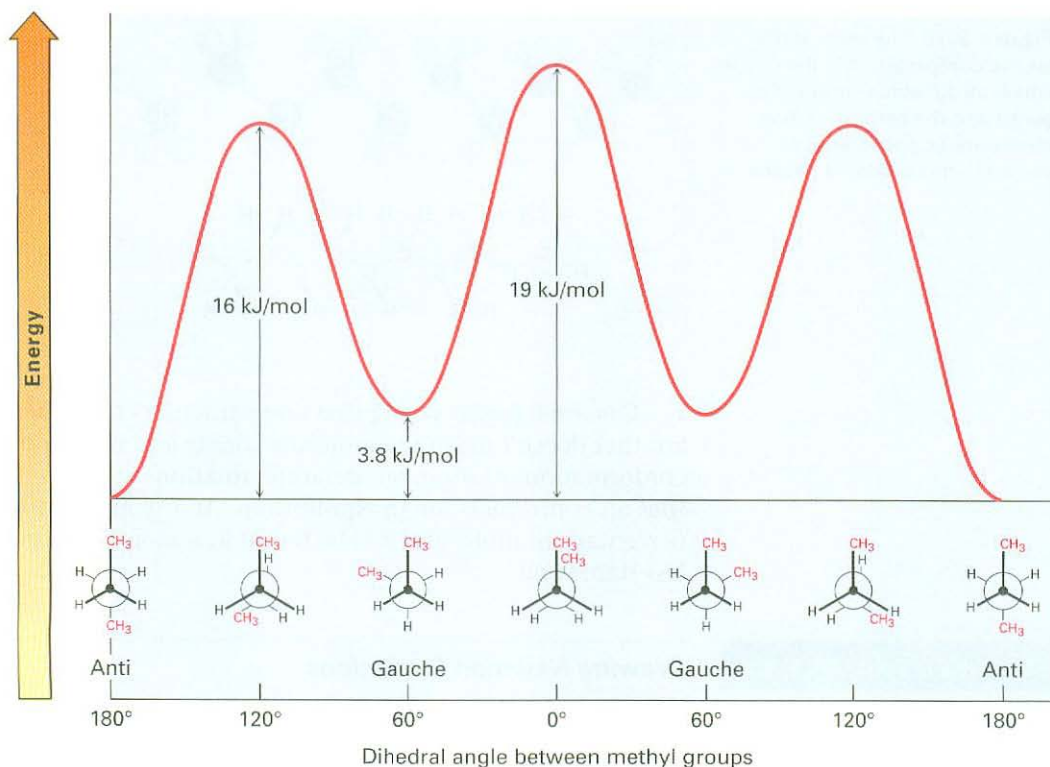


Figure 3.9 A plot of potential energy versus rotation for the C2–C3 bond in butane. The energy maximum occurs when the two methyl groups eclipse each other, and the energy minimum occurs when the two methyl groups are 180° apart (anti).

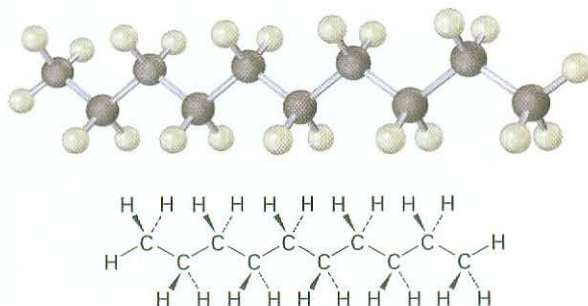
The notion of assigning definite energy values to specific interactions within a molecule is a very useful one that we'll return to in the next chapter. A summary of what we've seen thus far is given in Table 3.5.

Table 3.5 Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost	
		(kJ/mol)	(kcal/mol)
H↔H eclipsed	Torsional strain	4.0	1.0
H↔CH ₃ eclipsed	Mostly torsional strain	6.0	1.4
CH ₃ ↔CH ₃ eclipsed	Torsional and steric strain	11	2.6
CH ₃ ↔CH ₃ gauche	Steric strain	3.8	0.9

The same principles just developed for butane apply to pentane, hexane, and all higher alkanes. The most favorable conformation for any alkane has the carbon–carbon bonds in staggered arrangements, with large substituents arranged anti to one another. A generalized alkane structure is shown in Figure 3.10.

