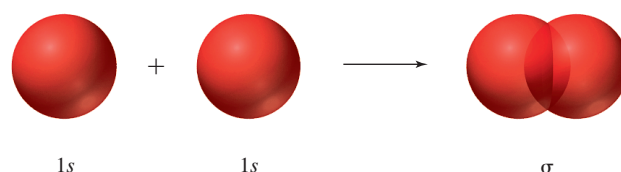


of structural types, you will find that the term sp^3 -hybridized carbon triggers associations in your mind that are different from those of some other term, such as sp^2 -hybridized carbon, for example.

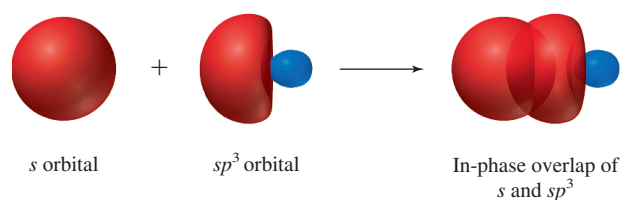
Molecular orbital theory can provide insights into structure and reactivity that the Lewis and orbital hybridization models can't. It is the least intuitive of the three methods, however, and requires the most training, background, and chemical knowledge to apply. We have *discussed* molecular orbital theory so far only in the context of the bonding in H_2 . We have *used* the results of molecular orbital theory, however, several times without acknowledging it until now. Electrostatic potential maps are obtained by molecular orbital calculations. Four molecular orbital calculations provided the drawings that we used in Figure 2.4 to illustrate how electron density builds up between the atoms in the valence bond (!) treatment of H_2 . Molecular orbital theory is well suited to quantitative applications and is becoming increasingly available for routine use via software that runs on personal computers. You will see the results of molecular orbital theory often in this text, but the theory itself will be developed only at an introductory level.

2.23 SUMMARY

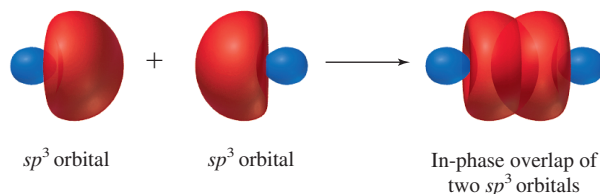
- Section 2.1 The classes of hydrocarbons are **alkanes**, **alkenes**, **alkynes**, and **arenes**. Alkanes are hydrocarbons in which all of the bonds are *single* bonds and are characterized by the molecular formula C_nH_{2n+2} .
- Section 2.2 Two theories of bonding, valence bond and molecular orbital theory, are based on the wave nature of an electron. Constructive interference between the electron wave of one atom and that of another gives a region between the two atoms in which the probability of sharing an electron is high—a bond.
- Section 2.3 In valence bond theory a covalent bond is described in terms of in-phase overlap of a half-filled orbital of one atom with a half-filled orbital of another. When applied to bonding in H_2 , the orbitals involved are the $1s$ orbitals of two hydrogen atoms and the bond is a σ bond.



- Section 2.4 In molecular orbital theory, the molecular orbitals (MOs) are approximated by combining the atomic orbitals (AOs) of all of the atoms in a molecule. The number of MOs must equal the number of AOs that are combined.
- Section 2.5 The first three alkanes are methane (CH_4), ethane (CH_3CH_3), and propane ($CH_3CH_2CH_3$).
- Section 2.6 Bonding in methane is most often described by an orbital hybridization model, which is a modified form of valence bond theory. Four equivalent sp^3 hybrid orbitals of carbon are generated by mixing the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals. In-phase overlap of each half-filled sp^3 hybrid orbital with a half-filled hydrogen $1s$ orbital gives a σ bond.



Section 2.7 The carbon–carbon bond in ethane is a σ bond in which an sp^3 hybrid orbital of one carbon overlaps with an sp^3 hybrid orbital of the other.



