

CHAPTER 2

ALKANES

Now that we've reviewed the various bonding models, we are ready to examine organic compounds in respect to their *structure, reactions, properties, and applications*. Were we to list the physical and chemical properties of each of the more than 8 million organic compounds separately, it would tax the capacity of even a powerful computer. Yet someone who is trained in organic chemistry can simply look at the structure of a substance and make reasonably confident predictions about its properties, including how it will behave in a chemical reaction.

Organic chemists associate particular structural units, called **functional groups**, with characteristic patterns of reactivity; they look at large molecules as collections of functional groups attached to nonreactive frameworks. Not only does this “functional group approach” have predictive power, but time and experience have shown that it organizes the material in a way that makes learning organic chemistry easier for most students.

We'll begin the chapter with a brief survey of various kinds of *hydrocarbons*—compounds that contain only carbon and hydrogen—introduce some functional groups, then return to hydrocarbons to discuss *alkanes* in some detail. The names of alkanes may seem strange at first, but they form the foundation for the most widely accepted system of *organic nomenclature*. The fundamentals of this nomenclature system, the **IUPAC rules**, constitute one of the main topics of this chapter.

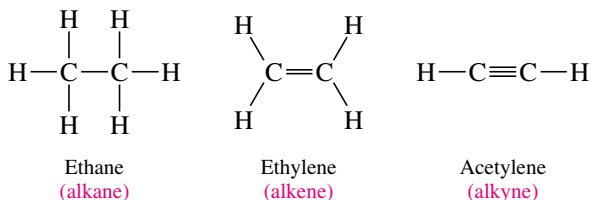
2.1 CLASSES OF HYDROCARBONS

Hydrocarbons are compounds that contain only carbon and hydrogen and are divided into two main classes: **aliphatic** hydrocarbons and **aromatic** hydrocarbons. This classification dates from the nineteenth century, when organic chemistry was almost exclusively devoted

to the study of materials from natural sources, and terms were coined that reflected a substance's origin. Two sources were fats and oils, and the word *aliphatic* was derived from the Greek word *aleiphar* ("fat"). Aromatic hydrocarbons, irrespective of their own odor, were typically obtained by chemical treatment of pleasant-smelling plant extracts.

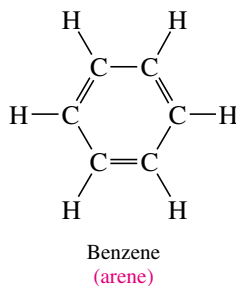
Aliphatic hydrocarbons include three major groups: *alkanes*, *alkenes*, and *alkynes*. **Alkanes** are hydrocarbons in which all the bonds are single bonds, **alkenes** contain a carbon–carbon double bond, and **alkynes** contain a carbon–carbon triple bond. Examples of the three classes of aliphatic hydrocarbons are the two-carbon compounds *ethane*, *ethylene*, and *acetylene*.

Bonding in ethane, ethylene, and acetylene was discussed in Sections 1.16–1.18.



Another name for aromatic hydrocarbons is **arenes**. Arenes have properties that are much different from alkanes, alkenes, and alkynes. The most important aromatic hydrocarbon is *benzene*.

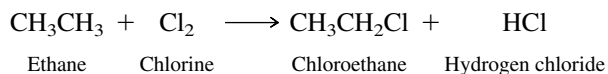
Bonding in benzene will be discussed in Section 11.5.



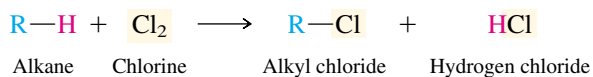
Many of the principles of organic chemistry can be developed by examining the series of hydrocarbons in the order: alkanes, alkenes, alkynes, and arenes. Alkanes are introduced in this chapter, alkenes in Chapters 5 and 6, alkynes in Chapter 9, and arenes in Chapters 11 and 12.

2.2 REACTIVE SITES IN HYDROCARBONS

A functional group is the structural unit responsible for a given molecule's reactivity under a particular set of conditions. It can be as small as a single hydrogen atom, or it can encompass several atoms. The functional group of an alkane is any one of its hydrogen substituents. A reaction that we shall discuss in Chapter 4 is one in which an alkane reacts with chlorine. For example:



One of the hydrogen atoms of ethane is replaced by chlorine. This replacement of hydrogen by chlorine is a characteristic reaction of all alkanes and can be represented for the general case by the equation:



In the general equation the functional group (—H) is shown explicitly while the remainder of the alkane molecule is abbreviated as R. This is a commonly used notation which helps focus our attention on the functional group transformation without being distracted by the parts of the molecule that remain unaffected. A hydrogen atom in one alkane is very much like the hydrogen of any other alkane in its reactivity toward chlorine. Our ability to write general equations such as the one shown illustrates why the functional group approach is so useful in organic chemistry.

A hydrogen atom is a functional unit in alkenes and alkynes as well as in alkanes. These hydrocarbons, however, contain a second functional group as well. The carbon–carbon double bond is a functional group in alkenes, and the carbon–carbon triple bond is a functional group in alkynes.

A hydrogen atom is a functional group in arenes, and we represent arenes as ArH to reflect this. What will become apparent when we discuss the reactions of arenes, however, is that their chemistry is much richer than that of alkanes, and it is therefore more appropriate to consider the ring in its entirety as the functional group.

2.3 THE KEY FUNCTIONAL GROUPS

As a class, alkanes are not particularly reactive compounds, and the H in RH is not a particularly reactive functional group. Indeed, when a group other than hydrogen is present on an alkane framework, that group is almost always the functional group. Table 2.1 lists examples of some compounds of this type. All will be discussed in later chapters.

Some of the most important families of organic compounds, those that contain the carbonyl group (C=O), deserve separate mention and are listed in Table 2.2. Carbonyl-containing compounds rank among the most abundant and biologically significant classes of naturally occurring substances.

Carbonyl group chemistry is discussed in a block of five chapters (Chapters 17–21).

PROBLEM 2.1 Many compounds contain more than one functional group. The structure of *prostaglandin E₁*, a hormone that regulates the relaxation of smooth muscles, contains two different kinds of carbonyl groups. Classify each one (aldehyde, ketone, carboxylic acid, ester, amide, acyl chloride, or carboxylic acid anhydride).

TABLE 2.1 Functional Groups in Some Important Classes of Organic Compounds

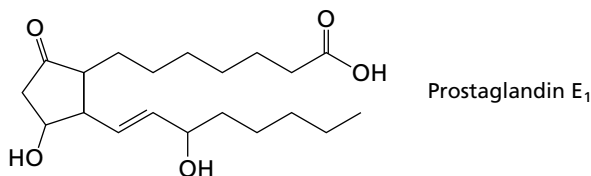
Class	Generalized abbreviation	Representative example	Name of example*
Alcohol	ROH	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol
Alkyl halide	RCl	$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane
Amine [†]	RNH_2	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethanamine
Epoxide	$\text{R}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{CR}_2$	$\text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{---} \end{array} \text{CH}_2$	Oxirane
Ether	ROR	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	Diethyl ether
Nitrile	$\text{RC}\equiv\text{N}$	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$	Propanenitrile
Nitroalkane	RNO_2	$\text{CH}_3\text{CH}_2\text{NO}_2$	Nitroethane
Thiol	RSH	$\text{CH}_3\text{CH}_2\text{SH}$	Ethanethiol

*Most compounds have more than one acceptable name.

[†]The example given is a *primary* amine (RNH_2). *Secondary* amines have the general structure R_2NH ; *tertiary* amines are R_3N .

TABLE 2.2 Classes of Compounds That Contain a Carbonyl Group

Class	Generalized abbreviation	Representative example	Name of example
Aldehyde	$\text{R}\overset{\text{O}}{\parallel}\text{CH}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CH}$	Ethanal
Ketone	$\text{R}\overset{\text{O}}{\parallel}\text{CR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$	2-Propanone
Carboxylic acid	$\text{R}\overset{\text{O}}{\parallel}\text{COH}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COH}$	Ethanoic acid
Carboxylic acid derivatives:			
Acyl halide	$\text{R}\overset{\text{O}}{\parallel}\text{CX}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCl}$	Ethanoyl chloride
Acid anhydride	$\text{R}\overset{\text{O}}{\parallel}\text{CO}\overset{\text{O}}{\parallel}\text{CR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CO}\overset{\text{O}}{\parallel}\text{CCH}_3$	Ethanoic anhydride
Ester	$\text{R}\overset{\text{O}}{\parallel}\text{COR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_3$	Ethyl ethanoate
Amide	$\text{R}\overset{\text{O}}{\parallel}\text{CNR}_2$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CNH}_2$	Ethanamide



The reactions of the carbonyl group feature prominently in *organic synthesis*—the branch of organic chemistry that plans and carries out the preparation of compounds of prescribed structure.

2.4 INTRODUCTION TO ALKANES: METHANE, ETHANE, AND PROPANE

See the boxed essay: "Methane and the Biosphere" that accompanies this section.

Alkanes have the general molecular formula $\text{C}_n\text{H}_{2n+2}$. The simplest one, **methane** (CH_4), is also the most abundant. Large amounts are present in our atmosphere, in the ground, and in the oceans. Methane has been found on Jupiter, Saturn, Uranus, Neptune, and Pluto, and even on Halley's Comet.

Ethane (C_2H_6 ; CH_3CH_3) and **propane** (C_3H_8 ; $\text{CH}_3\text{CH}_2\text{CH}_3$) are second and third, respectively, to methane in many ways. Ethane is the alkane next to methane in structural simplicity, followed by propane. Ethane ($\approx 10\%$) is the second and propane ($\approx 5\%$) the third most abundant component of natural gas, which is $\approx 75\%$ methane. The characteristic odor of natural gas we use for heating our homes and cooking comes from

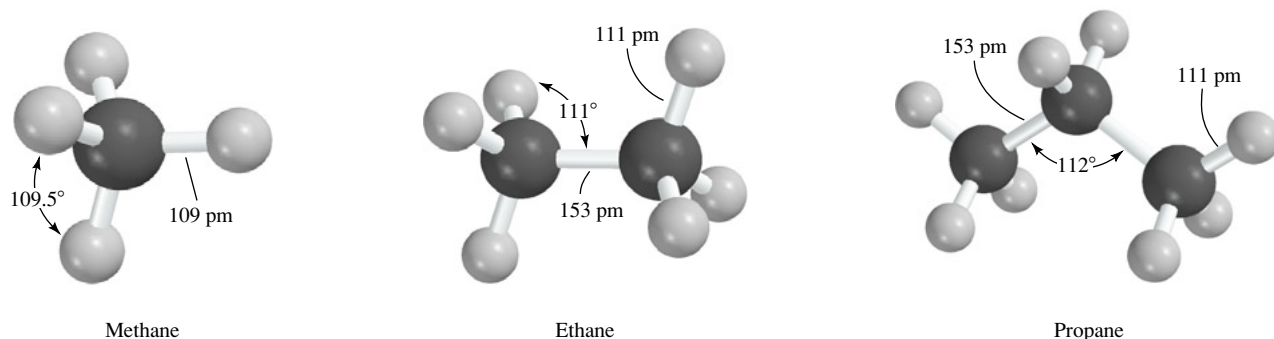


FIGURE 2.1 Structures of methane, ethane, and propane showing bond distances and bond angles.

trace amounts of unpleasant-smelling sulfur-containing compounds such as ethanethiol (see Table 2.1) that are deliberately added to it in order to warn us of potentially dangerous leaks. Natural gas is colorless and nearly odorless, as are methane, ethane, and propane.

Methane is the lowest boiling alkane, followed by ethane, then propane.

	CH ₄	CH ₃ CH ₃	CH ₃ CH ₂ CH ₃
	Methane	Ethane	Propane
Boiling point:	-160°C	-89°C	-42°C

Boiling points cited in this text are at 1 atm (760 mm of mercury) unless otherwise stated.

This will generally be true as we proceed to look at other alkanes; as the number of carbon atoms increases, so does the boiling point. All the alkanes with four carbons or less are gases at room temperature and atmospheric pressure. With the highest boiling point of the three, propane is the easiest one to liquefy. We are all familiar with “propane tanks.” These are steel containers in which a propane-rich mixture of hydrocarbons called *liquefied petroleum gas* (LPG) is maintained in a liquid state under high pressure as a convenient clean-burning fuel.

