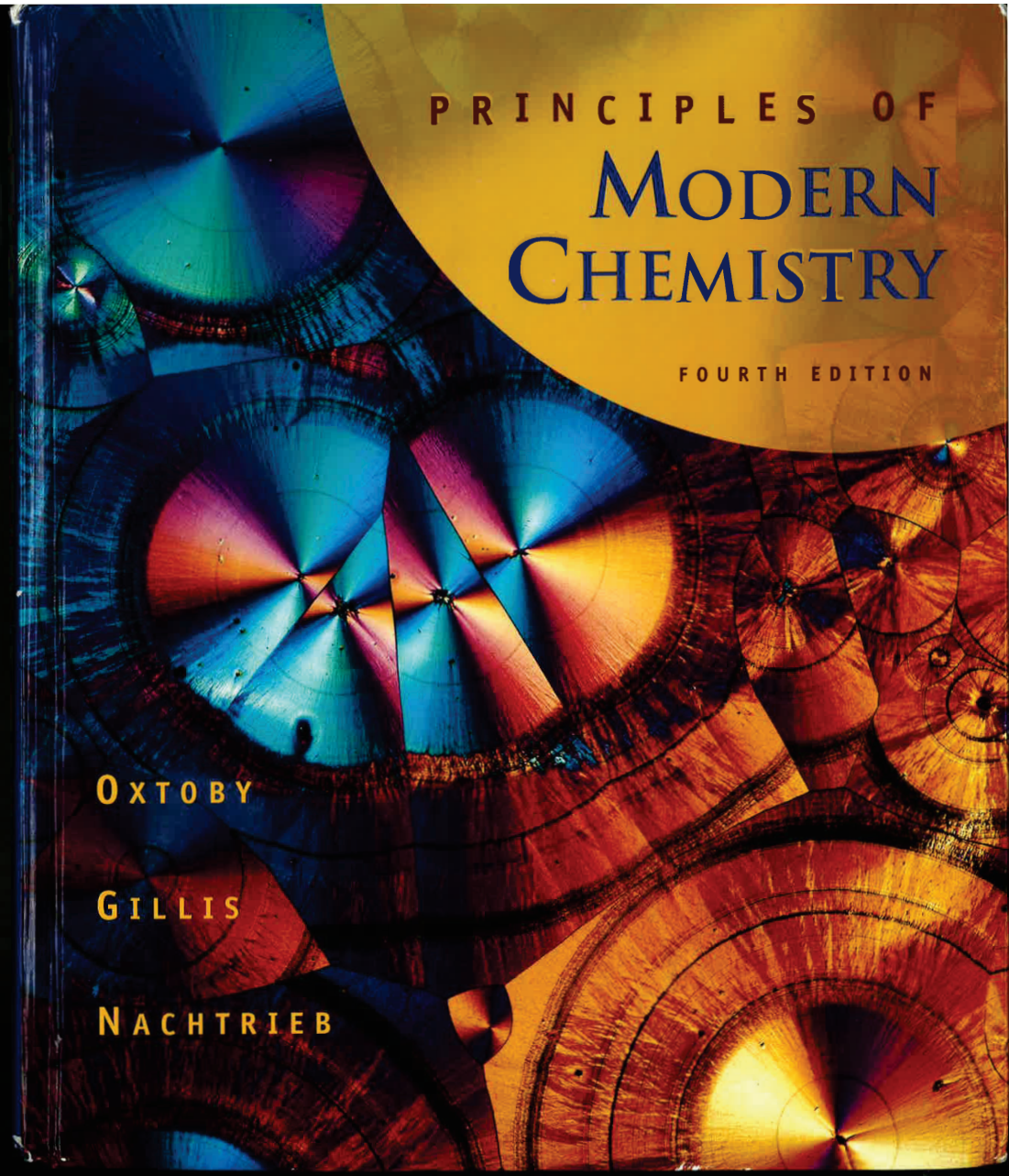

NEURELIS, INC., EX2052, page 1
PADAGIS US LLC v. NEURELIS, INC.
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PRINCIPLES OF

MODERN CHEMISTRY

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NEURELIS, INC., EX2052, page 2
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MODERN CHEMISTRY

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TO THE MEMORY OF NORMAN NACHTRIEB, OUR TEACHER, COLLEAGUE, AND FRIEND, WHOSE MANY CONTRIBUTIONS FILL THIS BOOK AND WHOSE SPIRIT CONTINUES TO INSPIRE US.

The search for truth is in one way hard and in another easy,
for it is evident that no one can master it fully or miss it completely.
But each adds a little to our knowledge of nature, and from all
the facts assembled there arises a certain grandeur.

(Greek inscription, taken from Aristotle, on the facade of
the National Academy of Sciences building in Washington, D.C.)