Section 2.8 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 2.9 Unbranched alkanes of the type $CH_3(CH_2)_xCH_3$ are often referred to as *n*-alkanes, and are said to belong to a **homologous series**.

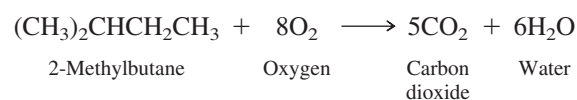
Section 2.10 There are three constitutional isomers of C_5H_{12} : ***n*-pentane** ($CH_3CH_2CH_2CH_2CH_3$), isopentane [$(CH_3)_2CHCH_2CH_3$], and neopentane [$(CH_3)_4C$].

Sections 2.11–2.15 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 2.6 summarizes the rules for alkanes and cycloalkanes. Table 2.7 gives the rules for naming alkyl groups.

Section 2.16 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 2.17 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 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 2.18 Alkanes and cycloalkanes burn in air to give carbon dioxide, water, and heat. This process is called **combustion**.



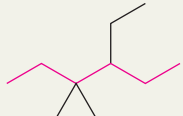
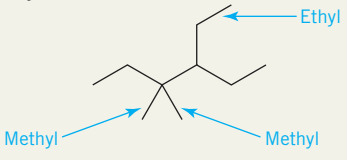
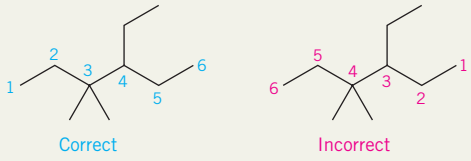
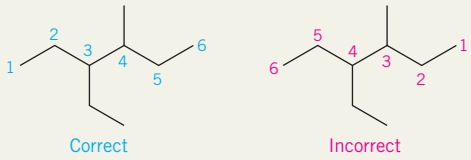
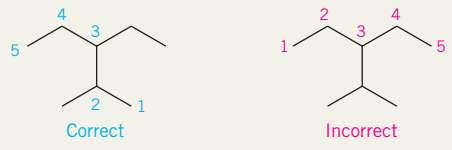
$$\Delta H^\circ = -3529 \text{ kJ } (-843.4 \text{ kcal})$$

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 2.19 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.

Section 2.20 Carbon is **sp^2 -hybridized** in ethylene, and the double bond has a σ component and a π component. The sp^2 hybridization state is derived by mixing the $2s$ and two of the three $2p$ orbitals. Three equivalent sp^2 orbitals result, and their axes are coplanar. Overlap of an sp^2 orbital of one carbon with an sp^2 orbital of another produces a σ bond between them. Each carbon still has one unhybridized p orbital available for bonding, and

TABLE 2.6 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes

Rule	Example
A. Alkanes	
<p>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>	<p>The longest continuous chain in the alkane shown is six carbons.</p>  <p>This alkane is named as a derivative of <i>hexane</i>.</p>
<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>	<p>The alkane bears two methyl groups and an ethyl group. It is an <i>ethyl</i><i>dimethylhexane</i>.</p> 
<p>3. Number from the end of the chain in the direction that gives the lower locant to a substituent at the first point of difference.</p>	<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>  <p>The correct name is <i>4-ethyl-3,3-dimethylhexane</i>.</p>
<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>	<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>
<p>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>	<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>

—Continued

TABLE 2.6 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes (*Continued*)

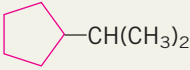
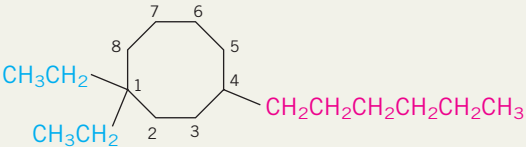