The structural features of methane, ethane, and propane are summarized in Figure 2.1. All of the carbon atoms are sp^3 -hybridized, all of the bonds are σ bonds, and the bond angles at carbon are close to tetrahedral.



Use your *Learning By Modeling* software to reproduce the models shown in Figure 2.1 so that you can better view their three-dimensional shapes.

2.5 ISOMERIC ALKANES: THE BUTANES

Methane is the only alkane of molecular formula CH₄, ethane the only one that is C₂H₆, and propane the only one that is C₃H₈. Beginning with C₄H₁₀, however, constitutional isomers (Section 1.8) are possible; two alkanes have this particular molecular formula. In one, called ***n*-butane**, four carbons are joined in a continuous chain. The *n* in *n*-butane stands for “normal” and means that the carbon chain is unbranched. The second isomer has a branched carbon chain and is called **isobutane**.

	CH ₃ CH ₂ CH ₂ CH ₃	CH ₃ CHCH ₃ CH ₃	or	(CH ₃) ₃ CH
	<i>n</i> -Butane	Isobutane		
Boiling point:	-0.4°C	-10.2°C		
Melting point:	-139°C	-160.9°C		

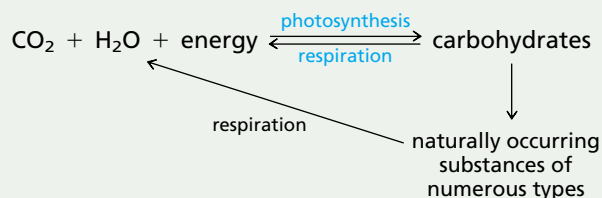


Make molecular models of the two isomers of C₄H₁₀.

As noted earlier (Section 1.16), CH₃ is called a *methyl* group. In addition to having methyl groups at both ends, *n*-butane contains two CH₂, or **methylene** groups. Isobutane contains three methyl groups bonded to a CH unit. The CH unit is called a **methine** group.

METHANE AND THE BIOSPHERE*

One of the things that environmental scientists do is to keep track of important elements in the biosphere—in what form do these elements normally occur, to what are they transformed, and how are they returned to their normal state? Careful studies have given clear, although complicated, pictures of the “nitrogen cycle,” the “sulfur cycle,” and the “phosphorus cycle,” for example. The “carbon cycle,” begins and ends with atmospheric carbon dioxide. It can be represented in an abbreviated form as:



Methane is one of literally millions of compounds in the carbon cycle, but one of the most abundant. It is formed when carbon-containing compounds decompose in the absence of air (*anaerobic* conditions). The organisms that bring this about are called *methanoarchaea*. Cells can be divided into three types: *archaea*, *bacteria*, and *eukarya*. Methanoarchaea are one kind of archaea and may rank among the oldest living things on earth. They can convert a number of carbon-containing compounds, including carbon dioxide and acetic acid, to methane.

Virtually anywhere water contacts organic matter in the absence of air is a suitable place for methanoarchaea to thrive—at the bottom of ponds, bogs, and rice fields, for example. *Marsh gas* (*swamp gas*) is mostly methane. Methanoarchaea live inside termites and grass-eating animals. One source quotes 20 L/day as the methane output of a large cow.

The scale on which methanoarchaea churn out methane, estimated to be 10^{11} – 10^{12} lb/year, is enormous. About 10% of this amount makes its way into

the atmosphere, but most of the rest simply ends up completing the carbon cycle. It exits the anaerobic environment where it was formed and enters the aerobic world where it is eventually converted to carbon dioxide by a variety of processes.

When we consider sources of methane we have to add “old” methane, methane that was formed millions of years ago but became trapped beneath the earth’s surface, to the “new” methane just described. *Firedamp*, an explosion hazard to miners, occurs in layers of coal and is mostly methane. Petroleum deposits, formed by microbial decomposition of plant material under anaerobic conditions, are always accompanied by pockets of natural gas, which is mostly methane.

An interesting thing happens when trapped methane leaks from sites under the deep ocean floor. If the pressure is high enough (50 atm) and the water cold enough (4°C), the methane doesn’t simply bubble to the surface. Individual methane molecules become trapped inside clusters of 6–18 water molecules forming *methane clathrates* or *methane hydrates*. Aggregates of these clathrates stay at the bottom of the ocean in what looks like a lump of dirty ice. Ice that burns. Far from being mere curiosities, methane clathrates are potential sources of energy on a scale greater than that of all known oil reserves combined. At present, it is not economically practical to extract the methane, however.

Methane clathrates have received recent attention from a different segment of the scientific community. While diving in the Gulf of Mexico in 1997, a research team of biologists and environmental scientists were surprised to find a new species of worm grazing on the mound of a methane clathrate. What were these worms feeding on? Methane? Bacteria that live on the methane? A host of questions having to do with deep-ocean ecosystems suddenly emerged. Stay tuned.

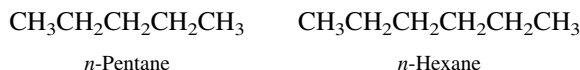
*The biosphere is the part of the earth where life is; it includes the surface, the oceans, and the lower atmosphere.

n-Butane and isobutane have the same molecular formula but differ in the order in which their atoms are connected. They are *constitutional isomers* of each other (Section 1.8). Because they are different in structure, they can have different properties. Both are gases at room temperature, but *n*-butane boils almost 10°C higher than isobutane and has a melting point that is over 20°C higher.

The bonding in *n*-butane and isobutane continues the theme begun with methane, ethane, and propane. All of the carbon atoms are sp^3 -hybridized, all of the bonds are σ bonds, and the bond angles at carbon are close to tetrahedral. This generalization holds for all alkanes regardless of the number of carbons they have.

2.6 HIGHER *n*-ALKANES

n-Alkanes are alkanes that have an unbranched carbon chain. ***n*-Pentane** and ***n*-hexane** are *n*-alkanes possessing five and six carbon atoms, respectively.

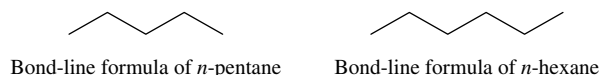


Their condensed structural formulas can be abbreviated even more by indicating within parentheses the number of methylene groups in the chain. Thus, *n*-pentane may be written as $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ and *n*-hexane as $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$. This shortcut is especially convenient with longer-chain alkanes. The laboratory synthesis of the “ultralong” alkane $\text{CH}_3(\text{CH}_2)_{388}\text{CH}_3$ was achieved in 1985; imagine trying to write a structural formula for this compound in anything other than an abbreviated way!

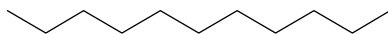
PROBLEM 2.2 An *n*-alkane of molecular formula $\text{C}_{28}\text{H}_{58}$ has been isolated from a certain fossil plant. Write a condensed structural formula for this alkane.

n-Alkanes have the general formula $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$ and are said to belong to a **homologous series** of compounds. A homologous series is one in which successive members differ by a $-\text{CH}_2-$ group.

Unbranched alkanes are sometimes referred to as “straight-chain alkanes,” but, as we’ll see in Chapter 3, their chains are not straight but instead tend to adopt the “zigzag” shape portrayed in the bond-line formulas introduced in Section 1.7.

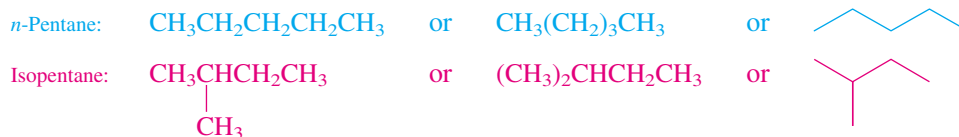


PROBLEM 2.3 Much of the communication between insects involves chemical messengers called *pheromones*. A species of cockroach secretes a substance from its mandibular glands that alerts other cockroaches to its presence and causes them to congregate. One of the principal components of this *aggregation pheromone* is the alkane shown in the bond-line formula that follows. Give the molecular formula of this substance, and represent it by a condensed formula.

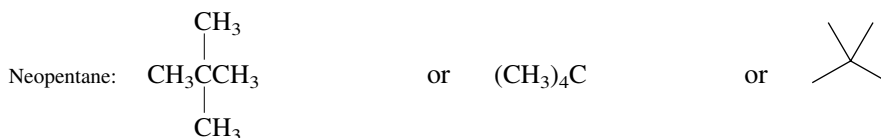


2.7 THE C_5H_{12} ISOMERS

Three isomeric alkanes have the molecular formula C_5H_{12} . The unbranched isomer is, as we have seen, *n*-pentane. The isomer with a single methyl branch is called **isopentane**. The third isomer has a three-carbon chain with two methyl branches. It is called **neopentane**.



Make molecular models of the three isomers of C_5H_{12} .

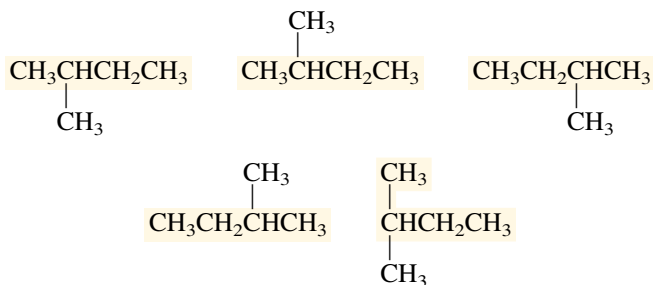


The number of $\text{C}_n\text{H}_{2n+2}$ isomers has been calculated for values of n from 1 to 400 and the comment made that the number of isomers of $\text{C}_{167}\text{H}_{336}$ exceeds the number of particles in the known universe (10^{80}). These observations and the historical background of isomer calculation are described in a paper in the April 1989 issue of the *Journal of Chemical Education* (pp. 278–281).

Table 2.3 presents the number of possible alkane isomers as a function of the number of carbon atoms they contain. As the table shows, the number of isomers increases enormously with the number of carbon atoms and raises two important questions:

1. How can we tell when we have written all the possible isomers corresponding to a particular molecular formula?
2. How can we name alkanes so that each one has a unique name?

The answer to the first question is that you cannot easily calculate the number of isomers. The data in Table 2.3 were determined by a mathematician who concluded that there was no simple expression from which to calculate the number of isomers. The best way to ensure that you have written all the isomers of a particular molecular formula is to work systematically, beginning with the unbranched chain and then shortening it while adding branches one by one. It is essential that you be able to recognize when two different-looking structural formulas are actually the same molecule written in different ways. The key point is the *connectivity* of the carbon chain. For example, the following group of structural formulas do *not* represent different compounds; they are just a portion of the many ways we could write a structural formula for isopentane. Each one has a continuous chain of four carbons with a methyl branch located one carbon from the end of the chain.



The fact that all of these structural formulas represent the same substance can be clearly seen by making molecular models.

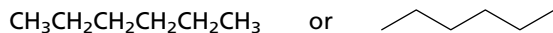


TABLE 2.3 The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas

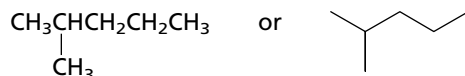
Molecular formula	Number of constitutional isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$\text{C}_{10}\text{H}_{22}$	75
$\text{C}_{15}\text{H}_{32}$	4,347
$\text{C}_{20}\text{H}_{42}$	366,319
$\text{C}_{40}\text{H}_{82}$	62,491,178,805,831

PROBLEM 2.4 Write condensed and bond-line formulas for the five isomeric C_6H_{14} alkanes.

SAMPLE SOLUTION When writing isomeric alkanes, it is best to begin with the unbranched isomer.



Next, remove a carbon from the chain and use it as a one-carbon (methyl) branch at the carbon atom next to the end of the chain.



Now, write structural formulas for the remaining three isomers. Be sure that each one is a unique compound and not simply a different representation of one written previously.

The answer to the second question—how to provide a name that is unique to a particular structure—is presented in the following section. It is worth noting, however, that being able to name compounds in a *systematic* way is a great help in deciding whether two structural formulas represent isomeric substances or are the same compound represented in two different ways. By following a precise set of rules, one will always get the same systematic name for a compound, regardless of how it is written. Conversely, two different compounds will always have different names.