CHAPTER

17

Bonding, Structure, and Reactions of Organic Molecules

17.1 Bonding and Structure in Organic Molecules

17.2 Petroleum Refining and the Hydrocarbons

17.3 Functional Groups and Organic Synthesis

Illustration
A petroleum refining tower. *(Courtesy of Ashland Oil, Inc.)*

Carbon is unique among the elements in the large number of compounds it forms and in the variety of their structures. In combination with hydrogen, it forms molecules with single, double, and triple bonds; chains; rings; branched structures; and cages (Fig. 17.1). The thousands of stable hydrocarbons are in sharp contrast with the mere two stable compounds between oxygen and hydrogen (water and hydrogen peroxide). Even the rather versatile elements nitrogen and oxygen form only six nitrogen oxides.

The unique properties of carbon relate to its position in the periodic table. As a second-period element, carbon has relatively small atoms, so it can easily form the

double and triple bonds that are rare in the compounds of related elements, such as silicon. As a Group IV element, carbon can form four bonds, more than the other second-period elements; this characteristic gives it wide scope for structural elaboration. Finally, as an element of intermediate electronegativity, carbon forms covalent compounds both with relatively electronegative elements, such as oxygen, nitrogen, and the halogens, and with relatively electropositive elements, such as hydrogen and the heavy metals mercury and lead.

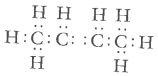
The study of the compounds of carbon is the discipline traditionally called **organic chemistry**, although the chemistry of carbon is intimately bound up with that of inorganic elements and with biochemistry. This chapter begins with a look at the variety of bonding and structures evidenced by organic molecules, made possible by the properties of the element carbon described in the previous paragraph. The description is based on the general principles of covalent bonding in polyatomic molecules presented in Section 16.2. The relation between molecular structure and properties of organic substances is illustrated by examining the composition, refining, and chemical processing of petroleum, the primary starting material for the production of hydrocarbons and their derivatives. The chapter concludes with an introduction to the types of compounds that result when elements such as chlorine, oxygen, and nitrogen combine with carbon and hydrogen, and with a survey of their importance in synthetic reactions.

FIGURE 17.1 One simple and unusual hydrocarbon is cubane (C_8H_8), in which the eight carbon atoms are arranged at the corners of a cube.

17.1 Bonding and Structure in Organic Molecules

Bonding in Organic Molecules

The structures of many organic molecules (compounds of carbon) can be described through the simple molecular orbital picture presented in Section 16.2. A helpful first step in analyzing molecular bonding is to write the Lewis electron-dot diagram. As an example, consider the molecule 2-butene ($CH_3CHCHCH_3$). Its Lewis diagram is



From the VSEPR theory, the steric number of the two outer carbon atoms is 4 (and so they have sp^3 hybridization), and that of the two central carbon atoms is 3 (giving sp^2 hybridization). The bonding about the outer carbon atoms will be tetrahedral, and that about the central ones will be trigonal planar. Electron pairs are placed into each localized (σ) molecular orbital, giving a single bond between each pair of bonding atoms. In the case of 2-butene, these placements use 22 out of the 24 available valence electrons, forming a total of 11 single bonds.

Next, the remaining p orbitals that were not involved in hybridization are combined to form π molecular orbitals. The p_z orbitals from the two central carbon

NEURELIS, INC., EX2052, page 5
PADAGIS US LLC v. NEURELIS, INC.
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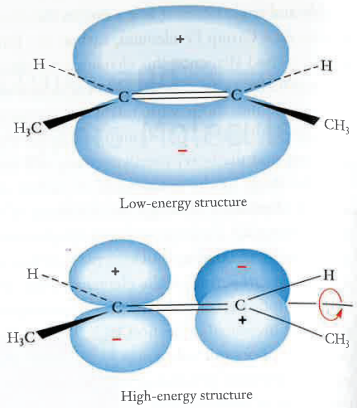


FIGURE 17.2 As the 2-butene molecule is twisted about the C=C bond, the overlap of the two *p* orbitals decreases, giving a higher energy.

atoms can be mixed to form a π (bonding) molecular orbital and a π^* (antibonding) molecular orbital. The remaining two valence electrons are placed into the π orbital, giving a double bond between the central carbon atoms. If the p_z orbital of one of these atoms is rotated about the central C—C axis, its overlap with the p_z orbital of the other carbon atom changes (Fig. 17.2). The overlap is greatest, and the energy lowest, when the two p_z orbitals are parallel to each other. In the most stable molecular geometry, the hydrogen atoms on the central carbon atoms lie in the same plane as the C—C—C—C carbon skeleton. This prediction is verified by experiment.

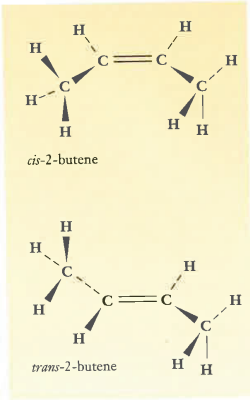


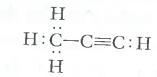
FIGURE 17.3 The two *cis-trans* isomers of 2-butene.