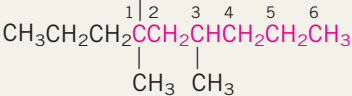
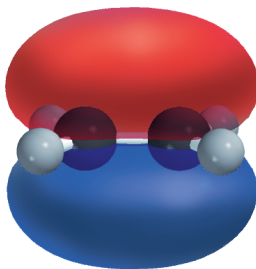
Rule	Example
B. Cycloalkanes	
<p>1. Count the number of carbons in the ring, and assign a basis name to the cycloalkane corresponding to the IUPAC name of the unbranched cycloalkane having the same number of carbons.</p>	<p>The compound shown contains five carbons in its ring.</p>  <p>It is named as a derivative of <i>cyclopentane</i>.</p>
<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>	<p>The previous compound is <i>isopropylcyclopentane</i>. Alternatively, the alkyl group can be named according to the rules summarized in Table 2.7, 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>
<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>	<p>The compound shown is <i>1,1-diethyl-4-hexylcyclooctane</i>.</p> 
<p>4. Name the compound as a cycloalkyl-substituted alkane if the substituent has more carbons than the ring.</p>	<p> $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ is <i>pentylcyclopentane</i> but  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ is <i>1-cyclopentylhexane</i></p>

TABLE 2.7 Summary of IUPAC Nomenclature of Alkyl Groups

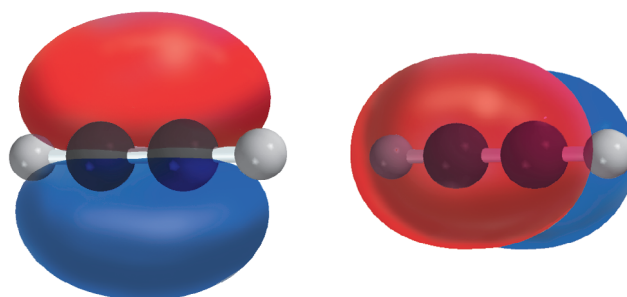
Rule	Example
<p>1. Number the carbon atoms beginning at the point of attachment, proceeding in the direction that follows the longest continuous chain.</p>	<p>The longest continuous chain that begins at the point of attachment in the group shown contains six carbons.</p> 
<p>2. Assign a basis name according to the number of carbons in the corresponding unbranched alkane. Drop the ending <i>-ane</i> and replace it with <i>-yl</i>.</p>	<p>The alkyl group shown in step 1 is named as a substituted <i>hexyl</i> group.</p>
<p>3. List the substituents attached to the basis group in alphabetical order using replicating prefixes when necessary.</p>	<p>The alkyl group in step 1 is a <i>dimethylpropylhexyl</i> group.</p>
<p>4. Locate the substituents according to the numbering of the main chain described in step 1.</p>	<p>The alkyl group is a <i>1,3-dimethyl-1-propylhexyl</i> group.</p>

“side-by-side” overlap of the p orbitals of adjacent carbons gives a π bond between them.



The π bond in ethylene is generated by overlap of p orbitals of adjacent carbons.

Section 2.21 Carbon is ***sp*-hybridized** in acetylene, and the triple bond is of the $\sigma + \pi + \pi$ type. The $2s$ orbital and one of the $2p$ orbitals combine to give two equivalent sp orbitals that have their axes in a straight line. A σ bond between the two carbons is supplemented by two π bonds formed by overlap of the remaining half-filled p orbitals.



The triple bond of acetylene has a σ bond component and two π bonds; the two π bonds are shown here and are perpendicular to each other.

Section 2.22 Lewis structures, orbital hybridization, and molecular orbital descriptions of bonding are all used in organic chemistry. Lewis structures are used the most, MO descriptions the least. All will be used in this text.

PROBLEMS

2.20 The general molecular formula for alkanes is C_nH_{2n+2} . What is the general molecular formula for:

- (a) Cycloalkanes (c) Alkynes
(b) Alkenes (d) Cyclic hydrocarbons that contain one double bond

2.21 A certain hydrocarbon has a molecular formula of C_5H_8 . Which of the following is *not* a structural possibility for this hydrocarbon?

- (a) It is a cycloalkane.
(b) It contains one ring and one double bond.
(c) It contains two double bonds and no rings.
(d) It is an alkyne.

2.22 Which of the hydrocarbons in each of the following groups are isomers?