2.8 IUPAC NOMENCLATURE OF UNBRANCHED ALKANES

Nomenclature in organic chemistry is of two types: **common** (or “trivial”) and **systematic**. Some common names existed long before organic chemistry became an organized branch of chemical science. Methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane are common names. One simply memorizes the name that goes with a compound in just the same way that one matches names with faces. So long as there are only a few names and a few compounds, the task is manageable. But there are millions of organic compounds already known, and the list continues to grow! A system built on common names is not adequate to the task of communicating structural information. Beginning in 1892, chemists developed a set of rules for naming organic compounds based on their structures, which we now call the **IUPAC rules**, in which *IUPAC* stands for the “International Union of Pure and Applied Chemistry.” (See the accompanying box, “A Brief History of Systematic Organic Nomenclature.”)

The IUPAC rules assign names to unbranched alkanes as shown in Table 2.4. Methane, ethane, propane, and butane are retained for CH_4 , CH_3CH_3 , $CH_3CH_2CH_3$, and $CH_3CH_2CH_2CH_3$, respectively. Thereafter, the number of carbon atoms in the chain is specified by a Latin or Greek prefix preceding the suffix *-ane*, which identifies the compound as a member of the alkane family. Notice that the prefix *n*- is not part of the IUPAC system. The IUPAC name for $CH_3CH_2CH_2CH_3$ is butane, not *n*-butane.

A more detailed account of the history of organic nomenclature may be found in the article “The Centennial of Systematic Organic Nomenclature” in the November 1992 issue of the *Journal of Chemical Education* (pp. 863–865).

PROBLEM 2.5 Refer to Table 2.4 as needed to answer the following questions:

- Beeswax contains 8–9% hentriacontane. Write a condensed structural formula for hentriacontane.
- Octacosane has been found to be present in a certain fossil plant. Write a condensed structural formula for octacosane.

TABLE 2.4 IUPAC Names of Unbranched Alkanes

Number of carbon atoms	Name	Number of carbon atoms	Name	Number of carbon atoms	Name
1	Methane	11	Undecane	21	Henicosane
2	Ethane	12	Dodecane	22	Docosane
3	Propane	13	Tridecane	23	Tricosane
4	Butane	14	Tetradecane	24	Tetracosane
5	Pentane	15	Pentadecane	30	Triacontane
6	Hexane	16	Hexadecane	31	Hentriacontane
7	Heptane	17	Heptadecane	32	Dotriacontane
8	Octane	18	Octadecane	40	Tetracontane
9	Nonane	19	Nonadecane	50	Pentacontane
10	Decane	20	Icosane*	100	Hectane

*Spelled "eicosane" prior to 1979 version of IUPAC rules.

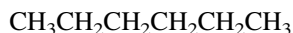
(c) What is the IUPAC name of the alkane described in Problem 2.3 as a component of the cockroach aggregation pheromone?

SAMPLE SOLUTION (a) Note in Table 2.4 that hentriacontane has 31 carbon atoms. All the alkanes in Table 2.4 have unbranched carbon chains. Hentriacontane has the condensed structural formula $\text{CH}_3(\text{CH}_2)_{29}\text{CH}_3$.

In Problem 2.4 you were asked to write structural formulas for the five isomeric alkanes of molecular formula C_6H_{14} . In the next section you will see how the IUPAC rules generate a unique name for each isomer.

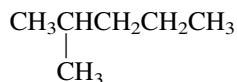
2.9 APPLYING THE IUPAC RULES: THE NAMES OF THE C_6H_{14} ISOMERS

We can present and illustrate the most important of the IUPAC rules for alkane nomenclature by naming the five C_6H_{14} isomers. By definition (Table 2.4), the unbranched C_6H_{14} isomer is hexane.



IUPAC name: hexane
(common name: *n*-hexane)

The IUPAC rules name branched alkanes as *substituted derivatives* of the unbranched alkanes listed in Table 2.4. Consider the C_6H_{14} isomer represented by the structure



Step 1

Pick out the *longest continuous carbon chain*, and find the IUPAC name in Table 2.4 that corresponds to the unbranched alkane having that number of carbons. This is the parent alkane from which the IUPAC name is to be derived.

You might find it helpful to make molecular models of all the C_6H_{14} isomers.



A BRIEF HISTORY OF SYSTEMATIC ORGANIC NOMENCLATURE

The first successful formal system of chemical nomenclature was advanced in France in 1787 to replace the babel of common names which then plagued the science. Hydrogen (instead of “inflammable air”) and oxygen (instead of “vital air”) are just two of the substances that owe their modern names to the proposals described in the *Méthode de nomenclature chimique*. It was then that important compounds such as sulfuric, phosphoric, and carbonic acid and their salts were named. The guidelines were more appropriate to inorganic compounds; it was not until the 1830s that names reflecting chemical composition began to appear in organic chemistry.

In 1889, a group with the imposing title of the International Commission for the Reform of Chemical Nomenclature was organized, and this group, in turn, sponsored a meeting of 34 prominent European chemists in Switzerland in 1892. Out of this meeting arose a system of organic nomenclature known as the **Geneva rules**. The principles on which the Geneva rules were based are the forerunners of our present system.

A second international conference was held in 1911, but the intrusion of World War I prevented any substantive revisions of the Geneva rules. The International Union of Chemistry was established in 1930 and undertook the necessary revision leading to publication in 1930 of what came to be known as the **Liège rules**.

After World War II, the International Union of Chemistry became the International Union of Pure and Applied Chemistry (known in the chemical community as the *IUPAC*). Since 1949, the IUPAC has issued reports on chemical nomenclature on a regular basis. The most recent **IUPAC rules** for organic chemistry were published in 1993. The IUPAC rules often offer several different ways to name a single compound. Thus although it is true that no two com-

pounds can have the same name, it is incorrect to believe that there is only a single IUPAC name for a particular compound.

The 1993 IUPAC recommendations and their more widely used 1979 predecessors may both be accessed at the same web site:

www.acdlabs.com/iupac/nomenclature

The IUPAC rules are not the only nomenclature system in use today. Chemical Abstracts Service surveys all the world's leading scientific journals that publish papers relating to chemistry and publishes brief abstracts of those papers. The publication *Chemical Abstracts* and its indexes are absolutely essential to the practice of chemistry. For many years *Chemical Abstracts* nomenclature was very similar to IUPAC nomenclature, but the tremendous explosion of chemical knowledge in recent years has required *Chemical Abstracts* to modify its nomenclature so that its indexes are better adapted to computerized searching. This means that whenever feasible, a compound has a single *Chemical Abstracts* name. Unfortunately, this *Chemical Abstracts* name may be different from any of the several IUPAC names. In general, it is easier to make the mental connection between a chemical structure and its IUPAC name than its *Chemical Abstracts* name.

It is worth noting that the **generic name** of a drug is not directly derived from systematic nomenclature. Furthermore, different pharmaceutical companies will call the same drug by their own trade name, which is different from its generic name. Generic names are invented on request (for a fee) by the U.S. Adopted Names Council, a private organization founded by the American Medical Association, the American Pharmaceutical Association, and the U.S. Pharmacopeial Convention.

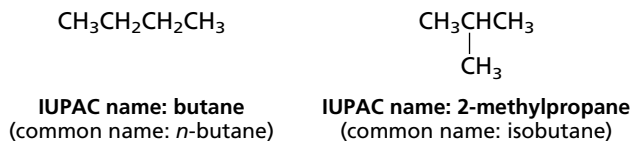
In this case, the longest continuous chain has *five* carbon atoms; the compound is named as a derivative of pentane. The key word here is *continuous*. It does not matter whether the carbon skeleton is drawn in an extended straight-chain form or in one with many bends and turns. All that matters is the number of carbons linked together in an uninterrupted sequence.

Step 2

Identify the substituent groups attached to the parent chain.

The parent pentane chain bears a methyl (CH₃) group as a substituent.

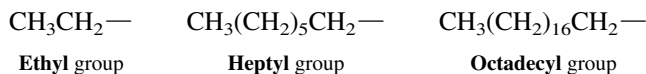
SAMPLE SOLUTION (a) There are two C_4H_{10} isomers. Butane (see Table 2.4) is the IUPAC name for the isomer that has an unbranched carbon chain. The other isomer has three carbons in its longest continuous chain with a methyl branch at the central carbon; its IUPAC name is 2-methylpropane.



So far, the only branched alkanes that we've named have methyl groups attached to the main chain. What about groups other than CH_3 ? What do we call these groups, and how do we name alkanes that contain them?

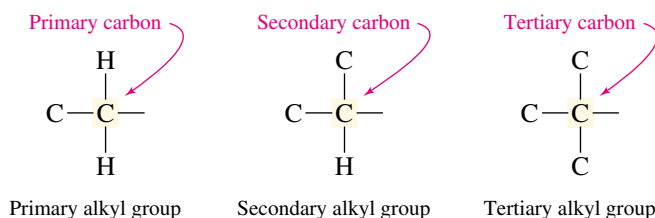
2.10 ALKYL GROUPS

An alkyl group lacks one of the hydrogen substituents of an alkane. A methyl group (CH_3-) is an alkyl group derived from methane (CH_4). Unbranched alkyl groups in which the point of attachment is at the end of the chain are named in IUPAC nomenclature by replacing the *-ane* endings of Table 2.4 by *-yl*.



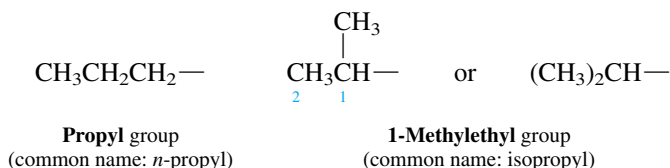
The dash at the end of the chain represents a potential point of attachment for some other atom or group.

Carbon atoms are classified according to their degree of substitution by other carbons. A **primary** carbon is one that is *directly* attached to one other carbon. Similarly, a **secondary** carbon is directly attached to two other carbons, a **tertiary** carbon to three, and a **quaternary** carbon to four. Alkyl groups are designated as primary, secondary, or tertiary according to the degree of substitution of the carbon at the potential point of attachment.



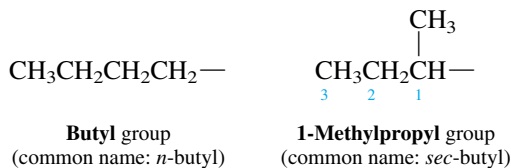
Ethyl (CH_3CH_2-), heptyl [$CH_3(CH_2)_5CH_2-$], and octadecyl [$CH_3(CH_2)_{16}CH_2-$] are examples of primary alkyl groups.

Branched alkyl groups are named by using the longest continuous chain that begins at the point of attachment as the base name. Thus, the systematic names of the two C_3H_7 alkyl groups are propyl and 1-methylethyl. Both are better known by their common names, *n*-propyl and isopropyl, respectively.

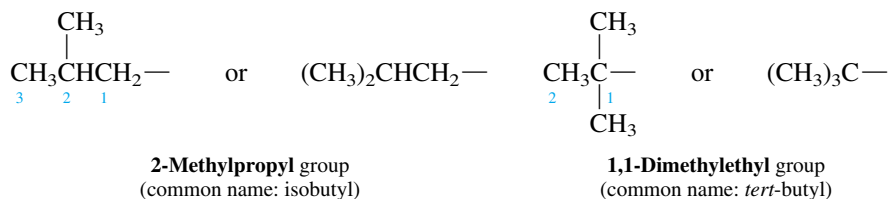


An isopropyl group is a *secondary* alkyl group. Its point of attachment is to a secondary carbon atom, one that is directly bonded to two other carbons.

The C₄H₉ alkyl groups may be derived either from the unbranched carbon skeleton of butane or from the branched carbon skeleton of isobutane. Those derived from butane are the butyl (*n*-butyl) group and the 1-methylpropyl (*sec*-butyl) group.

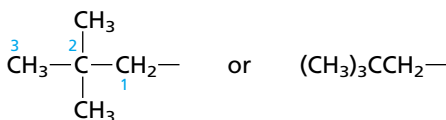


Those derived from isobutane are the 2-methylpropyl (isobutyl) group and the 1,1-dimethylethyl (*tert*-butyl) group. Isobutyl is a primary alkyl group because its potential point of attachment is to a primary carbon. *tert*-Butyl is a tertiary alkyl group because its potential point of attachment is to a tertiary carbon.