Structural Isomerism

In 2-butene there are two possible placements for the outer CH_3 groups relative to the double bond (Fig. 17.3). In one, called *cis*-2-butene, the two methyl (CH_3) groups lie on the same side of the double bond; in the other, *trans*-2-butene, they lie on opposite sides. Converting one form to the other requires breaking the central π bond (by rotating the two p_z orbitals 180° with respect to each other, as in Fig. 17.2), then re-forming it in the other configuration. Because breaking a π bond costs a significant amount of energy, both *cis* and *trans* forms are stable at room temperature, and interconversion between the two is very slow. The change in molecular structure from *trans* to *cis* can be accomplished by photochemistry without complete breaking of bonds (see Section 16.7). Molecules such as those of *trans*-2-butene can absorb ultraviolet light by the excitation of an electron from a π to a π^* molecular orbital, just as ethylene does (see Fig. 16.28). In the excited electronic state of *trans*-2-butene, the carbon–carbon double bond is effectively reduced to a single bond, and the one CH_3 group can rotate relative to the other to form *cis*-2-butene. Molecules that have the same chemical formula but different structures are called **geometrical isomers.** Absorption of ultraviolet light can cause interconversion of one geometrical isomer into another.

EXAMPLE 17.1

The Lewis diagram for propyne (CH_3CCH) is



Discuss its bonding and predict its geometry.

Solution

The leftmost carbon atom in the structure is sp^3 hybridized, and the other two carbon atoms are *sp* hybridized. The atoms in the molecule are on a single straight line with the exception of the three hydrogen atoms on the leftmost carbon atom, which point outward toward three of the vertices of a tetrahedron. There is a σ bond between each pair of bonded atoms. The p_x and p_y orbitals on carbon atoms 2 and 3 combine to form two π orbitals and two π^* orbitals; only the former are occupied in the ground-state electron configuration.

Related Problems: 1, 2

A second type of isomerism characteristic of organic molecules is **optical isomerism,** or **chirality.** A carbon atom that forms single bonds to four different atoms or groups of atoms can exist in two forms that are mirror images of each other but that cannot be interconverted without breaking and re-forming bonds (Fig. 17.4). If a mixture of the two forms is resolved into its optical isomers, the two forms rotate the plane of polarized light in different directions, and so such molecules are said to be "optically active." Although paired optical isomers have identical physical properties, their chemical properties can differ when they interact with other optically active molecules. As we will see in Section 25.3, proteins and other biomolecules are optically active. One goal of pharmaceutical research is to prepare particular optical isomers of carbon compounds for medicinal use. In many cases one optical isomer is beneficial and the other is useless or even harmful.

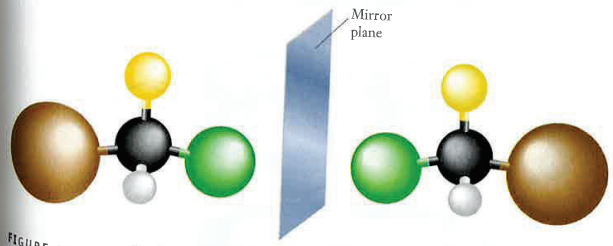


FIGURE 17.4 A molecule such as CHBrClF, which has four different atoms or groups of atoms bonded to a single carbon atom, exists in two mirror-image forms that cannot be superimposed by rotation. Such pairs of molecules are optical isomers; the carbon atom is called a chiral center.

NEURELIS, INC., EX2052, page 6
PADAGIS US LLC v. NEURELIS, INC.
IPR2025-00464, U.S. PATENT 8,895,546

Conjugated Molecules

When two or more double or triple bonds occur close to each other in a molecule, a delocalized molecular orbital picture of the bonding should be used. One example is 1,3-butadiene ($CH_2CHCHCH_2$), which has the Lewis diagram

All four carbon atoms have steric number 3, and so all are sp^2 hybridized. The remaining p_z orbitals have maximum overlap when the four carbon atoms lie in the same plane, and so this molecule is predicted to be planar. From these four p_z atomic orbitals, four molecular orbitals can be constructed by combining their phases as shown in Figure 17.5. The four electrons that remain after the σ orbitals are filled are placed in the two lowest π orbitals. The first of these is bonding among all four carbon atoms, and the second is bonding between the outer carbon atom pairs but antibonding between the central pair. Therefore, 1,3-butadiene has stronger and shorter bonds between the outer carbon pairs than between the two central carbon atoms. It is an example of a **conjugated π electron system,** in which two or more

