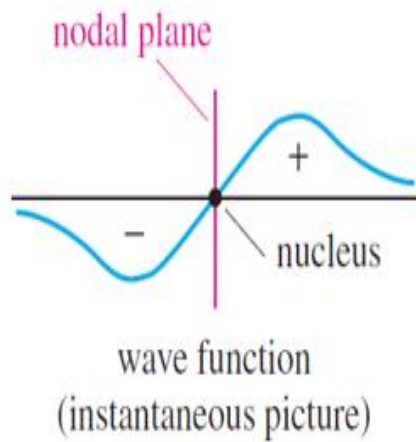


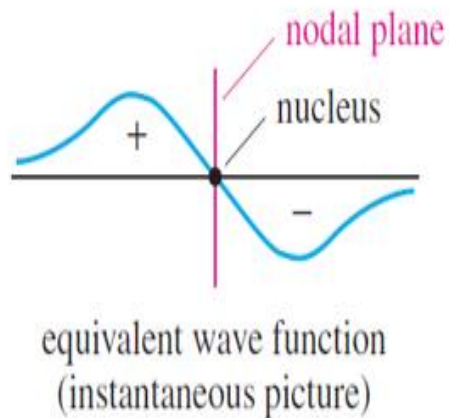
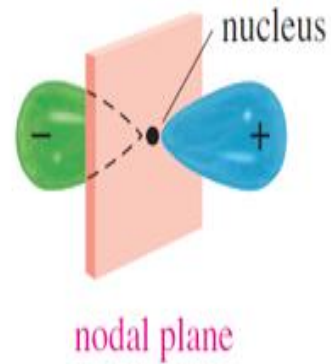
CHAPTER 2

Structure and Properties of Organic Molecules

1. Predict the hybridization and geometry of organic molecules based on their bonding.
2. Identify isomers and explain the differences between them.
3. Predict general trends in physical properties such as boiling points and solubilities.
4. Identify the general classes of organic compounds.



represented by



represented by

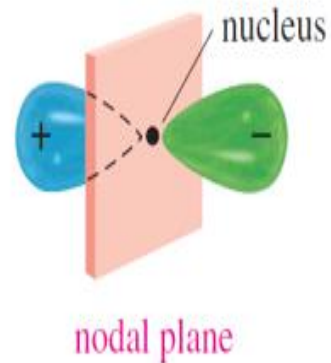


FIGURE 2-4

The $2p$ orbital. The $2p$ orbital has two lobes, separated by a nodal plane. The two lobes are out of phase with each other. When one has a plus sign, the other has a minus sign.

2-1A Linear Combination of Atomic Orbitals

- Atomic orbitals can combine and overlap to give more complex standing waves.
- When orbitals on *different* atoms interact, they produce **molecular orbitals** (MOs) that lead to bonding (or antibonding) interactions.
- When orbitals on the *same* atom interact, they give **hybrid atomic orbitals** that define the geometry of the bonds.

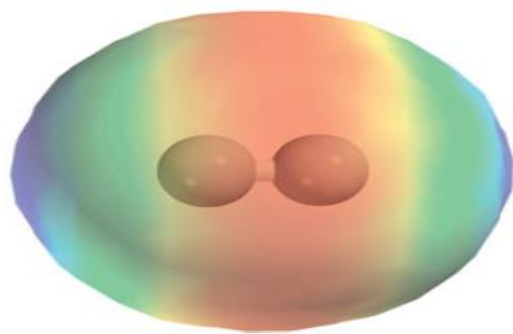
2-2 Molecular Orbitals

The internuclear distance where attraction and repulsion are balanced, which also gives the minimum energy (the strongest bond), is the *bond length*.

2-2A The Hydrogen Molecule; Sigma Bonding

Bonding molecular orbital (bonding MO): The bonding MO depicted in Figure 2-6 has most of its electron density centered *along the line connecting the nuclei*. This type of bond is called a *cylindrically symmetrical bond* or a **sigma bond** (**bond**).

The electrostatic potential map (EPM) of H_2 shows its cylindrically symmetrical sigma bond, with the highest electron density (red) in the bonding region between the two protons.



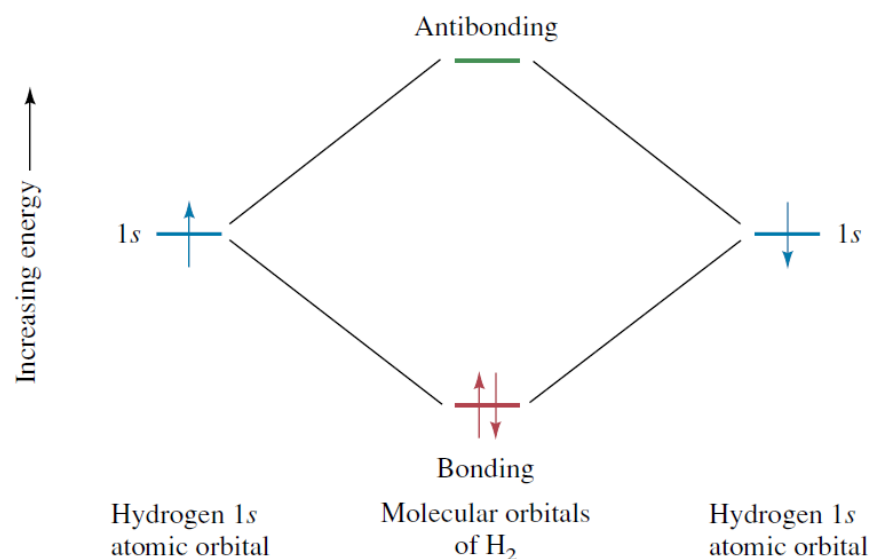
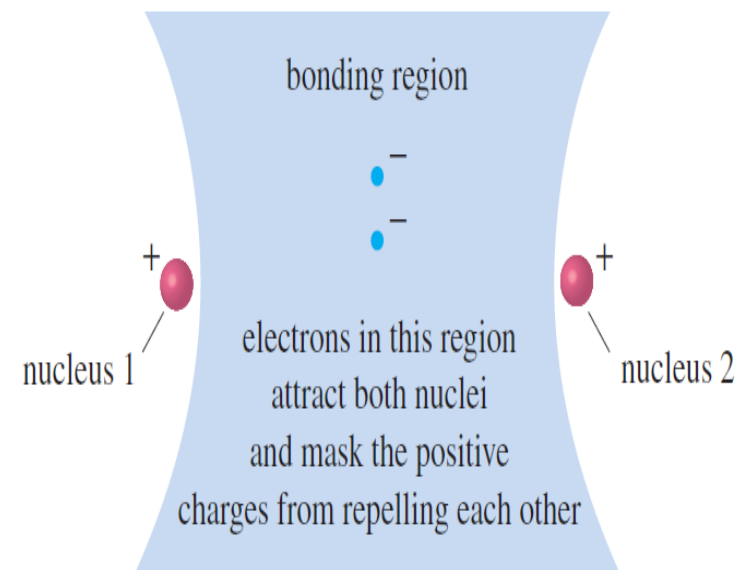
EPM of H_2

FIGURE 2-5

The bonding region. Electrons in the space between the two nuclei attract both nuclei and mask their positive charges. A bonding molecular orbital places a large amount of electron density in the bonding region.