PROBLEM 2.8 Give the structures and IUPAC names of all the C₅H₁₁ alkyl groups, and identify them as primary, secondary, or tertiary alkyl groups, as appropriate.

SAMPLE SOLUTION Consider the alkyl group having the same carbon skeleton as (CH₃)₄C. All the hydrogens are equivalent, so that replacing any one of them by a potential point of attachment is the same as replacing any of the others.



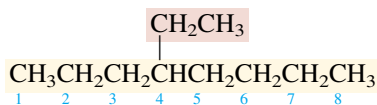
Numbering always begins at the point of attachment and continues through the longest continuous chain. In this case the chain is three carbons and there are two methyl groups at C-2. The IUPAC name of this alkyl group is **2,2-dimethylpropyl**. (The common name for this group is *neopentyl*.) It is a *primary* alkyl group because the carbon that bears the potential point of attachment (C-1) is itself directly bonded to one other carbon.

The names and structures of the most frequently encountered alkyl groups are given on the inside back cover.

In addition to methyl and ethyl groups, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, and neopentyl groups will appear often throughout this text. Although these are common names, they have been integrated into the IUPAC system and are an acceptable adjunct to systematic nomenclature. You should be able to recognize these groups on sight and to give their structures when needed.

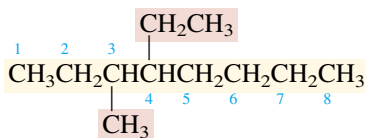
2.11 IUPAC NAMES OF HIGHLY BRANCHED ALKANES

By combining the basic principles of IUPAC notation with the names of the various alkyl groups, we can develop systematic names for highly branched alkanes. We'll start with the following alkane, name it, then increase its complexity by successively adding methyl groups at various positions.



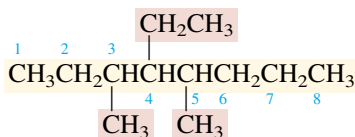
As numbered on the structural formula, the longest continuous chain contains eight carbons, and so the compound is named as a derivative of octane. Numbering begins at the end nearest the branch, and so the ethyl substituent is located at C-4, and the name of the alkane is **4-ethyloctane**.

What happens to the IUPAC name when a methyl replaces one of the hydrogens at C-3?



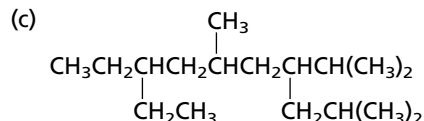
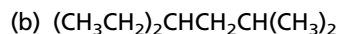
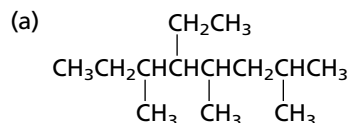
The compound becomes an octane derivative that bears a C-3 methyl group and a C-4 ethyl group. *When two or more different substituents are present, they are listed in alphabetical order in the name.* The IUPAC name for this compound is **4-ethyl-3-methyloctane**.

Replicating prefixes such as *di-*, *tri-*, and *tetra-* (see Section 2.9) are used as needed but are ignored when alphabetizing. Adding a second methyl group to the original structure, at C-5, for example, converts it to **4-ethyl-3,5-dimethyloctane**.

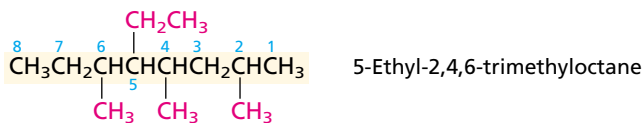


Italicized prefixes such as *sec-* and *tert-* are ignored when alphabetizing except when they are compared with each other. *tert*-Butyl precedes *isobutyl*, and *sec*-butyl precedes *tert*-butyl.

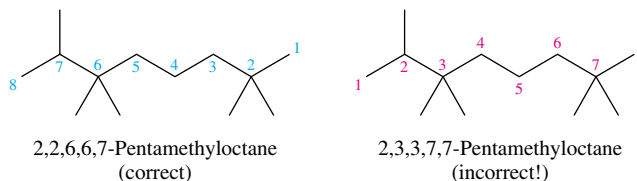
PROBLEM 2.9 Give an acceptable IUPAC name for each of the following alkanes:



SAMPLE SOLUTION (a) This problem extends the preceding discussion by adding a third methyl group to 4-ethyl-3,5-dimethyloctane, the compound just described. It is, therefore, an *ethyltrimethyloctane*. Notice, however, that the numbering sequence needs to be changed in order to adhere to the rule of numbering from the end of the chain nearest the first branch. When numbered properly, this compound has a methyl group at C-2 as its first-appearing substituent.



An additional feature of IUPAC nomenclature that concerns the direction of numbering is called the “first point of difference” rule. Consider the two directions in which the following alkane may be numbered:



When deciding on the proper direction, a point of difference occurs when one order gives a lower locant than another. Thus, while 2 is the first locant in both numbering schemes, the tie is broken at the second locant, and the rule favors 2,2,6,6,7, which has 2 as its second locant, whereas 3 is the second locant in 2,3,3,7,7. Notice that locants are *not* added together, but examined one by one.

Finally, when equal locants are generated from two different numbering directions, the direction is chosen which gives the lower number to the substituent that appears first in the name. (Remember, substituents are listed alphabetically.)

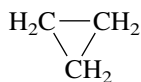
The IUPAC nomenclature system is inherently logical and incorporates healthy elements of common sense into its rules. Granted, some long, funny-looking, hard-to-pronounce names are generated. Once one knows the code (rules of grammar) though, it becomes a simple matter to convert those long names to unique structural formulas.

Tabular summaries of the IUPAC rules for alkane and alkyl group nomenclature appear on pages 81–83.

Cycloalkanes are one class of *alicyclic* (aliphatic cyclic) hydrocarbons.

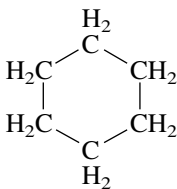
2.12 CYCLOALKANE NOMENCLATURE

Cycloalkanes are alkanes that contain a ring of three or more carbons. They are frequently encountered in organic chemistry and are characterized by the molecular formula C_nH_{2n} . Some examples include:



Cyclopropane

usually represented as



Cyclohexane

usually represented as

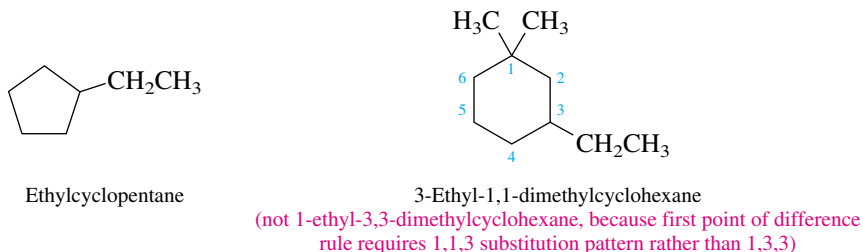


If you make a molecular model of cyclohexane, you will find its shape to be very different from a planar hexagon. We'll discuss the reasons why in Chapter 3.

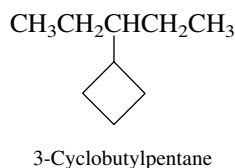


As you can see, cycloalkanes are named, under the IUPAC system, by adding the prefix *cyclo-* to the name of the unbranched alkane with the same number of carbons as

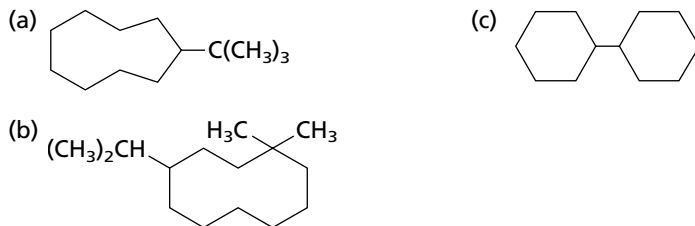
the ring. Substituent groups are identified in the usual way. Their positions are specified by numbering the carbon atoms of the ring in the direction that gives the lowest number to the substituents at the first point of difference.



When the ring contains fewer carbon atoms than an alkyl group attached to it, the compound is named as an alkane, and the ring is treated as a cycloalkyl substituent:



PROBLEM 2.10 Name each of the following compounds:



SAMPLE SOLUTION (a) The molecule has a *tert*-butyl group bonded to a nine-membered cycloalkane. It is *tert*-butylcyclononane. Alternatively, the *tert*-butyl group could be named systematically as a 1,1-dimethylethyl group, and the compound would then be named (1,1-dimethylethyl)cyclononane. (Parentheses are used when necessary to avoid ambiguity. In this case the parentheses alert the reader that the locants 1,1 refer to substituents on the alkyl group and not to ring positions.)

2.13 SOURCES OF ALKANES AND CYCLOALKANES

As noted earlier, natural gas is especially rich in methane and also contains ethane and propane, along with smaller amounts of other low-molecular-weight alkanes. Natural gas is often found associated with petroleum deposits. Petroleum is a liquid mixture containing hundreds of substances, including approximately 150 hydrocarbons, roughly half of which are alkanes or cycloalkanes. Distillation of crude oil gives a number of fractions, which by custom are described by the names given in Figure 2.2. High-boiling fractions such as kerosene and gas oil find wide use as fuels for diesel engines and furnaces, and the nonvolatile residue can be processed to give lubricating oil, greases, petroleum jelly, paraffin wax, and asphalt.

The word *petroleum* is derived from the Latin words for "rock" (*petra*) and "oil" (*oleum*).

Although both are closely linked in our minds and by our own experience, the petroleum industry predated the automobile industry by half a century. The first oil well, drilled in Titusville, Pennsylvania, by Edwin Drake in 1859, provided “rock oil,” as it was then called, on a large scale. This was quickly followed by the development of a process to “refine” it so as to produce kerosene. As a fuel for oil lamps, kerosene burned with a bright, clean flame and soon replaced the more expensive whale oil then in use. Other oil fields were discovered, and uses for other petroleum products were found—illuminating gas lit city streets, and oil heated homes and powered locomotives. There were oil refineries long before there were automobiles. By the time the first Model T rolled off Henry Ford’s assembly line in 1908, John D. Rockefeller’s Standard Oil holdings had already made him one of the half-dozen wealthiest people in the world.

Modern petroleum refining involves more than distillation, however, and includes two major additional operations:

1. **Cracking.** It is the more volatile, lower-molecular-weight hydrocarbons that are useful as automotive fuels and as a source of petrochemicals. Cracking increases the proportion of these hydrocarbons at the expense of higher molecular-weight ones by processes that involve the cleavage of carbon–carbon bonds induced by heat (*thermal cracking*) or with the aid of certain catalysts (*catalytic cracking*).
2. **Reforming.** The physical properties of the crude oil fractions known as *light gasoline* and *naphtha* (Figure 2.2) are appropriate for use as a motor fuel, but their ignition characteristics in high-compression automobile engines are poor and give rise to preignition, or “knocking.” Reforming converts the hydrocarbons in petroleum to aromatic hydrocarbons and highly branched alkanes, both of which show less tendency for knocking than unbranched alkanes and cycloalkanes.

The leaves and fruit of many plants bear a waxy coating made up of alkanes that prevents loss of water. In addition to being present in beeswax (see Problem 2.5), hentriacontane, $\text{CH}_3(\text{CH}_2)_{29}\text{CH}_3$, is a component of the wax of tobacco leaves.