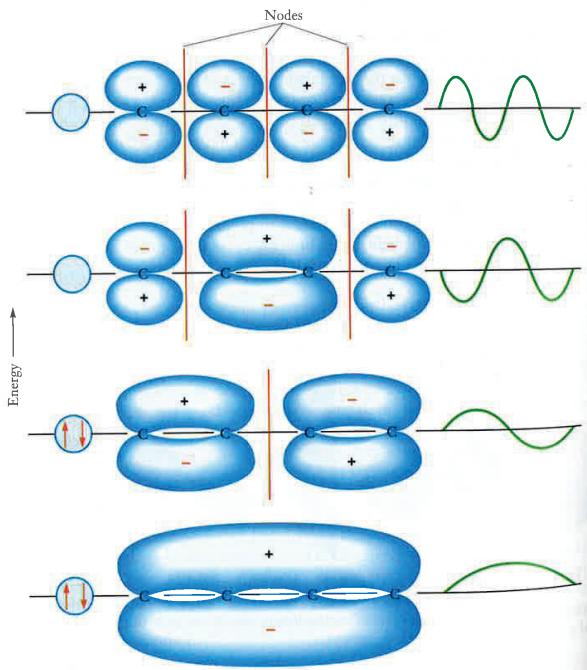
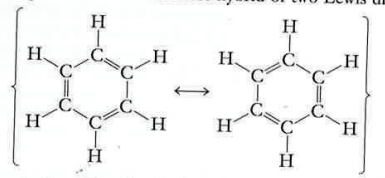


FIGURE 17.5 The four π molecular orbitals formed from four $2p_z$ atomic orbitals in 1,3-butadiene, viewed from the side. Planar nodes are indicated by red lines. Note the similarity in nodal properties to the first four harmonics of a vibrating string (right). Only the two lowest energy orbitals are occupied in the molecule in the ground state (left).

double or triple bonds alternate with single bonds. Such conjugated systems have lower energies than would be predicted from localized bond models and are best described with delocalized molecular orbitals extending over the entire π electron system.

Benzene is a ring molecule with the formula C_6H_6. In the language of Chapter 3, benzene is represented as a resonance hybrid of two Lewis diagrams:



The modern view is that the molecule does not jump between two structures but rather has a single, time-independent electron distribution in which the π bonding is described through delocalized molecular orbitals. Each carbon atom has sp^2 hybridization, and the remaining six p_z orbitals combine to give six molecular orbitals delocalized over the entire molecule. Figure 17.6 shows the π orbitals and their energy level diagram. The lowest energy π orbital has no nodes, the next two have two nodes, the next two have four nodes, and the highest energy orbital has six nodes.

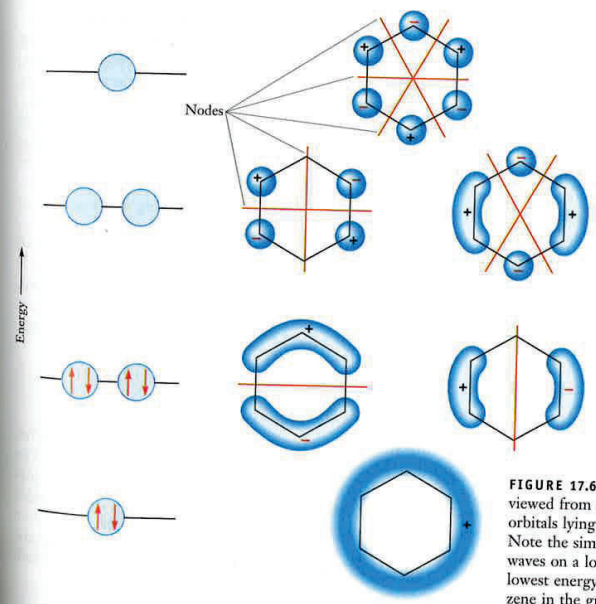


FIGURE 17.6 The six π molecular orbitals for benzene, viewed from the top, formed from the six $2p_z$ atomic orbitals lying perpendicular to the plane of the molecule. Note the similarity in nodal properties to the standing waves on a loop shown in Figure 15.16. Only the three lowest energy orbitals are occupied in molecules of benzene in the ground state.

NEURELIS, INC., EX2052, page 7
PADAGIS US LLC v. NEURELIS, INC.
IPR2025-00464, U.S. PATENT 8,895,546

The C_6H_6 molecule has 30 valence electrons, of which 24 occupy sp^2 hybrid orbitals and form σ bonds. When the six remaining valence electrons are placed in the three lowest energy π orbitals, the resulting electron distribution is the same in all six carbon–carbon bonds. As a result, benzene has six carbon–carbon bonds of equal length with properties intermediate between those of single and double bonds.