FIGURE 2-5

The bonding region. Electrons in the space between the two nuclei attract both nuclei and mask their positive charges. A bonding molecular orbital places a large amount of electron density in the bonding region.



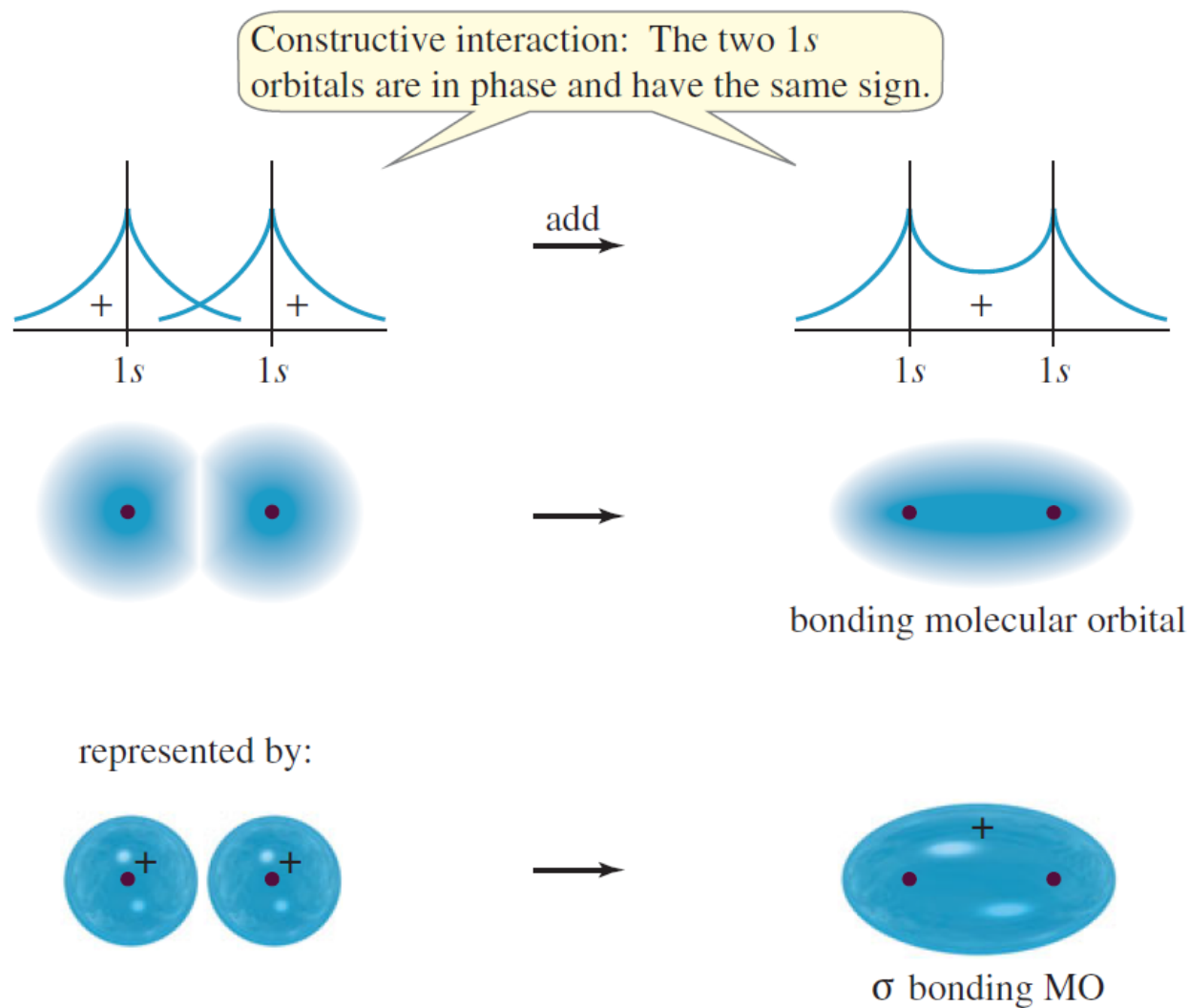


FIGURE 2-6

Formation of a σ bonding MO. When the $1s$ orbitals of two hydrogen atoms overlap in phase, they interact constructively to form a bonding MO. The electron density in the bonding region (between the nuclei) is increased. The result is a cylindrically symmetrical bond, or sigma (σ) bond.

When two hydrogen 1s orbitals overlap *out of phase* with each other, an **antibonding molecular orbital** results.

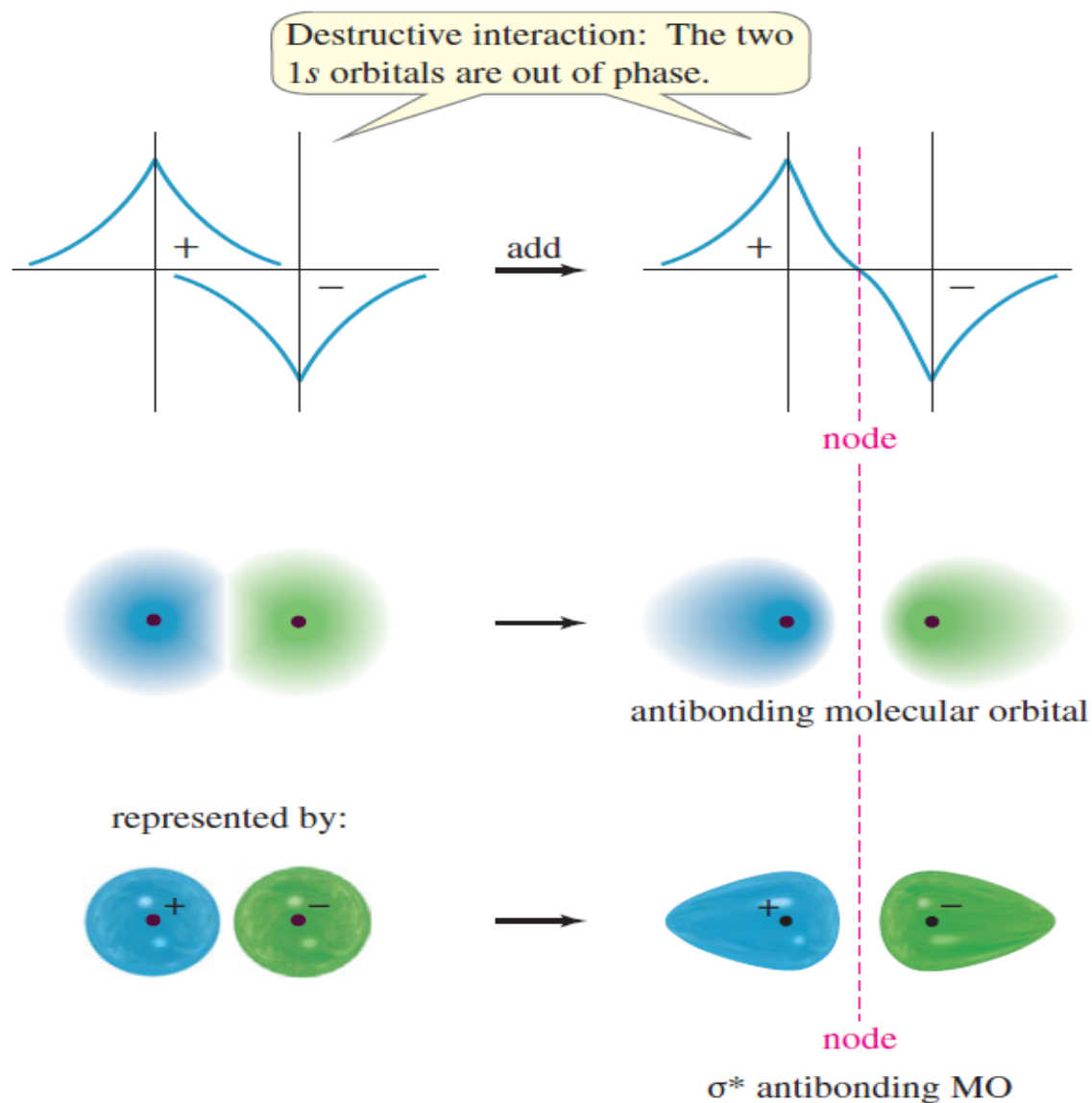
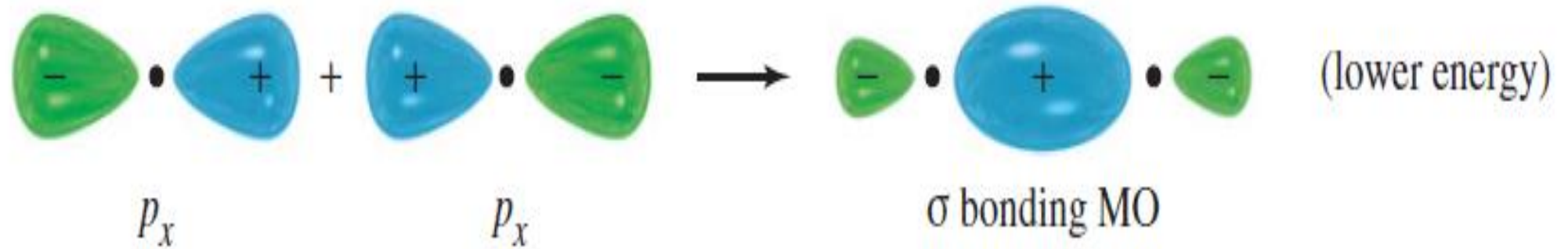