Cyclopentane and cyclohexane are present in petroleum, but as a rule, unsubsti-

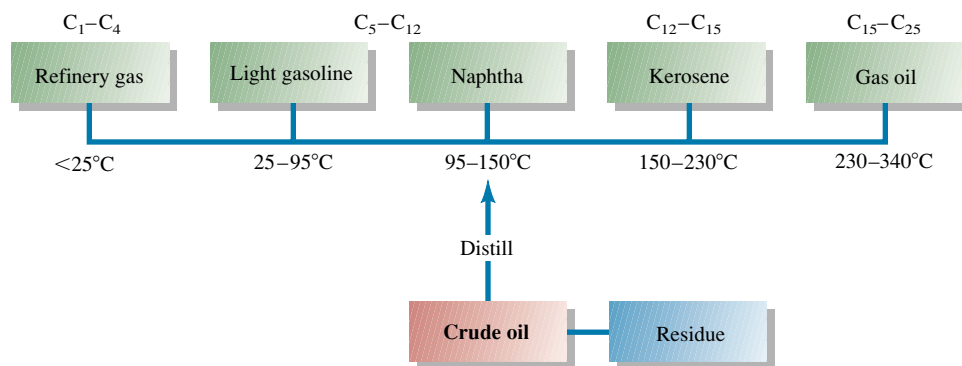
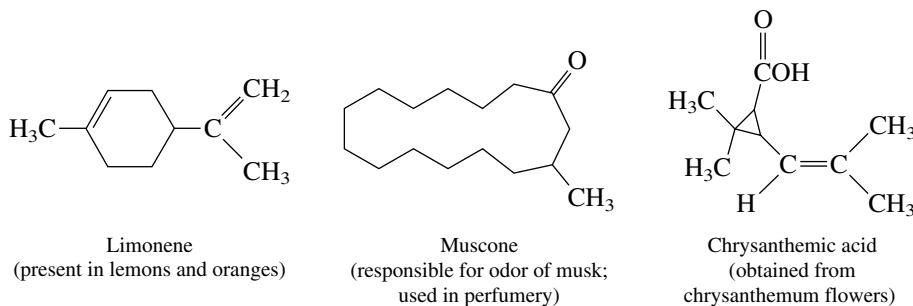


FIGURE 2.2 Distillation of crude oil yields a series of volatile fractions having the names indicated, along with a nonvolatile residue. The number of carbon atoms that characterize the hydrocarbons in each fraction is approximate.

The tendency of a gasoline to cause “knocking” in an engine is given by its octane number. The lower the octane number, the greater the tendency. The two standards are heptane (assigned a value of 0) and 2,2,4-trimethylpentane (assigned a value of 100). The octane number of a gasoline is equal to the percentage of 2,2,4-trimethylpentane in a mixture of 2,2,4-trimethylpentane and heptane that has the same tendency to cause knocking as that sample of gasoline.

tuted cycloalkanes are rarely found in natural sources. Compounds that contain rings of various types, however, are quite abundant.



2.14 PHYSICAL PROPERTIES OF ALKANES AND CYCLOALKANES

Boiling Point. As we have seen earlier in this chapter, methane, ethane, propane, and butane are gases at room temperature. The unbranched alkanes pentane (C_5H_{12}) through heptadecane ($C_{17}H_{36}$) are liquids, whereas higher homologs are solids. As shown in Figure 2.3, the boiling points of unbranched alkanes increase with the number of carbon atoms. Figure 2.3 also shows that the boiling points for 2-methyl-branched alkanes are lower than those of the unbranched isomer. By exploring at the molecular level the reasons for the increase in boiling point with the number of carbons and the difference in boiling point between branched and unbranched alkanes, we can begin to connect structure with properties.

A substance exists as a liquid rather than a gas because attractive forces between

Appendix 1 lists selected physical properties for representative alkanes as well as members of other families of organic compounds.

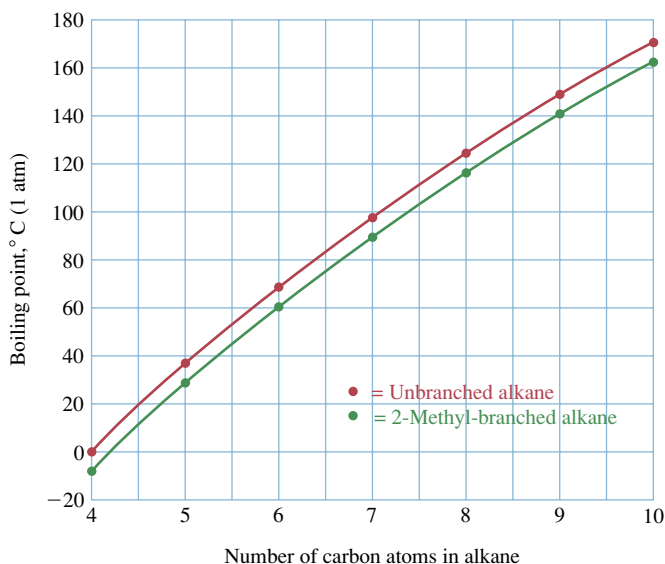


FIGURE 2.3 Boiling points of unbranched alkanes and their 2-methyl-branched isomers. (Temperatures in this text are expressed in degrees Celsius, °C. The SI unit of temperature is the kelvin, K. To convert degrees Celsius to kelvins add 273.15.)

molecules (**intermolecular attractive forces**) are greater in the liquid than in the gas phase. Attractive forces between neutral species (atoms or molecules, but not ions) are referred to as **van der Waals forces** and may be of three types:

1. dipole–dipole
2. dipole/induced-dipole
3. induced-dipole/induced-dipole

Van der Waals forces involving induced dipoles are often called *London forces*, or *dispersion forces*.

These forces are electrical in nature, and in order to vaporize a substance, enough energy must be added to overcome them. Most alkanes have no measurable dipole moment, and therefore the only van der Waals force to be considered is the induced-dipole/induced-dipole attractive force.

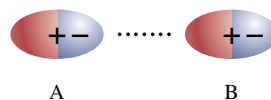
It might seem that two nearby molecules A and B of the same nonpolar substance would be unaffected by each other.



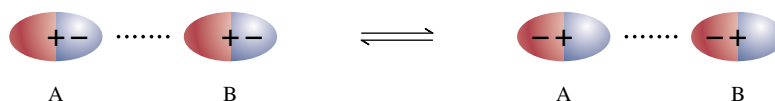
The electric field of a molecule, however, is not static, but fluctuates rapidly. Although, on average, the centers of positive and negative charge of an alkane nearly coincide, at any instant they may not, and molecule A can be considered to have a temporary dipole moment.



The neighboring molecule B “feels” the dipolar electric field of A and undergoes a spontaneous adjustment in its electron positions, giving it a temporary dipole moment that is complementary to that of A.



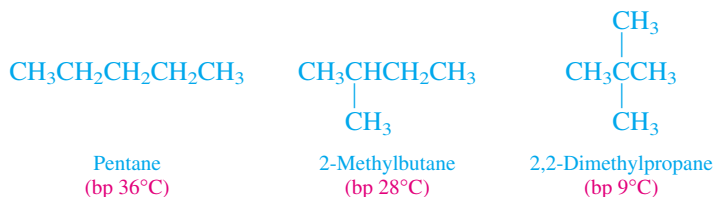
The electric fields of both A and B fluctuate, but always in a way that results in a weak attraction between them.



Extended assemblies of induced-dipole/induced-dipole attractions can accumulate to give substantial intermolecular attractive forces. An alkane with a higher molecular weight has more atoms and electrons and, therefore, more opportunities for intermolecular attractions and a higher boiling point than one with a lower molecular weight.

As noted earlier in this section, branched alkanes have lower boiling points than their unbranched isomers. Isomers have, of course, the same number of atoms and electrons, but a molecule of a branched alkane has a smaller surface area than an unbranched

one. The extended shape of an unbranched alkane permits more points of contact for intermolecular associations. Compare the boiling points of pentane and its isomers:



If you haven't already made models of the C_5H_{12} isomers, this would be a good time to do so.

The shapes of these isomers are clearly evident in the space-filling models depicted in Figure 2.4. Pentane has the most extended structure and the largest surface area available for “sticking” to other molecules by way of induced-dipole/induced-dipole attractive forces; it has the highest boiling point. 2,2-Dimethylpropane has the most compact structure, engages in the fewest induced-dipole/induced-dipole attractions, and has the lowest boiling point.

Induced-dipole/induced-dipole attractions are very weak forces individually, but a typical organic substance can participate in so many of them that they are collectively the most important of all the contributors to intermolecular attraction in the liquid state. They are the only forces of attraction possible between nonpolar molecules such as alkanes.

PROBLEM 2.11 Match the boiling points with the appropriate alkanes.
Alkanes: octane, 2-methylheptane, 2,2,3,3-tetramethylbutane, nonane
Boiling points (°C, 1 atm): 106, 116, 126, 151

Melting Point. Solid alkanes are soft, generally low-melting materials. The forces responsible for holding the crystal together are the same induced-dipole/induced-dipole interactions that operate between molecules in the liquid, but the degree of organization

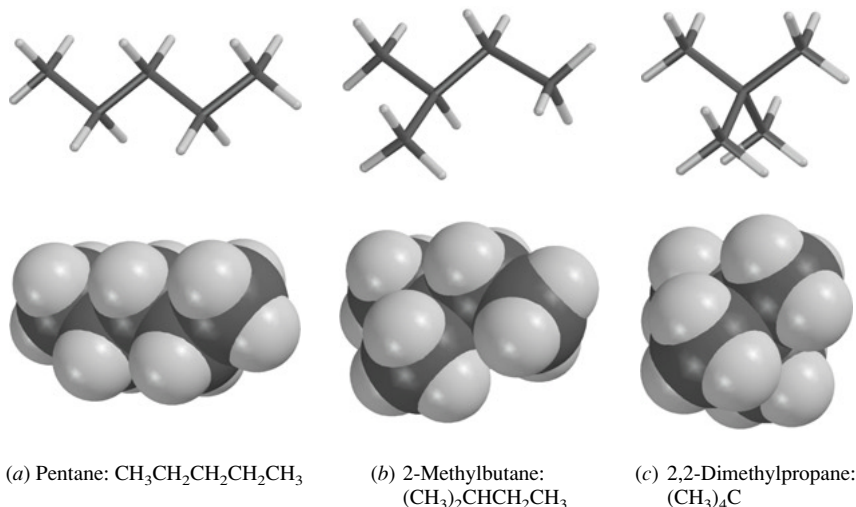


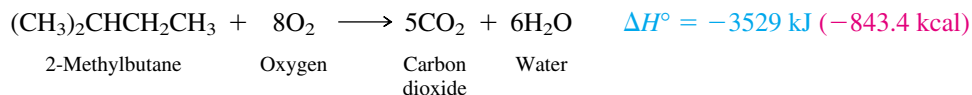
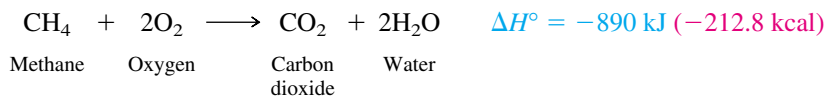
FIGURE 2.4 Space-filling models of (a) pentane, (b) 2-methylbutane, and (c) 2,2-dimethylpropane. The most branched isomer, 2,2-dimethylpropane, has the most compact, most spherical, three-dimensional shape.

is greater in the solid phase. By measuring the distances between the atoms of one molecule and its neighbor in the crystal, it is possible to specify a distance of closest approach characteristic of an atom called its **van der Waals radius**. In space-filling molecular models, such as those of pentane, 2-methylbutane, and 2,2-dimethylpropane shown in Figure 2.4, the radius of each sphere corresponds to the van der Waals radius of the atom it represents. The van der Waals radius for hydrogen is 120 pm. When two alkane molecules are brought together so that a hydrogen of one molecule is within 240 pm of a hydrogen of the other, the balance between electron–nucleus attractions versus electron–electron and nucleus–nucleus repulsions is most favorable. Closer approach is resisted by a strong increase in repulsive forces.

Solubility in Water. A familiar physical property of alkanes is contained in the adage “oil and water don’t mix.” Alkanes—indeed all hydrocarbons—are virtually insoluble in water. When a hydrocarbon dissolves in water, the framework of hydrogen bonds between water molecules becomes more ordered in the region around each molecule of the dissolved hydrocarbon. This increase in order, which corresponds to a decrease in entropy, signals a process that can be favorable only if it is reasonably exothermic. Such is not the case here. Being insoluble, and with densities in the 0.6–0.8 g/mL range, alkanes float on the surface of water (as the Alaskan oil spill of 1989 and the even larger Persian Gulf spill of 1991 remind us). The exclusion of nonpolar molecules, such as alkanes, from water is called the **hydrophobic effect**. We will encounter it again at several points later in the text.

2.15 CHEMICAL PROPERTIES. COMBUSTION OF ALKANES

An older name for alkanes is **paraffin hydrocarbons**. *Paraffin* is derived from the Latin words *parum affinis* (“with little affinity”) and testifies to the low level of reactivity of alkanes. Like most other organic compounds, however, alkanes burn readily in air. This combination with oxygen is known as **combustion** and is quite exothermic. All hydrocarbons yield carbon dioxide and water as the products of their combustion.