17.2 PETROLEUM REFINING AND THE HYDROCARBONS

When the first oil well was drilled in 1859 near Titusville, Pennsylvania, the future effects of the exploitation of petroleum on everyday life could not have been anticipated. Today, the petroleum and petrochemical industries span the world and touch the most minute details of our daily lives. In the early years of this century, the development of the automobile, fueled by low-cost gasoline derived from petroleum, dramatically changed many people's lifestyles. The subsequent use of gasoline and oil to power trains and planes, tractors and harvesters, pumps and coolers, transformed travel, agriculture, and industry. Natural gas and heating oil warm the vast majority of homes in the United States. Finally, the spectacular growth of the petrochemical industry since 1945 has led to the introduction of innumerable new products ranging from pharmaceuticals to plastics and synthetic fibers. More than half of the chemical compounds produced in greatest volumes stem directly or indirectly from petroleum.

As we look forward to the next century, the prospects for the continued enjoyment of cheap petroleum and petrochemicals are clouded. Many wells have been drained, and the remaining petroleum is relatively difficult and costly to extract. Petroleum is not easy to make. It originated from the deposition and decay of organic matter (of animal or vegetable origin) in oxygen-poor marine sediments. Subsequently, petroleum migrated to the porous sandstone rocks from which it is extracted today. In the last 100 years, we have consumed a significant fraction of the petroleum accumulated in the earth over many millions of years. The imperative for the future is to save the remaining reserves for uses for which few substitutes are available (such as the manufacture of specialty chemicals) while finding other sources of heat and energy.

Isolating individual hydrocarbon substances from the complex mixtures obtained as petroleum is therefore an industrial process of central importance. Moreover, it provides a fascinating story illustrating how the structure of molecules determines the properties of substances and therefore the behavior of those substances in particular processes. This section presents a brief introduction to this story, emphasizing the structure-property correlations.

TABLE 17.1

Straight-Chain Alkanes

Name	Formula
Methane	CH_4
Ethane	C_2H_6
Propane	C_3H_8
Butane	C_4H_{10}
Pentane	C_5H_{12}
Hexane	C_6H_{14}
Heptane	C_7H_{16}
Octane	C_8H_{18}
Nonane	C_9H_{20}
Decane	$C_{10}H_{22}$
Undecane	$C_{11}H_{24}$
Dodecane	$C_{12}H_{26}$
Tridecane	$C_{13}H_{28}$
Tetradecane	$C_{14}H_{30}$
Pentadecane	$C_{15}H_{32}$
⋮	⋮
Triacontane	$C_{30}H_{62}$

Petroleum Distillation and the Normal Alkanes

Although crude petroleum contains small amounts of oxygen, nitrogen, and sulfur, its major constituents are **hydrocarbons**, compounds of carbon and hydrogen. The most prevalent hydrocarbons in petroleum are the **straight-chain alkanes** (also called normal alkanes, or *n*-alkanes), which consist of chains of carbon atoms bonded to one another by single bonds, with enough hydrogen atoms on each carbon atom to bring it to the maximum bonding capacity of four. These alkanes have the generic formula C_nH_{2n+2}; Table 17.1 lists the names and formulas of the first few. The ends

of the molecules are methyl (—CH_3) groups, with methylene (—CH_2—) groups between. We could write pentane (C_5H_{12}) as $CH_3CH_2CH_2CH_2CH_3$ to indicate the structure more explicitly or, in abbreviated fashion, as $CH_3(CH_2)_3CH_3$.

Each carbon atom in a straight-chain alkane forms four single bonds, which point to the corners of a tetrahedron (exhibiting sp^3 hybridization). Although bond *lengths* do not change much through vibration, rotation about a C—C single bond occurs quite easily (Fig. 17.7), and so a given hydrocarbon molecule in a gas or liquid constantly changes its conformation. The term "straight chain" refers only to the bonding pattern in which each carbon atom is bonded to the next one in a sequence; it does not mean that the carbon atoms are positioned along a straight line. An alkane molecule with 10 to 20 carbon atoms looks quite different from its curled-up form when its bonds are extended to give a "stretched" molecule (Fig. 17.8). These two extreme conformations and many others interconvert rapidly at room temperature.

Figure 17.9 shows the melting and boiling points of the straight-chain alkanes; both increase with the number of carbon atoms and thus with molecular mass. This is a consequence of the increasing strength of dispersion forces between heavier molecules, as discussed in Section 4.7. Methane, ethane, propane, and butane are all gases at room temperature, but the hydrocarbons that follow them in the alkane series are liquids. Alkanes beyond about $C_{17}H_{36}$ are waxy solids at 20°C, with melting points that increase with the number of carbon atoms present. Paraffin wax, a low-melting solid, is a mixture of alkanes that have 20 to 30 carbon atoms per molecule. Petrolatum (petroleum jelly, or Vaseline) is a different mixture that is semisolid at room temperature.