FIGURE 2-7

Formation of a σ^* antibonding MO. When two 1s orbitals overlap out of phase, they interact destructively to form an antibonding MO. The positive and negative values of the wave functions tend to cancel out in the region between the nuclei, and a node separates the nuclei. We use an asterisk (*) to designate antibonding orbitals such as this sigma antibonding orbital, σ^* .

2-2B Sigma Overlap Involving p Orbitals



2-3 Pi Bonding

- A **pi bond (bond)** results from overlap between two *p* orbitals oriented perpendicular to the line connecting the nuclei (Figure 2-9). These parallel orbitals overlap sideways, with most of the electron density centered *above and below* the line connecting the nuclei.
- This overlap is parallel, not linear (a sigma bond is linear), so a pi molecular orbital is *not* cylindrically symmetrical. Figure 2-9 shows a π bonding MO and the corresponding π^* antibonding MO.

2-3A Single and Double Bonds

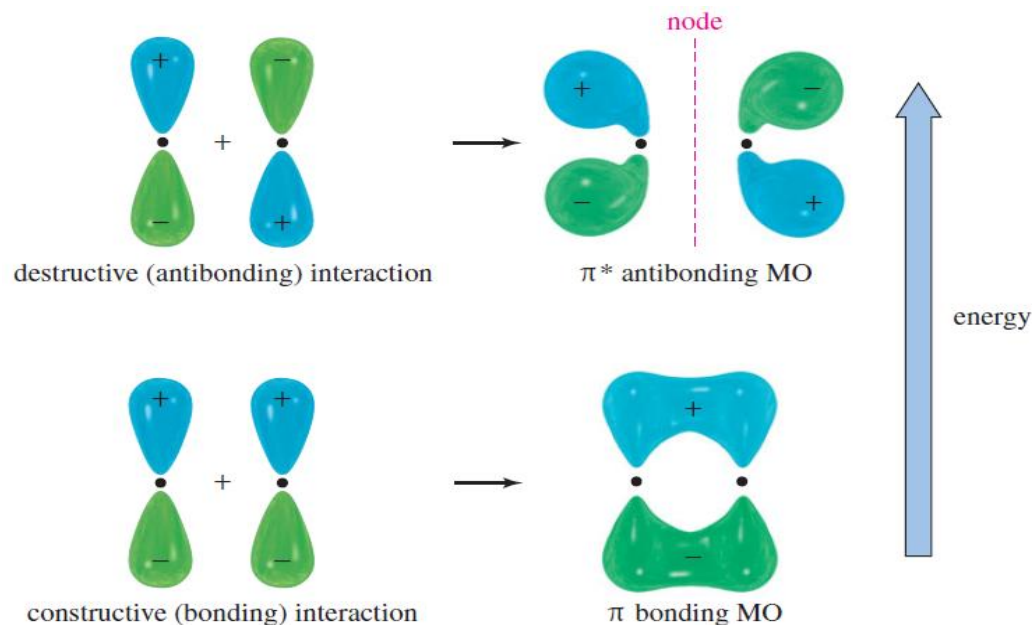
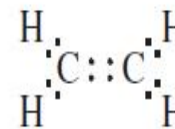
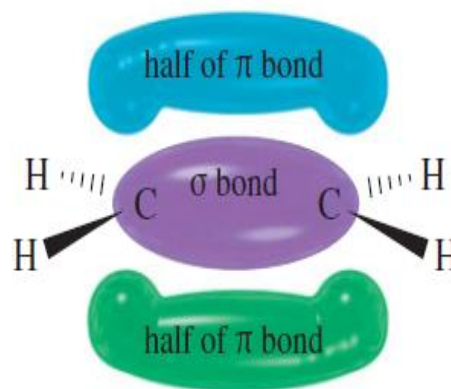


FIGURE 2-9

Pi bonding and antibonding molecular orbitals. The sideways overlap of two p orbitals leads to a π bonding MO and a π^* antibonding MO. A pi bond is not as strong as most sigma bonds.

FIGURE 2-10

Structure of the double bond in ethylene. The first pair of electrons forms a σ bond. The second pair forms a π bond. The π bond has its electron density centered in two lobes, above and below the σ bond. Together, the two lobes of the π bonding molecular orbital constitute one bond.



Lewis structure of ethylene

2-4 Hybridization and Molecular Shapes

Valence-shell electron-pair repulsion theory (VSEPR theory): Electron pairs repel each other, and the bonds and lone pairs around a central atom generally are separated by the largest possible angles.