Figure 3.10 The most stable alkane conformation is the one in which all substituents are staggered and the carbon-carbon bonds are arranged anti, as shown in this model of decane.



One final point: saying that one particular conformer is “more stable” than another doesn’t mean the molecule adopts and maintains only the more stable conformation. At room temperature, rotations around σ bonds occur so rapidly that all conformers are in equilibrium. At any given instant, however, a larger percentage of molecules will be found in a more stable conformation than in a less stable one.

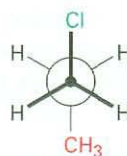
WORKED EXAMPLE 3.4

Drawing Newman Projections

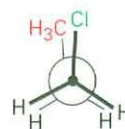
Sighting along the C1–C2 bond of 1-chloropropane, draw Newman projections of the most stable and least stable conformations.

Strategy The most stable conformation of a substituted alkane is generally a staggered one in which large groups have an anti relationship. The least stable conformation is generally an eclipsed one in which large groups are as close as possible.

Solution



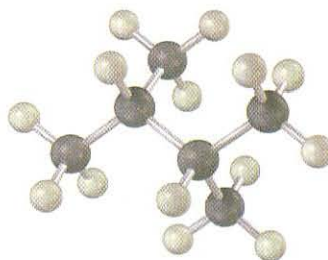
Most stable (staggered)



Least stable (eclipsed)

- Problem 3.15** Make a graph of potential energy versus angle of bond rotation for propane, and assign values to the energy maxima.
- Problem 3.16** Consider 2-methylpropane (isobutane). Sighting along the C2–C1 bond:
- Draw a Newman projection of the most stable conformation.
 - Draw a Newman projection of the least stable conformation.
 - Make a graph of energy versus angle of rotation around the C2–C1 bond.
 - Since an H↔H eclipsing interaction costs 4.0 kJ/mol and an H↔CH₃ eclipsing interaction costs 6.0 kJ/mol, assign relative values to the maxima and minima in your graph.
- Problem 3.17** Sight along the C2–C3 bond of 2,3-dimethylbutane, and draw a Newman projection of the most stable conformation.

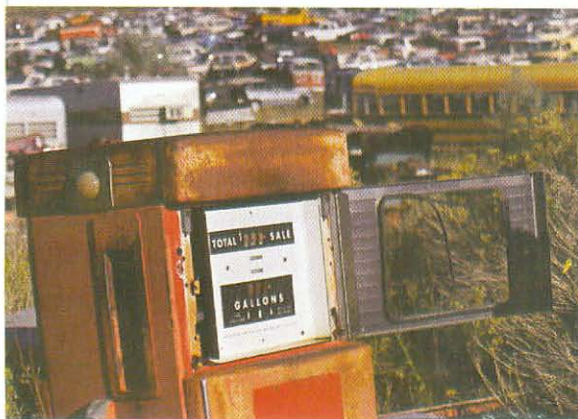
Problem 3.18 Draw a Newman projection along the C2–C3 bond of the following conformation of 2,3-dimethylbutane, and calculate a total strain energy:



Focus On . . .



Gasoline



© Sacha Burkard

British Foreign Minister Ernest Bevin once said that “The Kingdom of Heaven runs on righteousness, but the Kingdom of Earth runs on alkanes.” Well, actually he said “runs on oil” not “runs on alkanes,” but they’re essentially the same. By far, the major sources of alkanes are the world’s natural gas and petroleum deposits. Laid down eons ago, these deposits are thought to be derived from the decomposition of plant and animal matter, primarily of marine origin. *Natural gas* consists chiefly of methane but also contains ethane, propane, and butane. *Petroleum* is a complex mixture of hydrocarbons that must be separated into fractions and then further refined before it can be used.

Gasoline is a finite resource; it won’t be around forever.

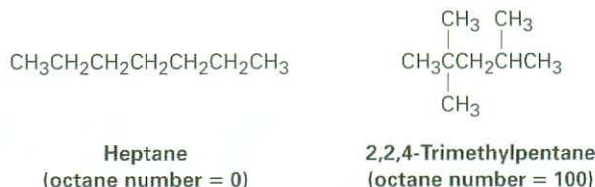
The petroleum era began in August 1859, when the world’s first oil well was drilled near Titusville, Pennsylvania. The petroleum was distilled into fractions according to boiling point, but it was high-boiling kerosene, or lamp oil, rather than gasoline that was primarily sought. Literacy was becoming widespread at the time, and people wanted better light for reading than was available from candles. Gasoline was too volatile for use in lamps and was initially considered a waste by-product. The world has changed greatly since those early days, however, and it is now gasoline rather than lamp oil that is prized.