A mixture of hydrocarbons such as petroleum does not boil at a single, sharply defined temperature. Instead, as such a mixture is heated, the compounds with lower boiling points (the most volatile) boil off first and, as the temperature rises, more and more of the material vaporizes. The existence of a boiling-point range permits components of a mixture to be separated by distillation, as Section 6.5 discussed. The earliest petroleum distillation was a simple batch process: the crude oil was heated in a still, the volatile fractions were removed at the top and condensed to

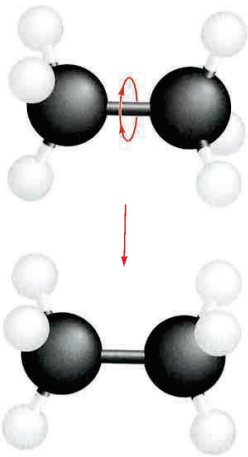


FIGURE 17.7 The two —CH_3 groups in ethane rotate easily about the bond that joins them.

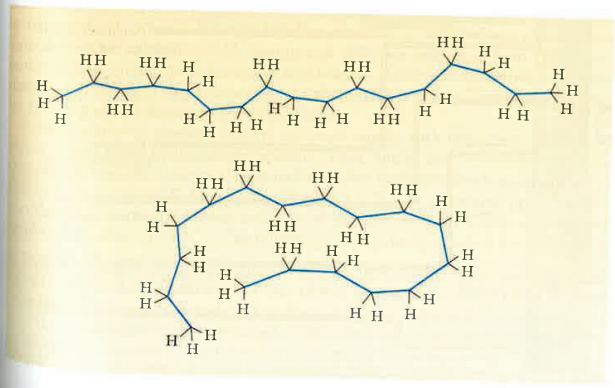


FIGURE 17.8 Two of the very many possible conformations of the alkane $C_{17}H_{36}$. The carbon atoms are not shown explicitly, but they lie at every intersection of four lines.

NEURELIS, INC., EX2052, page 8
PADAGIS US LLC v. NEURELIS, INC.
IPR2025-00464, U.S. PATENT 8,895,546

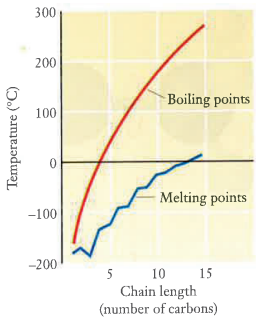


FIGURE 17.9 The melting and boiling points of the straight-chain alkanes increase with chain length n. Note the alternation in the melting points: alkanes with n odd tend to have lower melting points because they are more difficult to pack into a crystal lattice.

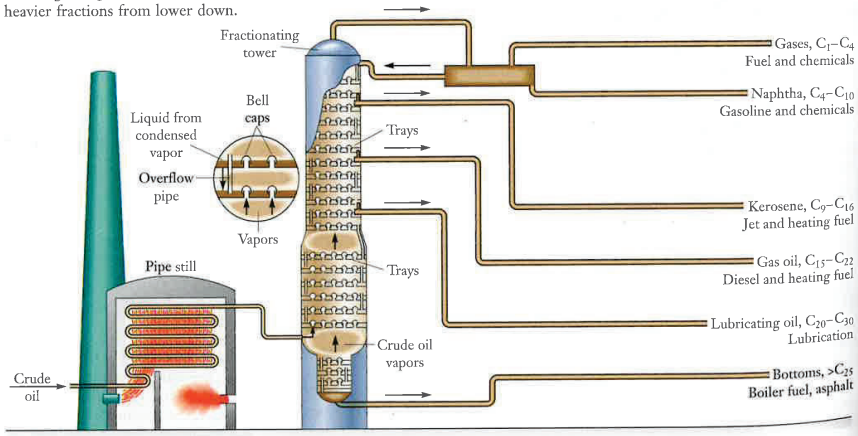
gasoline, and the still was cleaned for another batch. Modern petroleum refineries use much more sophisticated and efficient distillation methods, in which crude oil is added continuously and fractions of different volatility are tapped off at various points up and down the distillation column (Fig. 17.10). To save on energy costs, heat exchangers are employed to capture the heat from condensation of the liquid products.

Distillation allows hydrocarbons to be separated by boiling point and thus by molecular mass. The gases that emerge from the top of the column resemble the natural gas that collects in rock cavities above petroleum deposits. The gas mixtures can be separated further by redissolving the ethane, propane, and butane in a liquid solvent such as hexane. The methane-rich mixture of gases that remains is used for chemical synthesis or is shipped by pipeline to heat homes. Redistilling the hexane and its dissolved gases allows their separation and their use as chemical starting materials. Propane and butane are also bottled under pressure as liquefied petroleum gas (LPG), which is used for fuel in rural areas. After the gases, the next fraction to emerge from the petroleum distillation column is **naphtha**, which is used primarily in the manufacture of gasoline. Subsequent fractions of successively higher molecular mass are employed for jet and diesel fuel, heating oil, and machine lubricating oil. The heavy, involatile sludge that remains at the bottom of the distillation unit is pitch or asphalt, which is used for roofing and paving.