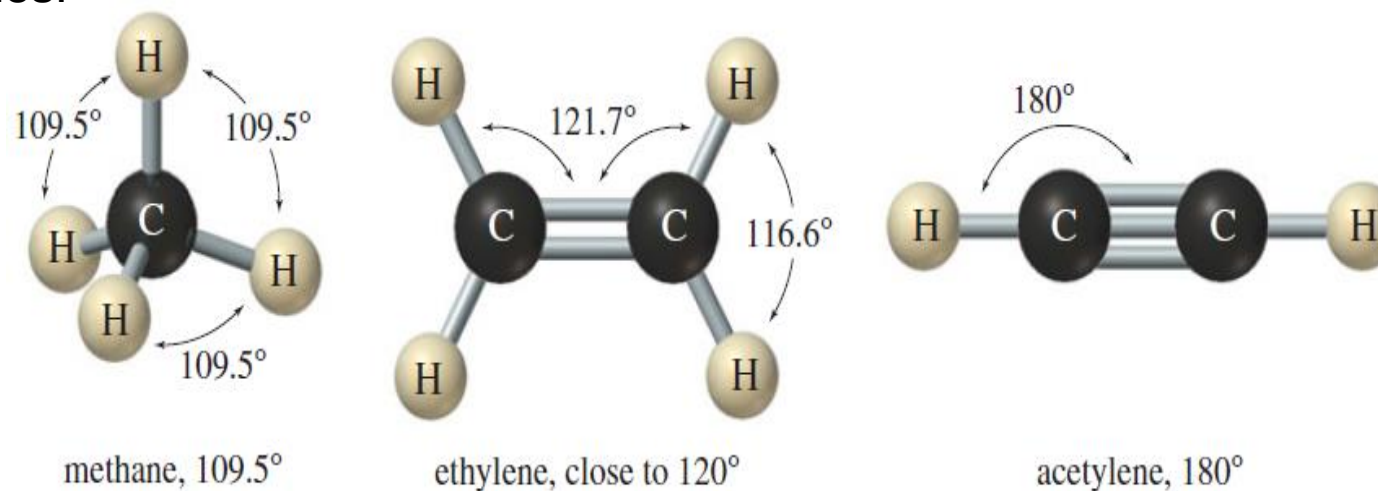


FIGURE 2-11

Common bond angles. Bond angles in organic compounds are usually close to 109°, 120°, or 180°.

Hybrid atomic orbitals. Hybrid atomic orbitals result from the mixing of orbitals on the *same* atom.

2-4A sp Hybrid Orbitals

sp hybrid orbital
 180°
Linear

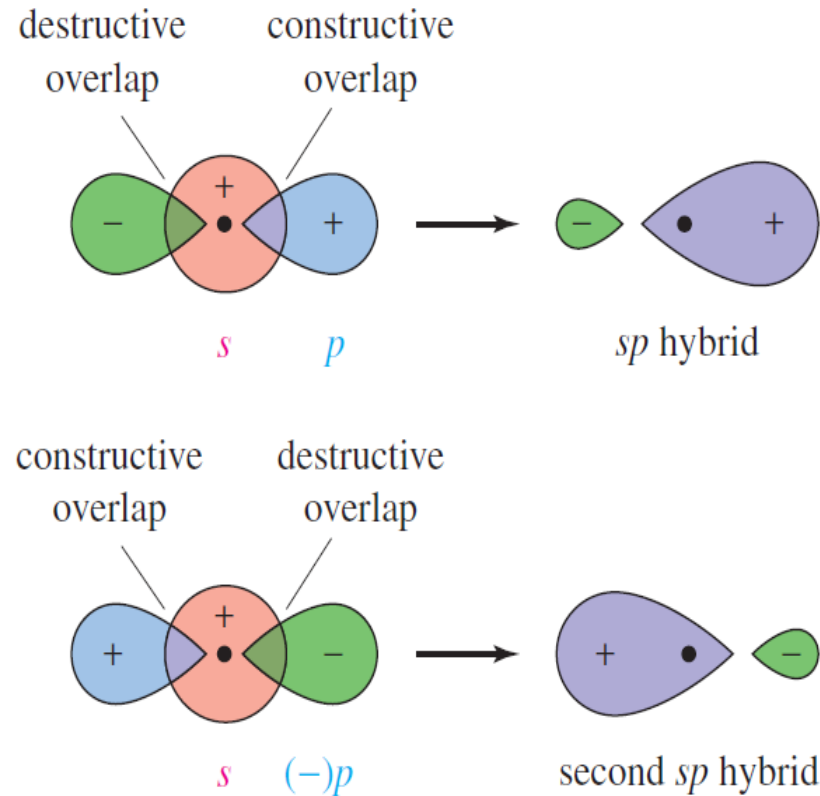
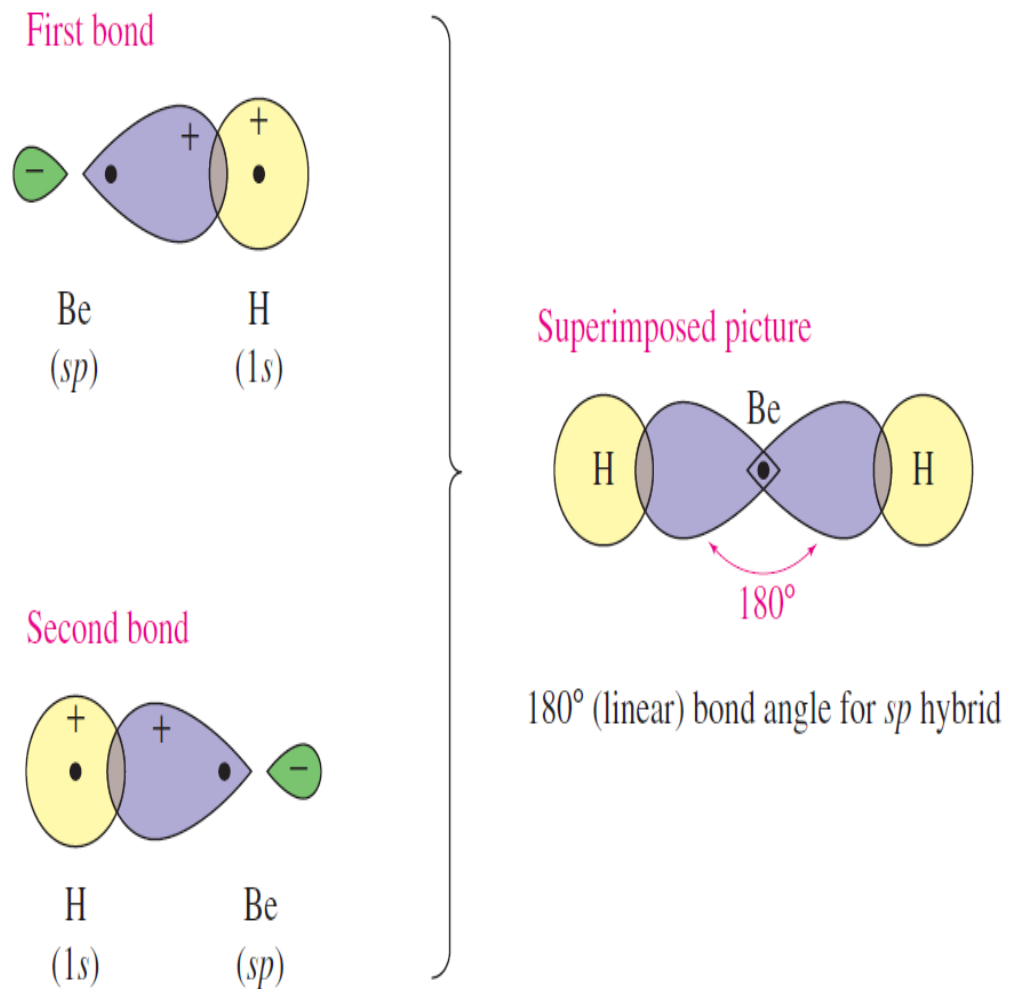