PROBLEM 2.12 Write a balanced chemical equation for the combustion of cyclohexane.

The heat released on combustion of a substance is called its **heat of combustion**. The heat of combustion is equal to $-\Delta H^\circ$ for the reaction written in the direction shown. By convention

$$\Delta H^\circ = H_{\text{products}}^\circ - H_{\text{reactants}}^\circ$$

where H° is the heat content, or **enthalpy**, of a compound in its standard state, that is, the gas, pure liquid, or crystalline solid at a pressure of 1 atm. In an exothermic process the enthalpy of the products is less than that of the starting materials, and ΔH° is a negative number.

Alkanes are so unreactive that George A. Olah of the University of Southern California was awarded the 1994 Nobel Prize in chemistry in part for developing novel substances that do react with alkanes.

Table 2.5 lists the heats of combustion of several alkanes. Unbranched alkanes have slightly higher heats of combustion than their 2-methyl-branched isomers, but the most important factor is the number of carbons. The unbranched alkanes and the 2-methyl-branched alkanes constitute two separate *homologous series* (see Section 2.6) in which there is a regular increase of about 653 kJ/mol (156 kcal/mol) in the heat of combustion for each additional CH₂ group.

PROBLEM 2.13 Using the data in Table 2.5, estimate the heat of combustion of
(a) 2-Methylnonane (in kcal/mol) (b) Icosane (in kJ/mol)

SAMPLE SOLUTION (a) The last entry for the group of 2-methylalkanes in the table is 2-methylheptane. Its heat of combustion is 1306 kcal/mol. Since 2-methylnonane has two more methylene groups than 2-methylheptane, its heat of combustion is 2×156 kcal/mol higher.

$$\text{Heat of combustion of 2-methylnonane} = 1306 + 2(156) = 1618 \text{ kcal/mol}$$

Heats of combustion can be used to measure the relative stability of isomeric hydrocarbons. They tell us not only which isomer is more stable than another, but by how much. Consider a group of C₈H₁₈ alkanes:

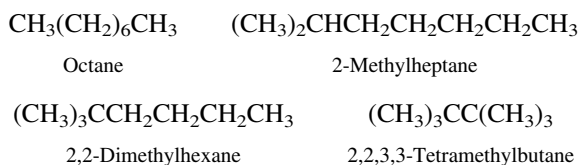


Figure 2.5 compares the heats of combustion of these C₈H₁₈ isomers on a *potential energy diagram*. **Potential energy** is comparable with enthalpy; it is the energy a molecule has exclusive of its kinetic energy. A molecule with more potential energy is less

TABLE 2.5 Heats of Combustion ($-\Delta H^\circ$) of Representative Alkanes

Compound	Formula	$-\Delta H^\circ$	
		kJ/mol	kcal/mol
Unbranched alkanes			
Hexane	CH ₃ (CH ₂) ₄ CH ₃	4,163	995.0
Heptane	CH ₃ (CH ₂) ₅ CH ₃	4,817	1151.3
Octane	CH ₃ (CH ₂) ₆ CH ₃	5,471	1307.5
Nonane	CH ₃ (CH ₂) ₇ CH ₃	6,125	1463.9
Decane	CH ₃ (CH ₂) ₈ CH ₃	6,778	1620.1
Undecane	CH ₃ (CH ₂) ₉ CH ₃	7,431	1776.1
Dodecane	CH ₃ (CH ₂) ₁₀ CH ₃	8,086	1932.7
Hexadecane	CH ₃ (CH ₂) ₁₄ CH ₃	10,701	2557.6
2-Methyl-branched alkanes			
2-Methylpentane	(CH ₃) ₂ CHCH ₂ CH ₂ CH ₃	4,157	993.6
2-Methylhexane	(CH ₃) ₂ CH(CH ₂) ₃ CH ₃	4,812	1150.0
2-Methylheptane	(CH ₃) ₂ CH(CH ₂) ₄ CH ₃	5,466	1306.3

stable than an isomer with less potential energy. Since these C_8H_{18} isomers all undergo combustion to the same final state according to the equation



the differences in their heats of combustion translate directly to differences in their potential energies. *When comparing isomers, the one with the lowest potential energy (in this case, the lowest heat of combustion) is the most stable.* Among the C_8H_{18} alkanes, the most highly branched isomer, 2,2,3,3-tetramethylbutane, is the most stable, and the unbranched isomer octane is the least stable. It is generally true for alkanes that a more branched isomer is more stable than a less branched one.

The small differences in stability between branched and unbranched alkanes result from an interplay between attractive and repulsive forces within a molecule (**intramolecular forces**). These forces are nucleus–nucleus repulsions, electron–electron repulsions, and nucleus–electron attractions, the same set of fundamental forces we met when talking about chemical bonding (see Section 1.12) and van der Waals forces between molecules (see Section 2.14). When the energy associated with these interactions is calculated for all of the nuclei and electrons within a molecule, it is found that the attractive forces increase more than the repulsive forces as the structure becomes more compact. Sometimes, though, two atoms in a molecule are held too closely together. We'll explore the consequences of that in Chapter 3.

PROBLEM 2.14 Without consulting Table 2.5, arrange the following compounds in order of decreasing heat of combustion: pentane, isopentane, neopentane, hexane.

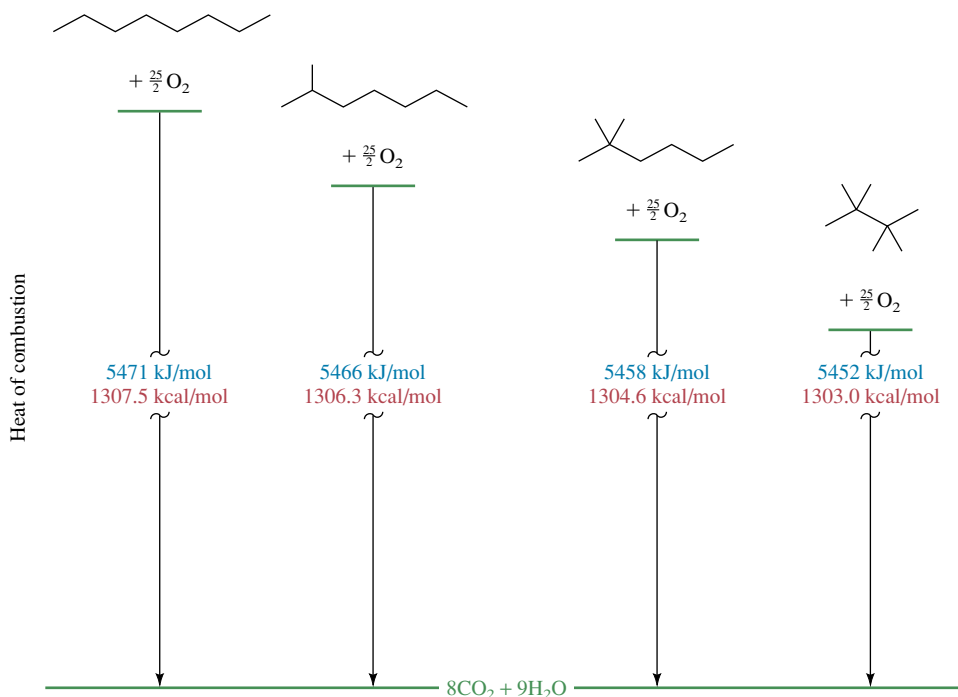


FIGURE 2.5 Energy diagram comparing heats of combustion of isomeric C_8H_{18} alkanes.

THERMOCHEMISTRY

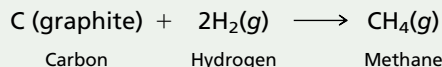
Thermochemistry is the study of the heat changes that accompany chemical processes. It has a long history dating back to the work of the French chemist Antoine Laurent Lavoisier in the late eighteenth century. Thermochemistry provides quantitative information that complements the qualitative description of a chemical reaction and can help us understand why some reactions occur and others do not. It is of obvious importance when assessing the relative value of various materials as fuels, when comparing the stability of isomers, or when determining the practicality of a particular reaction. In the field of bioenergetics, thermochemical information is applied to the task of sorting out how living systems use chemical reactions to store and use the energy that originates in the sun.

By allowing compounds to react in a calorimeter, it is possible to measure the heat evolved in an exothermic reaction or the heat absorbed in an endothermic reaction. Thousands of reactions have been studied to produce a rich library of thermochemical data. These data take the form of **heats of reaction** and correspond to the value of the enthalpy change ΔH° for a particular reaction of a particular substance.

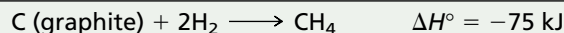
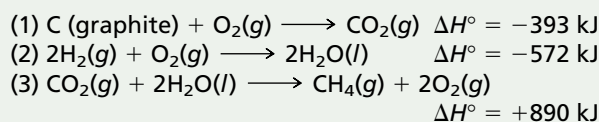
In this section you have seen how heats of combustion can be used to determine relative stabilities of isomeric alkanes. In later sections we shall expand our scope to include the experimentally determined heats of certain other reactions, such as *bond dissociation energies* (Section 4.17) and *heats of hydrogenation* (Section 6.2), to see how ΔH° values from various sources can aid our understanding of structure and reactivity.

Heat of formation (ΔH_f°), the enthalpy change for formation of a compound directly from the elements, is one type of heat of reaction. In cases such as the formation of CO_2 or H_2O from the combustion of carbon or hydrogen, respectively, the heat of formation of a substance can be measured directly. In most

other cases, heats of formation are not measured experimentally but are calculated from the measured heats of other reactions. Consider, for example, the heat of formation of methane. The reaction that defines the formation of methane from the elements,



can be expressed as the sum of three reactions:



Equations (1) and (2) are the heats of formation of carbon dioxide and water, respectively. Equation (3) is the reverse of the combustion of methane, and so the heat of reaction is equal to the heat of combustion but opposite in sign. The **molar heat of formation** of a substance is the enthalpy change for formation of one mole of the substance from the elements. For methane $\Delta H_f^\circ = -75 \text{ kJ/mol}$.

The heats of formation of most organic compounds are derived from heats of reaction by arithmetic manipulations similar to that shown. Chemists find a table of ΔH_f° values to be convenient because it replaces many separate tables of ΔH° values for individual reaction types and permits ΔH° to be calculated for any reaction, real or imaginary, for which the heats of formation of reactants and products are available. It is more appropriate for our purposes, however, to connect thermochemical data to chemical processes as directly as possible, and therefore we will cite heats of particular reactions, such as heats of combustion and heats of hydrogenation, rather than heats of formation.

2.16 OXIDATION–REDUCTION IN ORGANIC CHEMISTRY

As we have just seen, the reaction of alkanes with oxygen to give carbon dioxide and water is called *combustion*. A more fundamental classification of reaction types places it in the *oxidation–reduction* category. To understand why, let's review some principles of oxidation–reduction, beginning with the **oxidation number** (also known as **oxidation state**).

There are a variety of methods for calculating oxidation numbers. In compounds that contain a single carbon, such as methane (CH₄) and carbon dioxide (CO₂), the oxidation number of carbon can be calculated from the molecular formula. Both molecules are neutral, and so the algebraic sum of all the oxidation numbers must equal zero. Assuming, as is customary, that the oxidation state of hydrogen is +1, the oxidation state of carbon in CH₄ is calculated to be −4. Similarly, assuming an oxidation state of −2 for oxygen, carbon is +4 in CO₂. This kind of calculation provides an easy way to develop a list of one-carbon compounds in order of increasing oxidation state, as shown in Table 2.6.

The carbon in methane has the lowest oxidation number (−4) of any of the compounds in Table 2.6. Methane contains carbon in its most *reduced* form. Carbon dioxide and carbonic acid have the highest oxidation numbers (+4) for carbon, corresponding to its most *oxidized* state. When methane or any alkane undergoes combustion to form carbon dioxide, carbon is oxidized and oxygen is reduced.