Petroleum refining begins by fractional distillation of crude oil into three principal cuts according to boiling point (bp): straight-run gasoline (bp 30–200 °C), kerosene (bp 175–300 °C), and heating oil, or diesel fuel (bp 275–400 °C). Further distillation under reduced pressure then yields

(continued)

lubricating oils and waxes and leaves a tarry residue of asphalt. The distillation of crude oil is only the first step in gasoline production, however. Straight-run gasoline turns out to be a poor fuel in automobiles because of *engine knock*, an uncontrolled combustion that can occur in a hot engine.

The *octane number* of a fuel is the measure by which its antiknock properties are judged. It was recognized long ago that straight-chain hydrocarbons are far more prone to induce engine knock than are highly branched compounds. Heptane, a particularly bad fuel, is assigned a base value of 0 octane number, and 2,2,4-trimethylpentane, commonly known as isooctane, has a rating of 100.



Because straight-run gasoline burns so poorly in engines, petroleum chemists have devised numerous methods for producing higher-quality fuels. One of these methods, *catalytic cracking*, involves taking the high-boiling kerosene cut (C_{11} – C_{14}) and “cracking” it into smaller branched molecules suitable for use in gasoline. Another process, called *reforming*, is used to convert C_6 – C_8 alkanes to aromatic compounds such as benzene and toluene, which have substantially higher octane numbers than alkanes. The final product that goes in your tank has an approximate composition of 15% C_4 – C_8 straight-chain alkanes, 25% to 40% C_4 – C_{10} branched-chain alkanes, 10% cyclic alkanes, 10% straight-chain and cyclic alkenes, and 25% arenes (aromatics).

SUMMARY AND KEY WORDS

A **functional group** is a group of atoms within a larger molecule that has a characteristic chemical reactivity. Because functional groups behave in approximately the same way in all molecules where they occur, the chemical reactions of an organic molecule are largely determined by its functional groups.

Alkanes are a class of **saturated hydrocarbons** with the general formula $\text{C}_n\text{H}_{2n+2}$. They contain no functional groups, are relatively inert, and can be either **straight-chain** (*normal*) or **branched**. Alkanes are named by a series of IUPAC rules of nomenclature. Compounds that have the same chemical formula but different structures are called **isomers**. More specifically, compounds such as butane and isobutane, which differ in their connections between atoms, are called **constitutional isomers**.

Carbon–carbon single bonds in alkanes are formed by σ overlap of carbon sp^3 hybrid orbitals. Rotation is possible around σ bonds because of their cylindrical

aliphatic, 79
alkane, 79
alkyl group, 83
anti conformation, 95
branched-chain alkane, 80
conformation, 93
conformers, 93
constitutional isomers, 81
eclipsed conformation, 94
functional group, 73
gauche conformation, 95

hydrocarbon, 79
 isomers, 81
 Newman projection, 93
 R group, 84
 saturated, 79
 staggered conformation, 94
 stereochemistry, 93
 steric strain, 96
 straight-chain alkane, 80
 substituent, 86
 torsional strain, 94

symmetry, and alkanes therefore exist in a large number of rapidly interconverting **conformations**. **Newman projections** make it possible to visualize the spatial consequences of bond rotation by sighting directly along a carbon-carbon bond axis. Not all alkane conformations are equally stable. The **staggered** conformation of ethane is 12 kJ/mol (2.9 kcal/mol) more stable than the **eclipsed** conformation because of **torsional strain**. In general, any alkane is most stable when all its bonds are staggered.

EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW Sign in at www.thomsonedu.com to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.



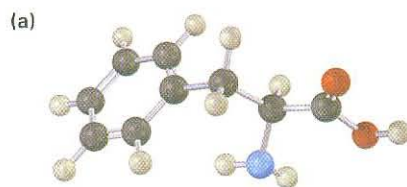
Online homework for this chapter may be assigned in Organic OWL.

■ indicates problems assignable in Organic OWL.