FIGURE 2-12

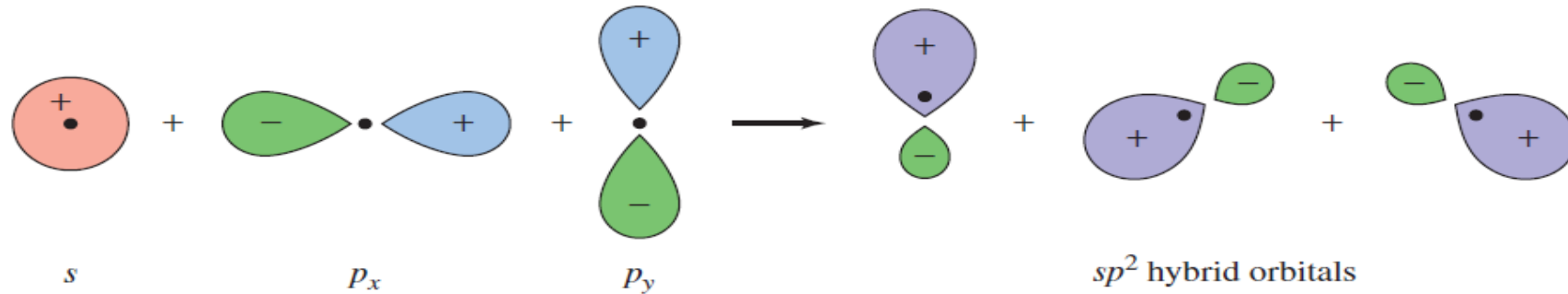
Formation of a pair of sp hybrid atomic orbitals. Addition of an s orbital to a p orbital gives an sp hybrid atomic orbital, with most of its electron density on one side of the nucleus. Adding the p orbital with opposite phase gives the other sp hybrid orbital, with most of its electron density on the opposite side of the nucleus from the first hybrid.

FIGURE 2-13

Linear geometry in the bonding of BeH_2 . To form two sigma bonds, the two sp hybrid atomic orbitals on Be overlap with the $1s$ orbitals of hydrogen. The bond angle is 180° (linear).



2-4B sp^2 Hybrid Orbitals



sp^2 hybrid orbitals
trigonal geometry
 120°

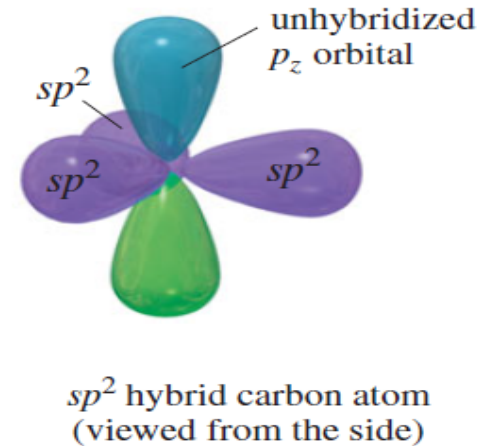
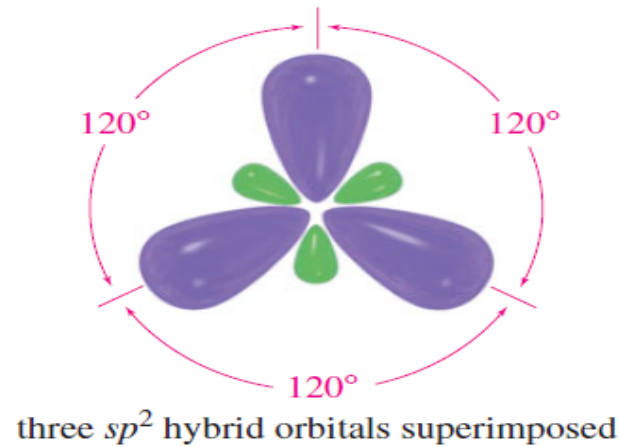
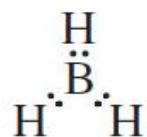
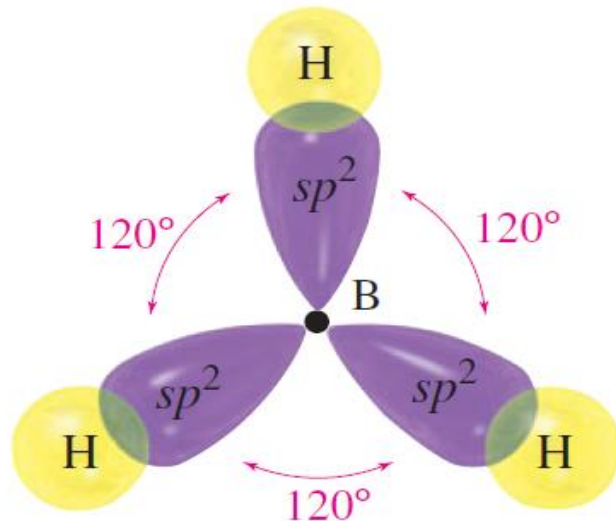


FIGURE 2-14

Trigonal geometry with sp^2 hybrid orbitals. Hybridization of an s orbital with two p orbitals gives a set of three sp^2 hybrid orbitals. This trigonal structure has bond angles of about 120° . The remaining p orbital is perpendicular to the plane of the three hybrid orbitals.



The best bonding orbitals are those that provide the greatest electron density in the bonding region while keeping the three pairs of bonding electrons as far apart as possible. Hybridization of an s orbital with two p orbitals gives three sp^2 hybrid orbitals directed 120° apart. Overlap of these orbitals with the hydrogen $1s$ orbitals gives a planar, trigonal molecule. (Note that the small back lobes of the hybrid orbitals have been omitted.)