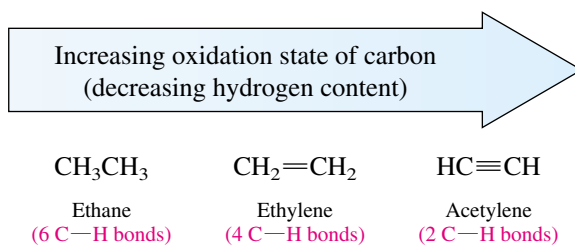
A useful generalization from Table 2.6 is the following:

Oxidation of carbon corresponds to an increase in the number of bonds between carbon and oxygen or to a decrease in the number of carbon–hydrogen bonds. Conversely, reduction corresponds to an increase in the number of carbon–hydrogen bonds or to a decrease in the number of carbon–oxygen bonds. From Table 2.6 it can be seen that each successive increase in oxidation state increases the number of bonds between carbon and oxygen and decreases the number of carbon–hydrogen bonds. Methane has four C–H bonds and no C–O bonds; carbon dioxide has four C–O bonds and no C–H bonds.

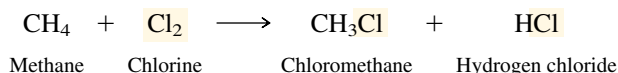
Among the various classes of hydrocarbons, alkanes contain carbon in its most reduced state, and alkynes contain carbon in its most oxidized state.

TABLE 2.6 Oxidation Number of Carbon in One-Carbon Compounds

Compound	Structural formula	Molecular formula	Oxidation number
Methane	CH ₄	CH ₄	−4
Methanol	CH ₃ OH	CH ₄ O	−2
Formaldehyde	H ₂ C=O	CH ₂ O	0
Formic acid	$\begin{array}{c} \text{O} \\ \\ \text{HCOH} \end{array}$	CH ₂ O ₂	+2
Carbonic acid	$\begin{array}{c} \text{O} \\ \\ \text{HOCOH} \end{array}$	H ₂ CO ₃	+4
Carbon dioxide	O=C=O	CO ₂	+4



We can extend the generalization by recognizing that the pattern is not limited to increasing hydrogen or oxygen content. Any element *more electronegative* than carbon will have the same effect on oxidation number as oxygen. Thus, the oxidation numbers of carbon in CH_3Cl and in CH_3OH are the same (-2), and the reaction of methane with chlorine (to be discussed in Section 4.16) involves *oxidation* of carbon.

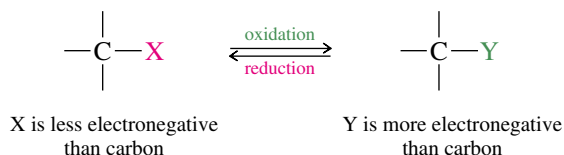


Any element *less electronegative* than carbon will have the same effect on oxidation number as hydrogen. Thus, the oxidation numbers of carbon in CH_3Li and in CH_4 are the same (-4), and the reaction of CH_3Cl with lithium (to be discussed in Section 14.3) involves *reduction* of carbon.



The oxidation number of carbon *decreases* from -2 in CH_3Cl to -4 in CH_3Li .

The generalization can be expressed in terms broad enough to cover both the preceding reactions and many others as well, as follows: *Oxidation of carbon occurs when a bond between carbon and an atom which is less electronegative than carbon is replaced by a bond to an atom that is more electronegative than carbon. The reverse process is reduction.*



Organic chemists are much more concerned with whether a particular reaction is an oxidation or a reduction of carbon than with determining the precise change in oxidation number. The generalizations described permit reactions to be examined in this way and eliminate the need for calculating oxidation numbers themselves.

PROBLEM 2.15 The reactions shown will all be encountered in Chapter 6. Classify each according to whether it proceeds by oxidation of carbon, by reduction of carbon, or by a process other than oxidation-reduction.

- (a) $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$
 (b) $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{BrCH}_2\text{CH}_2\text{Br}$
 (c) $6\text{CH}_2=\text{CH}_2 + \text{B}_2\text{H}_6 \longrightarrow 2(\text{CH}_3\text{CH}_2)_3\text{B}$

Methods for calculating oxidation numbers in complex molecules are available. They are time-consuming to apply, however, and are rarely used in organic chemistry.

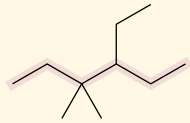
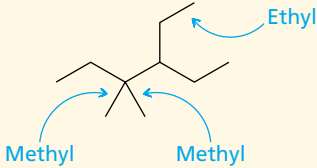
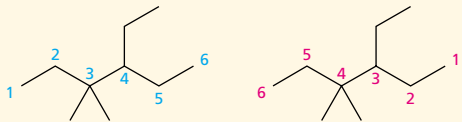
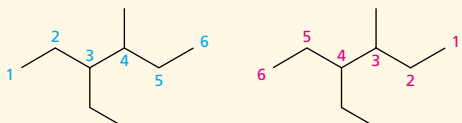
SAMPLE SOLUTION (a) In this reaction one new C—H bond and one new C—O bond are formed. One carbon is reduced, the other is oxidized. Overall, there is no net change in oxidation state, and the reaction is not classified as an oxidation–reduction.

The ability to recognize when oxidation or reduction occurs is of value when deciding on the kind of reactant with which an organic molecule must be treated in order to convert it into some desired product. Many of the reactions to be discussed in subsequent chapters involve oxidation–reduction.

2.17 SUMMARY

- Section 2.1 The classes of hydrocarbons are **alkanes, alkenes, alkynes, and arenes**. Alkanes are hydrocarbons in which all of the bonds are *single* bonds and are characterized by the molecular formula C_nH_{2n+2} .
- Section 2.2 **Functional groups** are the structural units responsible for the characteristic reactions of a molecule. The functional groups in an alkane are its hydrogen atoms.
- Section 2.3 The families of organic compounds listed on the inside front cover and in Tables 2.1 and 2.2 bear functional groups that are more reactive than H, and the hydrocarbon chain to which they are attached can often be considered as simply a supporting framework. For example, ethanolamine ($H_2NCH_2CH_2OH$) contains both amine (RNH_2) and alcohol (ROH) functional groups.
- Section 2.4 The first three alkanes are **methane** (CH_4), **ethane** (CH_3CH_3), and **propane** ($CH_3CH_2CH_3$). All can be described according to the orbital hybridization model of bonding based on sp^3 hybridization of carbon.
- Section 2.5 Two constitutionally isomeric alkanes have the molecular formula C_4H_{10} . One has an unbranched chain ($CH_3CH_2CH_2CH_3$) and is called ***n*-butane**; the other has a branched chain [$(CH_3)_3CH$] and is called **isobutane**. Both *n*-butane and isobutane are **common names**.
- Section 2.6 Unbranched alkanes of the type $CH_3(CH_2)_nCH_3$ are often referred to as *n*-alkanes.
- Section 2.7 There are three constitutional isomers of C_5H_{12} : ***n*-pentane** ($CH_3CH_2CH_2CH_2CH_3$), **isopentane** [$(CH_3)_2CHCH_2CH_3$], and **neopentane** [$(CH_3)_4C$].
- Sections 2.8–2.12 A single alkane may have several different names; a name may be a common name, or it may be a *systematic name* developed by a well-defined set of rules. The most widely used system is **IUPAC nomenclature**. Table 2.7 summarizes the rules for alkanes and cycloalkanes. Table 2.8 gives the rules for naming alkyl groups.
- Section 2.13 Natural gas is an abundant source of methane, ethane, and propane. Petroleum is a liquid mixture of many hydrocarbons, including alkanes. Alkanes also occur naturally in the waxy coating of leaves and fruits.
- Section 2.14 Alkanes and cycloalkanes are nonpolar and insoluble in water. The forces of attraction between alkane molecules are **induced-dipole/induced-dipole** attractive forces. The boiling points of alkanes increase as the

TABLE 2.7 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes

Rule	Example
A. Alkanes	
1. Find the longest continuous chain of carbon atoms, and assign a basis name to the compound corresponding to the IUPAC name of the unbranched alkane having the same number of carbons.	<p>The longest continuous chain in the alkane shown is six carbons.</p> 
2. List the substituents attached to the longest continuous chain in alphabetical order. Use the prefixes <i>di-</i> , <i>tri-</i> , <i>tetra-</i> , and so on, when the same substituent appears more than once. Ignore these prefixes when alphabetizing.	<p>This alkane is named as a derivative of <i>hexane</i>.</p> <p>The alkane bears two methyl groups and an ethyl group. It is an <i>ethyl</i><i>dimethyl</i>hexane.</p> 
3. Number the chain in the direction that gives the lower locant to a substituent at the first point of difference.	<p>When numbering from left to right, the substituents appear at carbons 3, 3, and 4. When numbering from right to left the locants are 3, 4, and 4; therefore, number from left to right.</p> 
4. When two different numbering schemes give equivalent sets of locants, choose the direction that gives the lower locant to the group that appears first in the name.	<p>The correct name is <i>4-ethyl-3,3-dimethylhexane</i>.</p> <p>In the following example, the substituents are located at carbons 3 and 4 regardless of the direction in which the chain is numbered.</p>  <p>Ethyl precedes methyl in the name; therefore <i>3-ethyl-4-methylhexane</i> is correct.</p>

(Continued)

TABLE 2.7 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes (Continued)

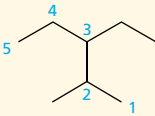
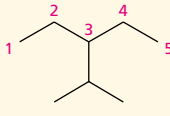
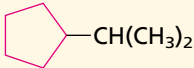
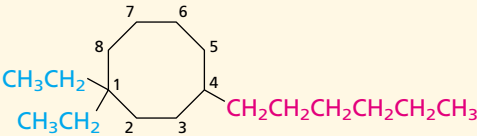


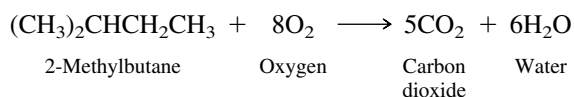
Rule	Example
5. When two chains are of equal length, choose the one with the greater number of substituents as the parent. (Although this requires naming more substituents, the substituents have simpler names.)	<p>Two different chains contain five carbons in the alkane:</p>   <p>The correct name is <i>3-ethyl-2-methylpentane</i> (disubstituted chain), rather than <i>3-isopropylpentane</i> (monosubstituted chain).</p>
B. Cycloalkanes	
1. Count the number of carbons in the ring, and assign a basis name to the cycloalkane corresponding to the IUPAC name of the unbranched alkane having the same number of carbons.	<p>The compound shown contains five carbons in its ring.</p>  <p>It is named as a derivative of <i>cyclopentane</i>.</p>
2. Name the alkyl group, and append it as a prefix to the cycloalkane. No locant is needed if the compound is a monosubstituted cycloalkane. It is understood that the alkyl group is attached to C-1.	<p>The previous compound is <i>isopropylcyclopentane</i>. Alternatively, the alkyl group can be named according to the rules summarized in Table 2.8, whereupon the name becomes <i>(1-methylethyl)cyclopentane</i>. Parentheses are used to set off the name of the alkyl group as needed to avoid ambiguity.</p>
3. When two or more different substituents are present, list them in alphabetical order, and number the ring in the direction that gives the lower number at the first point of difference.	<p>The compound shown is <i>1,1-diethyl-4-hexylcyclooctane</i>.</p> 
4. Name the compound as a cycloalkyl-substituted alkane if the substituent has more carbons than the ring.	<p> <i>CH₂CH₂CH₂CH₂CH₂CH₃</i> is <i>pentylcyclopentane</i> but  <i>CH₂CH₂CH₂CH₂CH₂CH₃</i> is <i>1-cyclopentylhexane</i></p>

TABLE 2.8 Summary of IUPAC Nomenclature of Alkyl Groups

Rule	Example
1. Number the carbon atoms beginning at the point of attachment, proceeding in the direction that follows the longest continuous chain.	The longest continuous chain that begins at the point of attachment in the group shown contains six carbons. $\begin{array}{cccccccc} & & & 1 & 2 & 3 & 4 & 5 & 6 \\ & & & & & & & & \\ \text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{C} & \text{CH}_2 & \text{CH} & \text{CH}_2 & \text{CH}_2 & \text{CH}_3 \\ & & & & & & & & \\ & & & \text{CH}_3 & & \text{CH}_3 & & & \end{array}$
2. Assign a basis name according to the number of carbons in the corresponding unbranched alkane. Drop the ending <i>-ane</i> and replace it by <i>-yl</i> .	The alkyl group shown in step 1 is named as a substituent <i>hexyl</i> group.
3. List the substituents on the basis group in alphabetical order using replicating prefixes when necessary.	The alkyl group in step 1 is a <i>dimethylpropylhexyl</i> group.
4. Locate the substituents according to the numbering of the main chain described in step 1.	The alkyl group is a <i>1,3-dimethyl-1-propylhexyl</i> group.

number of carbon atoms increases. Branched alkanes have lower boiling points than their unbranched isomers. There is a limit to how closely two molecules can approach each other, which is given by the sum of their **van der Waals radii**.