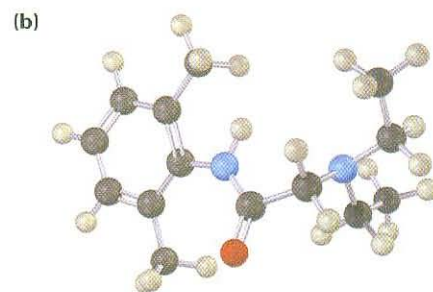
VISUALIZING CHEMISTRY

(Problems 3.1–3.18 appear within the chapter.)

3.19 ■ Identify the functional groups in the following substances, and convert each drawing into a molecular formula (red = O, blue = N):



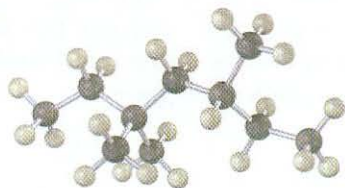
Phenylalanine



Lidocaine

3.20 ■ Give IUPAC names for the following alkanes, and convert each drawing into a skeletal structure:

(a)



(b)



(c)

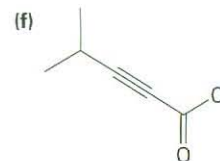
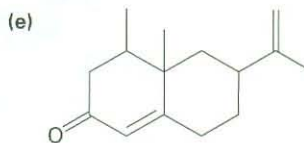
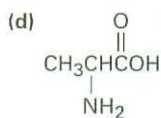
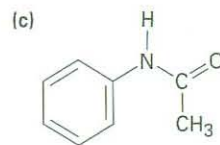
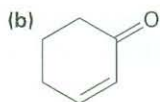
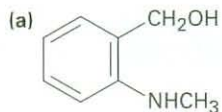


(d)



ADDITIONAL PROBLEMS

3.21 ■ Locate and identify the functional groups in the following molecules. In these representations, each intersection of lines and the end of each line represents a carbon atom with the appropriate number of hydrogens attached.



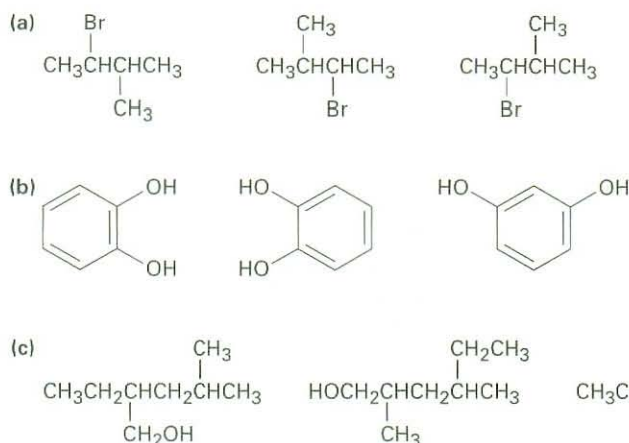
3.22 Draw structures that meet the following descriptions (there are many possibilities):

(a) Three isomers with the formula C_8H_{18}

(b) Two isomers with the formula $C_4H_8O_2$

3.23 Draw structures of the nine isomers of C_7H_{16} .

3.24 ■ In each of the following sets, which structures represent the same compound and which represent different compounds?



3.25 There are seven constitutional isomers with the formula $C_4H_{10}O$. Draw as many as you can.

3.26 ■ Propose structures that meet the following descriptions:

- (a) A ketone with five carbons (b) A four-carbon amide
 (c) A five-carbon ester (d) An aromatic aldehyde
 (e) A keto ester (f) An amino alcohol

3.27 ■ Propose structures for the following:

- (a) A ketone, C_4H_8O (b) A nitrile, C_5H_9N
 (c) A dialdehyde, $C_4H_6O_2$ (d) A bromoalkene, $C_6H_{11}Br$
 (e) An alkane, C_6H_{14} (f) A *cyclic* saturated hydrocarbon, C_6H_{12}
 (g) A diene (dialkene), C_5H_8 (h) A keto alkene, C_5H_8O

3.28 Draw as many compounds as you can that fit the following descriptions:

- (a) Alcohols with formula $C_4H_{10}O$ (b) Amines with formula $C_5H_{13}N$
 (c) Ketones with formula $C_5H_{10}O$ (d) Aldehydes with formula $C_5H_{10}O$
 (e) Esters with formula $C_4H_8O_2$ (f) Ethers with formula $C_4H_{10}O$

3.29 ■ Draw compounds that contain the following:

- (a) A primary alcohol (b) A tertiary nitrile
 (c) A secondary thiol (d) Both primary and secondary alcohols
 (e) An isopropyl group (f) A quaternary carbon

3.30 Draw and name all monobromo derivatives of pentane, $C_5H_{11}Br$.

3.31 Draw and name all monochloro derivatives of 2,5-dimethylhexane, $C_8H_{17}Cl$.

3.32 Predict the hybridization of the carbon atom in each of the following functional groups:

- (a) Ketone (b) Nitrile (c) Carboxylic acid

3.33 ■ Draw the structures of the following molecules:

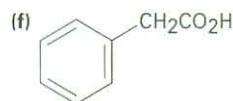
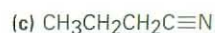
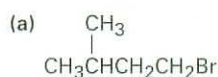
- (a) *Biacetyl*, $C_4H_6O_2$, a substance with the aroma of butter; it contains no rings or carbon-carbon multiple bonds.
 (b) *Ethylenimine*, C_2H_5N , a substance used in the synthesis of melamine polymers; it contains no multiple bonds.
 (c) *Glycerol*, $C_3H_8O_3$, a substance isolated from fat and used in cosmetics; it has an $-OH$ group on each carbon.

- 3.34** ■ Draw structures for the following:
- | | |
|------------------------------------|---------------------------------|
| (a) 2-Methylheptane | (b) 4-Ethyl-2,2-dimethylhexane |
| (c) 4-Ethyl-3,4-dimethyloctane | (d) 2,4,4-Trimethylheptane |
| (e) 3,3-Diethyl-2,5-dimethylnonane | (f) 4-Isopropyl-3-methylheptane |

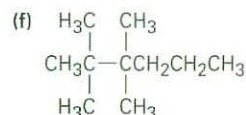
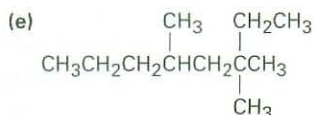
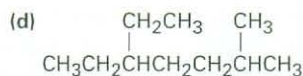
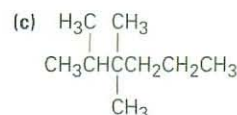
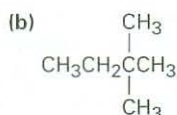
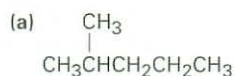
- 3.35** Draw a compound that:
- Has only primary and tertiary carbons
 - Has no secondary or tertiary carbons
 - Has four secondary carbons

- 3.36** Draw a compound that:
- Has nine primary hydrogens
 - Has only primary hydrogens

- 3.37** For each of the following compounds, draw an isomer that has the same functional groups. Each intersection of lines represents a carbon atom with the appropriate number of hydrogens attached.



- 3.38** ■ Give IUPAC names for the following compounds:



- 3.39** Name the five isomers of C_6H_{14} .

- 3.40** Explain why each of the following names is incorrect:

- | | |
|---------------------------------|---------------------------------|
| (a) 2,2-Dimethyl-6-ethylheptane | (b) 4-Ethyl-5,5-dimethylpentane |
| (c) 3-Ethyl-4,4-dimethylhexane | (d) 5,5,6-Trimethyloctane |
| (e) 2-Isopropyl-4-methylheptane | |

- 3.41** Propose structures and give IUPAC names for the following:

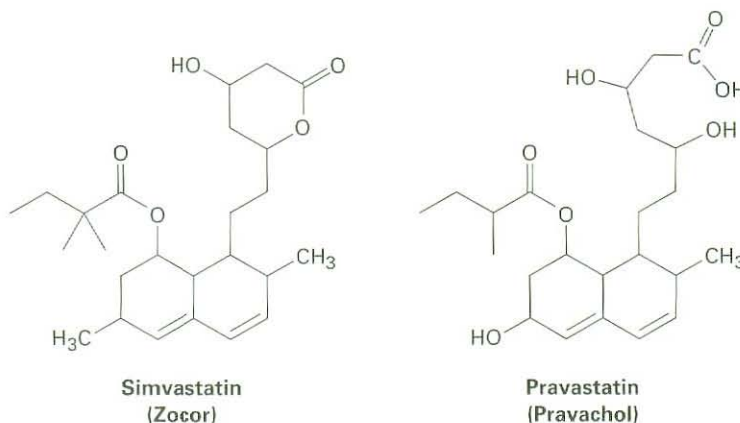
- | | |
|-----------------------------|--|
| (a) A diethyldimethylhexane | (b) A (3-methylbutyl)-substituted alkane |
|-----------------------------|--|