2-4C sp^3 Hybrid Orbitals

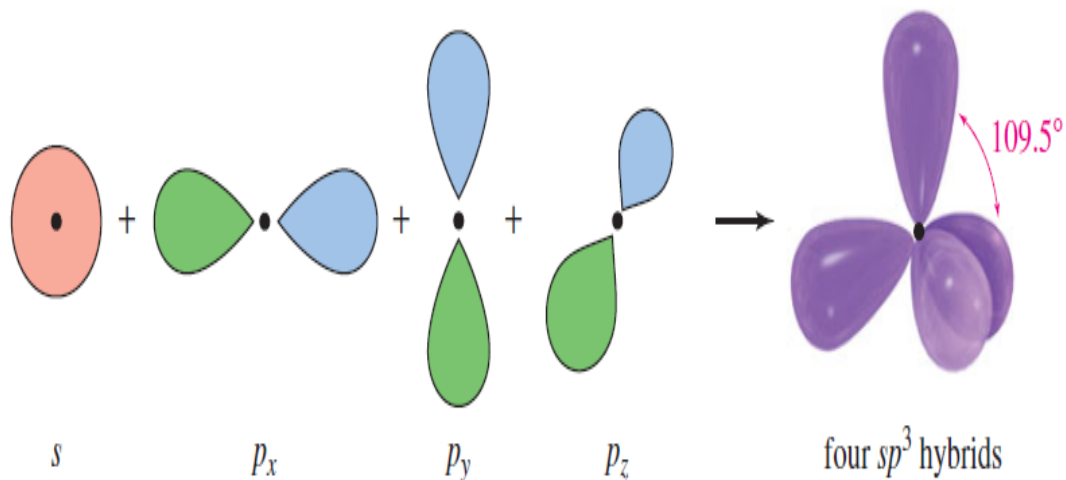
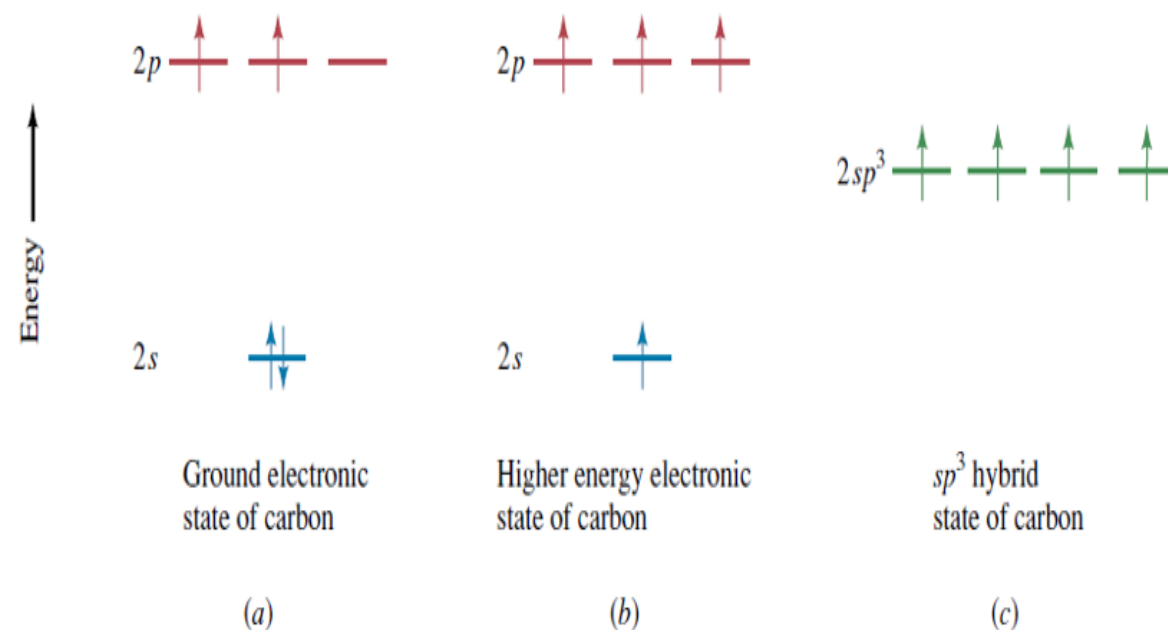


FIGURE 2-15

Tetrahedral geometry with sp^3 hybrid orbitals. Hybridization of an s orbital with all three p orbitals gives four sp^3 hybrid orbitals with tetrahedral geometry corresponding to 109.5° bond angles.

Bonding in methane and hybridization:



Tetrahedral; sp^3 hybrid orbitals; 109.5° .

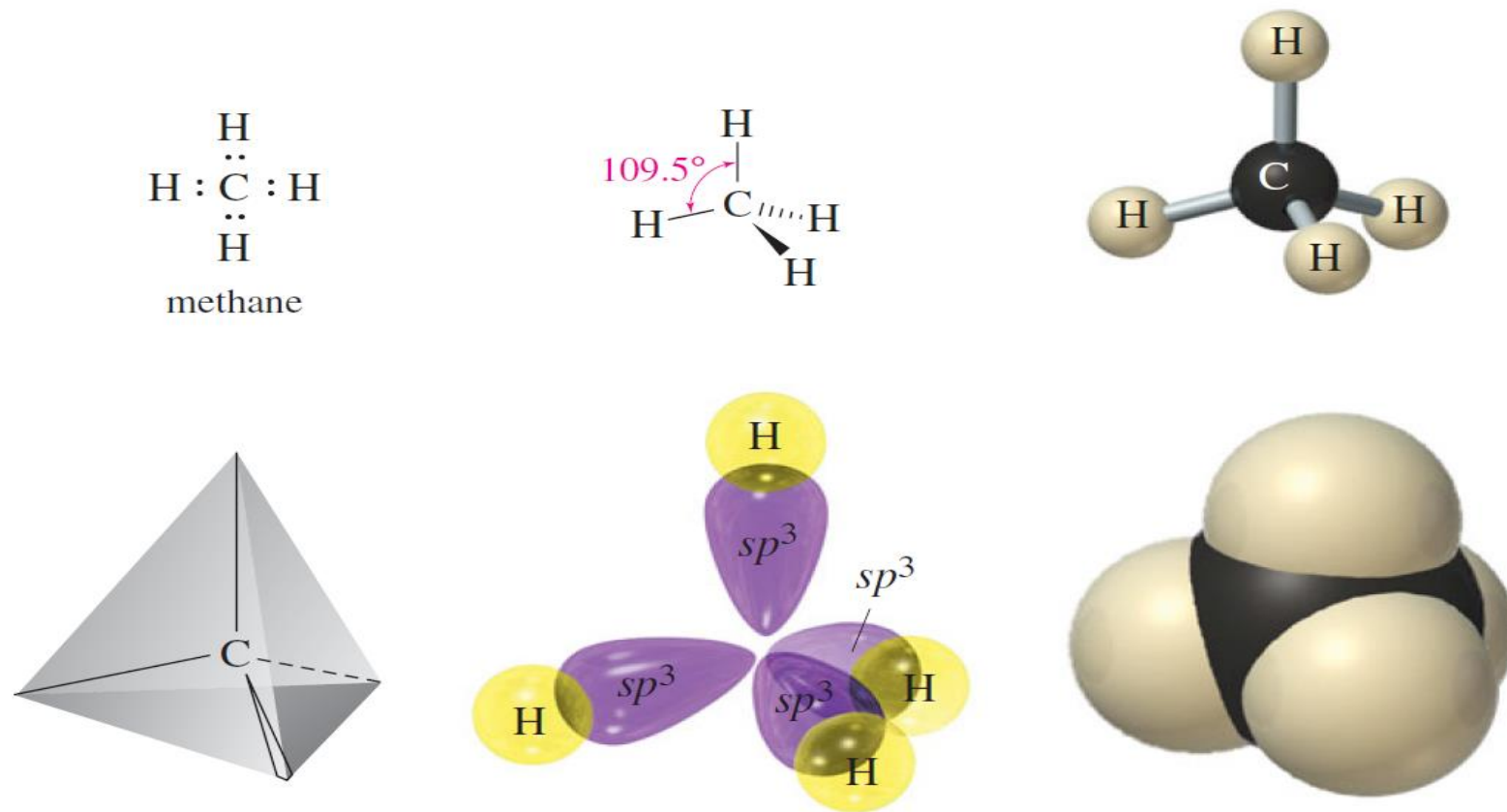
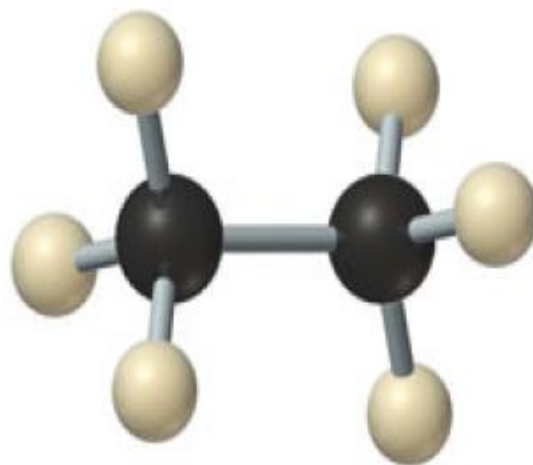
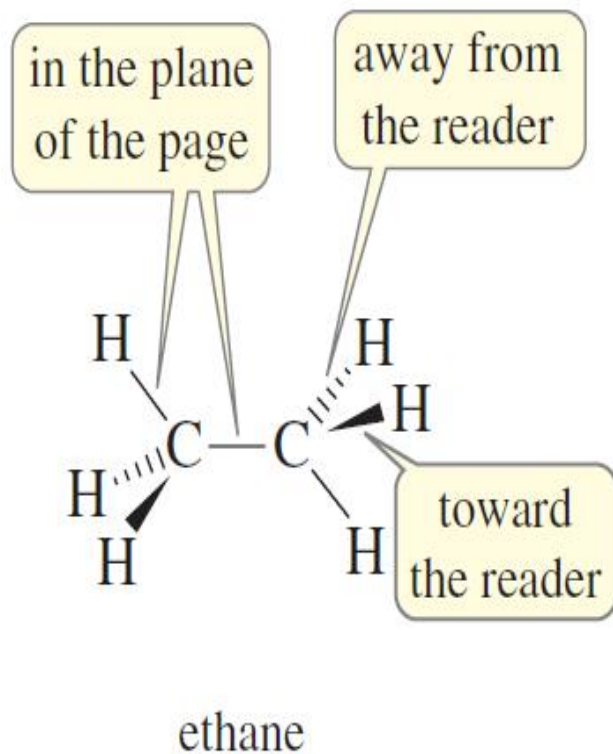