Section 2.15 Alkanes and cycloalkanes burn in air to give carbon dioxide, water, and heat. This process is called **combustion**.



$$\Delta H^\circ = -3529 \text{ kJ } (-843.4 \text{ kcal})$$

The heat evolved on burning an alkane increases with the number of carbon atoms. The relative stability of isomers may be determined by comparing their respective **heats of combustion**. The more stable of two isomers has the lower heat of combustion.

Section 2.16 Combustion of alkanes is an example of **oxidation–reduction**. Although it is possible to calculate oxidation numbers of carbon in organic molecules, it is more convenient to regard oxidation of an organic substance as an increase in its oxygen content or a decrease in its hydrogen content.

PROBLEMS

2.16 Write structural formulas, and give the IUPAC names for the nine alkanes that have the molecular formula C_7H_{16} .

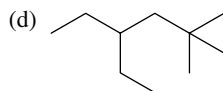
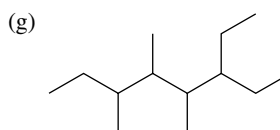
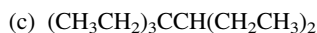
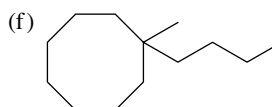
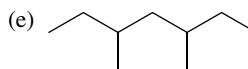
2.17 From among the 18 constitutional isomers of C_8H_{18} , write structural formulas, and give the IUPAC names for those that are named as derivatives of

- (a) Heptane
(b) Hexane
(c) Pentane
(d) Butane

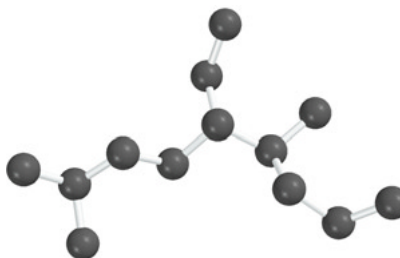
2.18 Write a structural formula for each of the following compounds:

- (a) 6-Isopropyl-2,3-dimethylnonane
(b) 4-*tert*-Butyl-3-methylheptane
(c) 4-Isobutyl-1,1-dimethylcyclohexane
(d) *sec*-Butylcycloheptane
(e) Cyclobutylcyclopentane
(f) (2,2-Dimethylpropyl)cyclohexane
(g) Pentacosane
(h) 10-(1-methylpentyl)pentacosane

2.19 Give the IUPAC name for each of the following compounds:

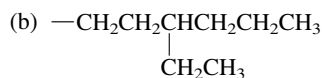


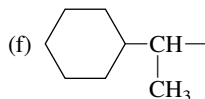
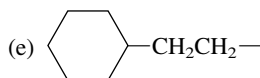
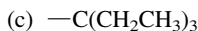
2.20 All the parts of this problem refer to the alkane having the carbon skeleton shown.



- (a) What is the molecular formula of this alkane?
(b) What is its IUPAC name?
(c) How many methyl groups are present in this alkane? Methylene groups? Methine groups?
(d) How many carbon atoms are primary? Secondary? Tertiary? Quaternary?

2.21 Give the IUPAC name for each of the following alkyl groups, and classify each one as primary, secondary, or tertiary:





2.22 *Pristane* is an alkane that is present to the extent of about 14% in shark liver oil. Its IUPAC name is 2,6,10,14-tetramethylpentadecane. Write its structural formula.

2.23 Hectane is the IUPAC name for the unbranched alkane that contains 100 carbon atoms.

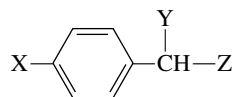
- How many σ bonds are there in hectane?
- How many alkanes have names of the type x -methylhectane?
- How many alkanes have names of the type 2, x -dimethylhectane?

2.24 Which of the compounds in each of the following groups are isomers?

- Butane, cyclobutane, isobutane, 2-methylbutane
- Cyclopentane, neopentane, 2,2-dimethylpentane, 2,2,3-trimethylbutane
- Cyclohexane, hexane, methylcyclopentane, 1,1,2-trimethylcyclopropane
- Ethylcyclopropane, 1,1-dimethylcyclopropane, 1-cyclopropylpropane, cyclopentane
- 4-Methyltetradecane, 2,3,4,5-tetramethyldecane, pentadecane, 4-cyclobutyldecane

2.25 *Epichlorohydrin* is the common name of an industrial chemical used as a component in epoxy cement. The molecular formula of epichlorohydrin is $\text{C}_3\text{H}_5\text{ClO}$. Epichlorohydrin has an epoxide functional group; it does not have a methyl group. Write a structural formula for epichlorohydrin.

2.26 (a) Complete the structure of the pain-relieving drug *ibuprofen* on the basis of the fact that ibuprofen is a carboxylic acid that has the molecular formula $\text{C}_{13}\text{H}_{18}\text{O}_2$, X is an isobutyl group, and Y is a methyl group.

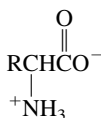


(b) *Mandelonitrile* may be obtained from peach flowers. Derive its structure from the template in part (a) given that X is hydrogen, Y is the functional group that characterizes alcohols, and Z characterizes nitriles.

2.27 *Isoamyl acetate* is the common name of the substance most responsible for the characteristic odor of bananas. Write a structural formula for isoamyl acetate, given the information that it is an ester in which the carbonyl group bears a methyl substituent and there is a 3-methylbutyl group attached to one of the oxygens.

2.28 *n-Butyl mercaptan* is the common name of a foul-smelling substance obtained from skunk fluid. It is a thiol of the type RX , where R is an n -butyl group and X is the functional group that characterizes a thiol. Write a structural formula for this substance.

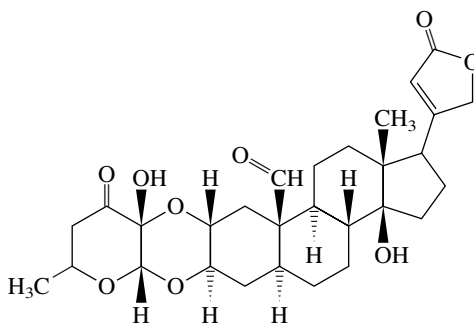
2.29 Some of the most important organic compounds in biochemistry are the α -amino acids, represented by the general formula shown.



Write structural formulas for the following α -amino acids.

- Alanine (R = methyl)
- Valine (R = isopropyl)
- Leucine (R = isobutyl)
- Isoleucine (R = *sec*-butyl)
- Serine (R = XCH_2 , where X is the functional group that characterizes alcohols)
- Cysteine (R = XCH_2 , where X is the functional group that characterizes thiols)
- Aspartic acid (R = XCH_2 , where X is the functional group that characterizes carboxylic acids)

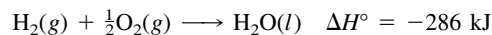
2.30 Uscharidin is the common name of a poisonous natural product having the structure shown. Locate all of the following in uscharidin:



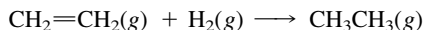
- Alcohol, aldehyde, ketone, and ester functional groups
 - Methylene groups
 - Primary carbons
- 2.31** Write the structural formula of a compound of molecular formula $C_4H_8Cl_2$ in which
- All the carbons belong to methylene groups
 - None of the carbons belong to methylene groups
- 2.32** Female tiger moths signify their presence to male moths by giving off a sex attractant. The sex attractant has been isolated and found to be a 2-methyl-branched alkane having a molecular weight of 254. What is this material?
- 2.33** Write a balanced chemical equation for the combustion of each of the following compounds:
- Decane
 - Cyclodecane
 - Methylcyclononane
 - Cyclopentylcyclopentane
- 2.34** The heats of combustion of methane and butane are 890 kJ/mol (212.8 kcal/mol) and 2876 kJ/mol (687.4 kcal/mol), respectively. When used as a fuel, would methane or butane generate more heat for the same mass of gas? Which would generate more heat for the same volume of gas?
- 2.35** In each of the following groups of compounds, identify the one with the largest heat of combustion and the one with the smallest. (Try to do this problem without consulting Table 2.5.)
- Hexane, heptane, octane
 - Isobutane, pentane, isopentane
 - Isopentane, 2-methylpentane, neopentane

- (d) Pentane, 3-methylpentane, 3,3-dimethylpentane
 (e) Ethylcyclopentane, ethylcyclohexane, ethylcycloheptane

2.36 (a) Given ΔH° for the reaction



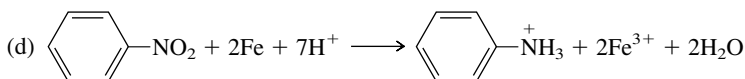
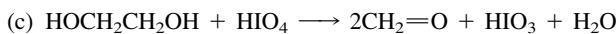
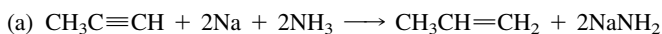
along with the information that the heat of combustion of ethane is 1560 kJ/mol and that of ethylene is 1410 kJ/mol, calculate ΔH° for the hydrogenation of ethylene:



- (b) If the heat of combustion of acetylene is 1300 kJ/mol, what is the value of ΔH° for its hydrogenation to ethylene? To ethane?
 (c) What is the value of ΔH° for the hypothetical reaction



2.37 Each of the following reactions will be encountered at some point in this text. Classify each one according to whether the organic substrate is oxidized or reduced in the process.

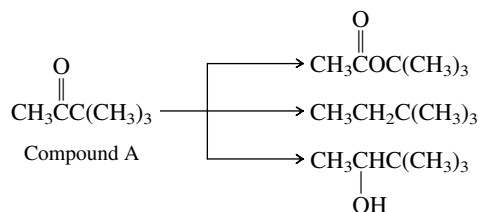


2.38 The reaction shown is important in the industrial preparation of dichlorodimethylsilane for eventual conversion to silicone polymers.



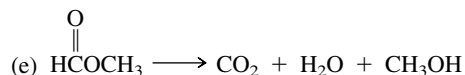
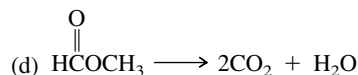
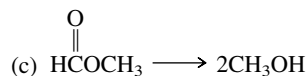
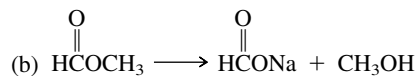
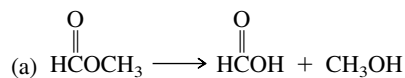
Is carbon oxidized, or is it reduced in this reaction?

2.39 Compound A undergoes the following reactions:

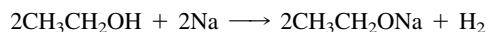


- (a) To what class of compounds does compound A belong?
 (b) Which of the reactions shown require(s) an oxidizing agent?
 (c) Which of the reactions shown require(s) a reducing agent?
 (d) Identify the class to which each of the reaction products belongs.

2.40 Each of the following equations describes a reaction of a compound called *methyl formate*. To what class of compounds does methyl formate belong? Which reactions require a reducing agent? Which require an oxidizing agent? Which reactions are not oxidation–reduction?



2.41 Which atoms in the following reaction undergo changes in their oxidation state? Which atom is oxidized? Which one is reduced?



2.42 We have not talked about heats of combustion of compounds other than hydrocarbons. Nevertheless, from among the compounds shown here, you should be able to deduce which one gives off the most heat on combustion (to give CO_2 and H_2O) and which one the least.



2.43 Make a molecular model of each of the compounds given as a representative example of the various functional group classes in Table 2.1.



2.44 The compound identified as “ethanoic acid” in Table 2.2 is better known as acetic acid. Make a molecular model of acetic acid, and compare the two C—O bond distances. Compare these with the C—O bond distance in ethanol (Problem 2.43).



2.45 You have seen that a continuous chain of sp^3 -hybridized carbons, as in an alkane, is not “straight,” but rather adopts a zigzag geometry. What would the hybridization state of carbon have to be in order for the chain to be truly straight?