Cyclic and Branched-Chain Alkanes

The straight-chain alkanes are not the only hydrocarbons in petroleum. Two other important classes of compounds, the cyclic and branched-chain alkanes, are also represented. A **cycloalkane** consists of at least one chain of carbon atoms attached at

FIGURE 17.10 In the distillation of petroleum, the lighter, more volatile hydrocarbon fractions are removed from higher up the column and the heavier fractions from lower down.



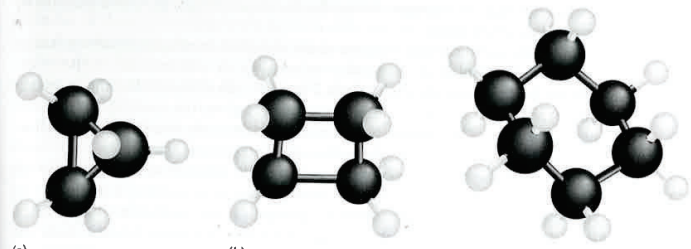


FIGURE 17.11 Three cyclic hydrocarbons. (a) Cyclopropane, C_3H_6. (b) Cyclobutane, C_4H_8. (c) Cyclohexane, C_6H_{12}.

the ends to form a closed loop. In the formation of this additional C—C bond, two hydrogen atoms must be eliminated, and so the general formula for cycloalkanes with one ring is C_nH_{2n} (Fig. 17.11). The smallest cycloalkanes, cyclopropane and cyclobutane, are very strained compounds because the C—C—C bond angle is 60° (in C_3H_6) or 90° (in C_4H_8), far less than the normal tetrahedral angle of 109.5°. As a result, these compounds are more reactive than the heavier cycloalkanes or their straight-chain analogs, propane and butane.

Branched-chain alkanes are hydrocarbons that contain only C—C and C—H single bonds but in which the carbon atoms are no longer arranged in a straight chain. One or more carbon atoms in each molecule are bonded to three or four other carbon atoms rather than to only one or two as in the normal alkanes or cycloalkanes. The simplest branched-chain molecule (Fig. 17.12b) is that of 2-methylpropane, sometimes referred to as isobutane. This molecule has the same molecular formula as butane (C_4H_{10}) but a different bonding structure in which the central carbon atom is bonded to three —CH_3 groups and only one hydrogen atom. The compounds butane and 2-methylpropane are **isomers.** Their molecules have the same formula but different three-dimensional structures that can be interconverted only by breaking and re-forming chemical bonds.

The number of possible isomers increases rapidly with increasing numbers of carbon atoms in the hydrocarbon molecule. Thus, butane and 2-methylpropane are the only two isomers of chemical formula C_4H_{10}, but there are three isomers of C_5H_{12}, five of C_6H_{14}, nine of C_7H_{16}, and millions of $C_{30}H_{62}$. A systematic procedure for naming these isomers has been codified by the International Union of Pure and Applied Chemistry (IUPAC). The following set of rules is a part of that procedure.

1. Find the longest continuous chain of carbon atoms in the molecule. The molecule is named as a derivative of this alkane. In Figure 17.12b a chain of three carbon atoms can be found, and so the molecule is a derivative of propane.
2. The hydrocarbon groups attached to the chain are called alkyl groups. Their names are obtained by dropping the ending *-ane* from the corresponding alkane and replacing it with *-yl* (Table 17.2). The methyl group, —CH_3, is derived from

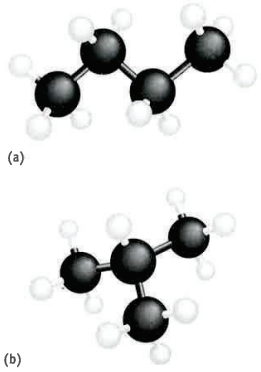


FIGURE 17.12 Two isomeric hydrocarbons with the molecular formula C_4H_{10}. (a) Butane. (b) 2-methylpropane.

NEURELIS, INC., EX2052, page 9
PADAGIS US LLC v. NEURELIS, INC.
IPR2025-00464, U.S. PATENT 8,895,546

TABLE 17.2

Alkyl Side Groups

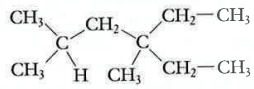
Name	Formula
Methyl	$-CH_3$
Ethyl	$-CH_2CH_3$
Propyl	$-CH_2CH_2CH_3$
Isopropyl	$-CH(CH_3)_2$
Butyl	$-CH_2CH_2CH_2CH_3$

methane (CH_4), for example. Note also the isopropyl group, which attaches by its middle carbon atom.

3. Number the carbon atoms along the chain identified in rule 1. Identify each alkyl group by the number of the carbon atom at which it is attached to the chain. The methyl group in the molecule in Figure 17.12b is attached to the second of the three carbon atoms in the propane chain, and so the molecule is called 2-methylpropane. The carbon chain is numbered from the end that gives the lowest number for the position of the first attached group.
4. If more than one alkyl group of the same type is attached to the chain, use the prefixes *di-* (two), *tri-* (three), *tetra-* (four), *penta-* (five), and so forth to specify the total number of such attached groups in the molecule. Thus, 2,2,3-trimethylbutane has two methyl groups attached to the second carbon atom and one to the third carbon atom of the four-atom butane chain. It is an isomer of heptane (C_7H_{16}).
5. If several types of alkyl groups appear, name them in alphabetical order. Ethyl is listed before methyl, which appears before propyl.