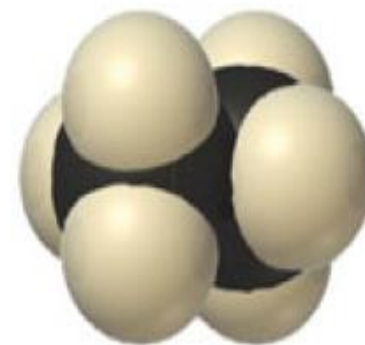
FIGURE 2-16

Several views of methane. Methane has tetrahedral geometry, using four sp^3 hybrid orbitals to form sigma bonds to the four hydrogen atoms.

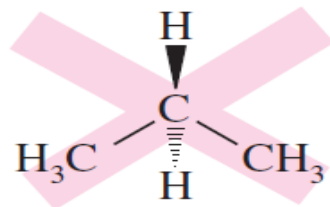
2-5 Drawing Three- Dimensional Molecules



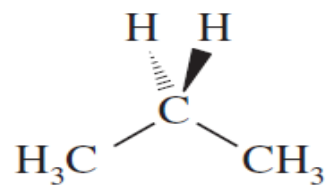
ethane



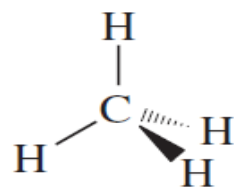
ethane



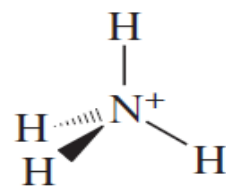
incorrect



correct



correct



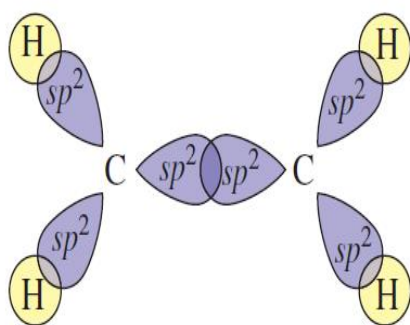
General Rules of Hybridization and Geometry

Rule 1: Both sigma bonding electrons and lone pairs can occupy hybrid orbitals. The number of hybrid orbitals on an atom is computed by adding the number of sigma bonds and the number of lone pairs of electrons on that atom.

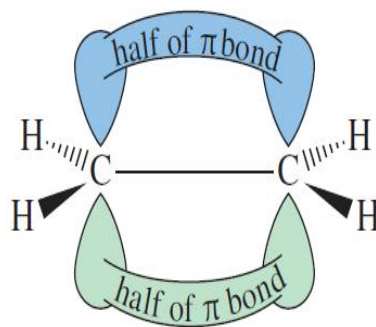
Rule 2: Use the hybridization and geometry that give the widest possible separation of the calculated number of bonds and lone pairs.

Rule 3: If two or three pairs of electrons form a multiple bond between two atoms, the first bond is a sigma bond formed by a hybrid orbital. The second bond is a pi bond, consisting of two lobes above and below the sigma bond, formed by two unhybridized *p* orbitals (see the structure of ethylene in Figure 2-17). The third bond of a triple bond is another pi bond, perpendicular to the first pi bond (shown in Figure 2-18).

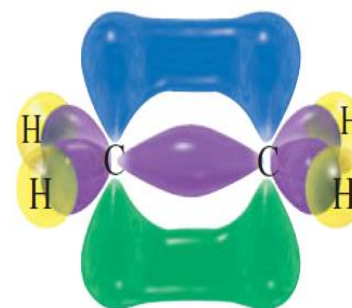
Summary of Hybridization and Geometry			
Hybrid Orbitals	Hybridization	Geometry	Approximate Bond Angles
2	$s + p = sp$	linear	180°
3	$s + p + p = sp^2$	trigonal	120°
4	$s + p + p + p = sp^3$	tetrahedral	109.5°



σ bond framework
(viewed from above the plane)



π bond
(viewed from alongside the plane)