- 3.42** ■ Consider 2-methylbutane (isopentane). Sighting along the C2–C3 bond:

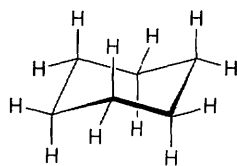
- Draw a Newman projection of the most stable conformation.
- Draw a Newman projection of the least stable conformation.
- Since a $\text{CH}_3 \leftrightarrow \text{CH}_3$ eclipsing interaction costs 11 kJ/mol (2.5 kcal/mol) and a $\text{CH}_3 \leftrightarrow \text{CH}_3$ gauche interaction costs 3.8 kJ/mol (0.9 kcal/mol), make a quantitative plot of energy versus rotation about the C2–C3 bond.

- 3.43** ■ What are the relative energies of the three possible staggered conformations around the C2–C3 bond in 2,3-dimethylbutane? (See Problem 3.42.)

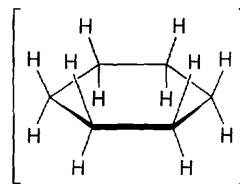
- 3.44** Construct a qualitative potential-energy diagram for rotation about the C–C bond of 1,2-dibromoethane. Which conformation would you expect to be more stable? Label the anti and gauche conformations of 1,2-dibromoethane.
- 3.45** Which conformation of 1,2-dibromoethane (Problem 3.44) would you expect to have the larger dipole moment? The observed dipole moment of 1,2-dibromoethane is $\mu = 1.0$ D. What does this tell you about the actual structure of the molecule?
- 3.46** ■ The barrier to rotation about the C–C bond in bromoethane is 15 kJ/mol (3.6 kcal/mol).
 (a) What energy value can you assign to an H–Br eclipsing interaction?
 (b) Construct a quantitative diagram of potential energy versus bond rotation for bromoethane.
- 3.47** Draw the most stable conformation of pentane, using wedges and dashes to represent bonds coming out of the paper and going behind the paper, respectively.
- 3.48** Draw the most stable conformation of 1,4-dichlorobutane, using wedges and dashes to represent bonds coming out of the paper and going behind the paper, respectively.
- 3.49** Malic acid, $C_4H_6O_5$, has been isolated from apples. Because this compound reacts with 2 molar equivalents of base, it is a dicarboxylic acid.
 (a) Draw at least five possible structures.
 (b) If malic acid is a secondary alcohol, what is its structure?
- 3.50** ■ Formaldehyde, $H_2C=O$, is known to all biologists because of its usefulness as a tissue preservative. When pure, formaldehyde *trimerizes* to give trioxane, $C_3H_6O_3$, which, surprisingly enough, has no carbonyl groups. Only one monobromo derivative ($C_3H_5BrO_3$) of trioxane is possible. Propose a structure for trioxane.
- 3.51** ■ Increased substitution around a bond leads to increased strain. Take the four substituted butanes listed below, for example. For each compound, sight along the C2–C3 bond and draw Newman projections of the most stable and least stable conformations. Use the data in Table 3.5 to assign strain energy values to each conformation. Which of the eight conformations is most strained? Which is least strained?
 (a) 2-Methylbutane (b) 2,2-Dimethylbutane
 (c) 2,3-Dimethylbutane (d) 2,2,3-Trimethylbutane
- 3.52** The cholesterol-lowering agents called *statins*, such as simvastatin (Zocor) and pravastatin (Pravachol), are among the most widely prescribed drugs in the world. Identify the functional groups in both, and tell how the two substances differ.



3.53 We'll look in the next chapter at *cycloalkanes*—saturated cyclic hydrocarbons—and we'll see that the molecules generally adopt puckered, nonplanar conformations. Cyclohexane, for instance, has a puckered shape like a lounge chair rather than a flat shape. Why?

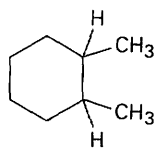


Nonplanar cyclohexane



Planar cyclohexane

3.54 We'll see in the next chapter that there are two isomeric substances both named 1,2-dimethylcyclohexane. Explain.



1,2-Dimethylcyclohexane