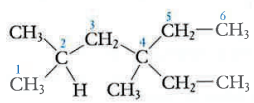
EXAMPLE 17.2

Name the following branched-chain alkane:



Solution

The longest continuous chain of carbon atoms is six, and so this is a derivative of hexane. Number the carbon atoms starting from the left.



Methyl groups are attached to carbon atoms 2 and 4, and an ethyl group is attached to atom 4. The name is thus 4-ethyl-2,4-dimethylhexane. Note that if we had started numbering from the right, the higher number 3 would have appeared for the position of the first methyl group, and so the numbering from the left is preferred.

Related Problems: 13, 14

The fraction of branched-chain alkanes in a gasoline affects how it burns in an engine. Gasoline composed entirely of straight-chain alkanes burns very unevenly, causing "knocking" that can damage the engine. Blends that are richer in branched-chain and cyclic alkanes burn with much less knocking. Smoothness of combustion is rated quantitatively via the **octane number** of the gasoline, which was defined in 1927 by selecting two compounds that lie at extremes in the knocking they cause. Pure 2,2,4-trimethylpentane (commonly known as isooctane) burns very smoothly and was assigned an octane number of 100. Of the compounds examined at the time, pure heptane caused the most knocking and was assigned octane number 0. Mixtures of heptane and isooctane cause intermediate amounts of knocking. Standard mixtures of these two compounds define a scale for evaluating the knocking caused by real gasolines, which are complex mixtures of branched-chain and straight-chain hydrocarbons. If a gasoline sample produces the same amount of knocking in a test engine as a mixture of 90% (by volume) 2,2,4-trimethylpentane and 10% heptane, it is assigned the octane number 90.

Certain additives increase the octane rating of gasoline. The least expensive of these is tetraethyllead, $Pb(C_2H_5)_4$, a compound that has very weak bonds between the central lead atom and the ethyl carbon atoms. It readily releases ethyl radicals ($\cdot C_2H_5$) into the gasoline during combustion; these reactive species speed and smooth the combustion process, reducing knocking and giving better fuel performance. The lead is released into the atmosphere and causes serious long-term health hazards, however. As a result, the use of lead in gasoline is being phased out, and other low-cost additives are being sought to increase octane number. Chemical processing to make branched-chain compounds from straight-chain compounds represents another solution to the problem, although only a partial one.

Alkenes and Alkynes

The hydrocarbons discussed so far are referred to as **saturated,** because all the carbon–carbon bonds are single bonds. Hydrocarbons that have double and triple carbon–carbon bonds are referred to as **unsaturated** (Fig. 17.13). Ethylene (C_2H_4) has a double bond between its carbon atoms and is called an **alkene.** The simplest **alkyne** is acetylene (C_2H_2), which has a triple bond between its carbon atoms. In naming these compounds, the *-ane* ending of the corresponding alkane is replaced by *-ene* when a double bond is present and by *-yne* when a triple bond is present. Ethene is thus the systematic name for ethylene, and ethyne for acetylene, although we will continue to use their more common names. For any compound with a carbon backbone of four or more carbon atoms, it is necessary to specify the location of the double or triple bond. This is done by numbering the carbon–carbon bonds and putting the number of the lower numbered carbon involved in the multiple bond before the name of the alkene or alkyne. Thus, the two different isomeric alkynes with the formula C_4H_6 are

$HC{\equiv}C{-}CH_2{-}CH_3$ 1-butyne

$CH_3{-}C{\equiv}C{-}CH_3$ 2-butyne

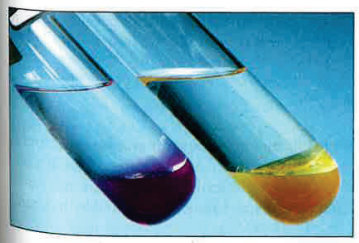


FIGURE 17.13 One way to distinguish alkanes from alkenes is by their reactions with aqueous $KMnO_4$. This strong oxidizing agent undergoes no reaction with hexane and retains its purple color (left). When $KMnO_4$ is placed in contact with 1-hexene, however, a redox reaction takes place in which the brown solid MnO_2 forms (right) and —OH groups are added to both sides of the double bond in the 1-hexene, giving a compound with the formula $CH_3(CH_2)_3CH(OH)CH_2OH$. *(Charles Steele)*

NEURELIS, INC., EX2052, page 10
PADAGIS US LLC v. NEURELIS, INC.
IPR2025-00464, U.S. PATENT 8,895,546