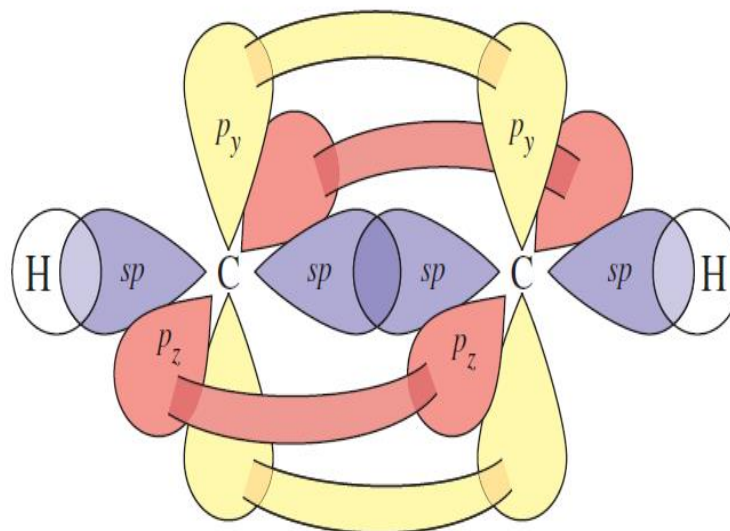
ethylene

FIGURE 2-17

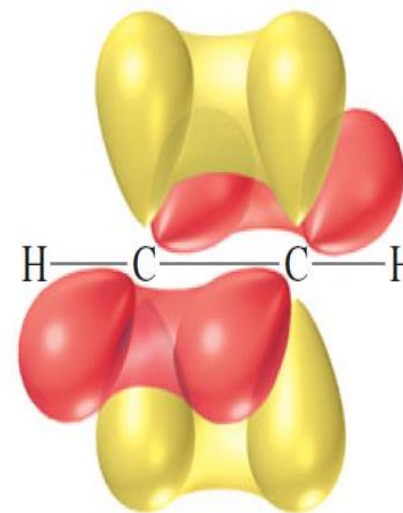
Planar geometry of ethylene. The carbon atoms in ethylene are sp^2 hybridized, with trigonal bond angles of about 120° . All the carbon and hydrogen atoms lie in the same plane.

FIGURE 2-18

Linear geometry of acetylene. The carbon atoms in acetylene are sp hybridized, with linear (180°) bond angles. The triple bond contains one sigma bond and two perpendicular pi bonds.



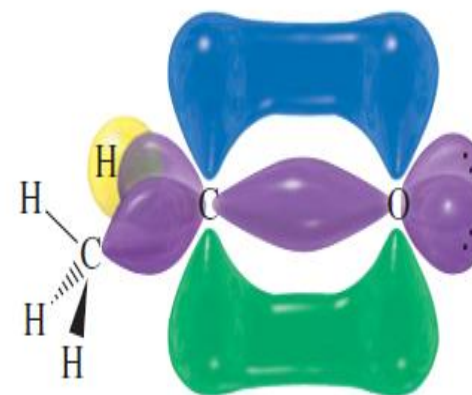
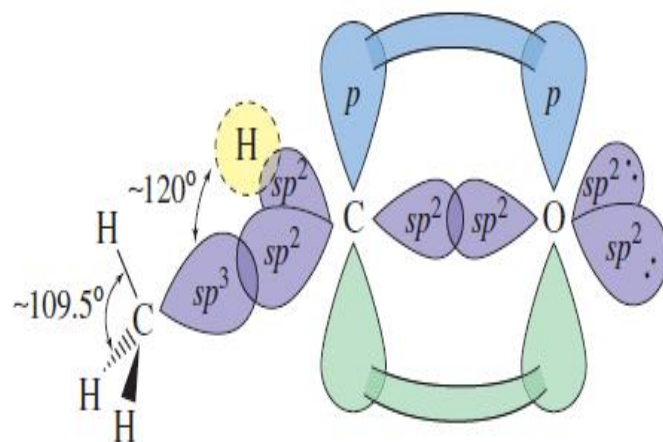
acetylene

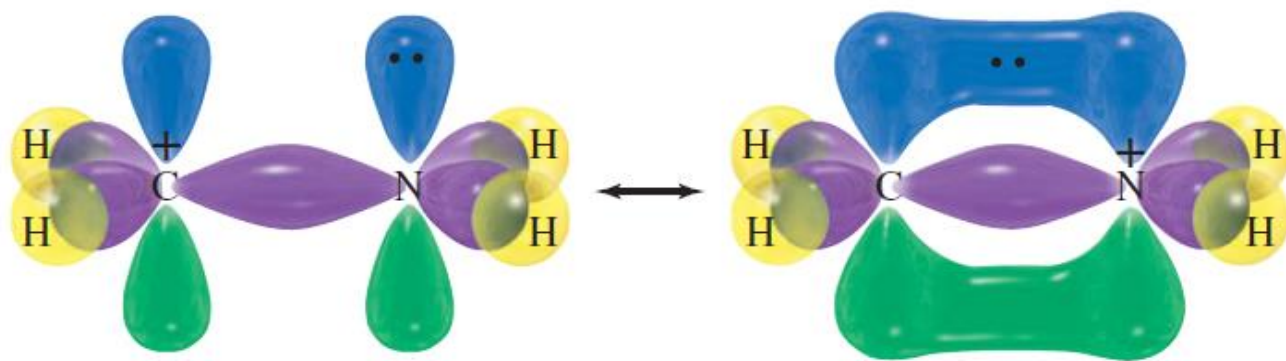


acetylene

FIGURE 2-19

Structure of acetaldehyde. The CH_3 carbon in acetaldehyde is sp^3 hybridized, with tetrahedral bond angles of about 109.5° . The carbonyl ($\text{C}=\text{O}$) carbon is sp^2 hybridized, with bond angles of about 120° . The oxygen atom is probably sp^2 hybridized, but we cannot measure any bond angles





Looking at either resonance form for $[\text{CH}_2\text{NH}_2]^+$ we would predict SP^2 hybridization (120° bond angles) for the carbon atom; however, the first resonance form suggests SP^3 hybridization for nitrogen (109° bond angles), and the second suggests SP^2 hybridization (120° bond angles). Which is correct?

Experiments show that the bond angles on both carbon and nitrogen are about 120° , implying SP^2 hybridization.

2-7 Bond Rotation

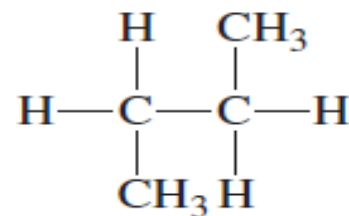
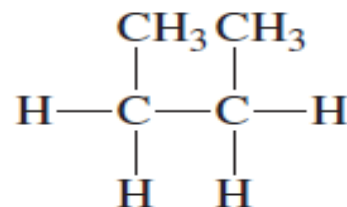
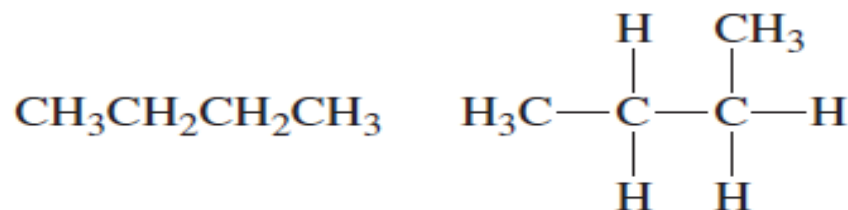
2-7A Rotation of Single Bonds

Drawings that differ only by rotations of single bonds usually represent the same compound. For example, the following drawings all represent *n*-butane:

Conformations

Eclipsed

Staggered



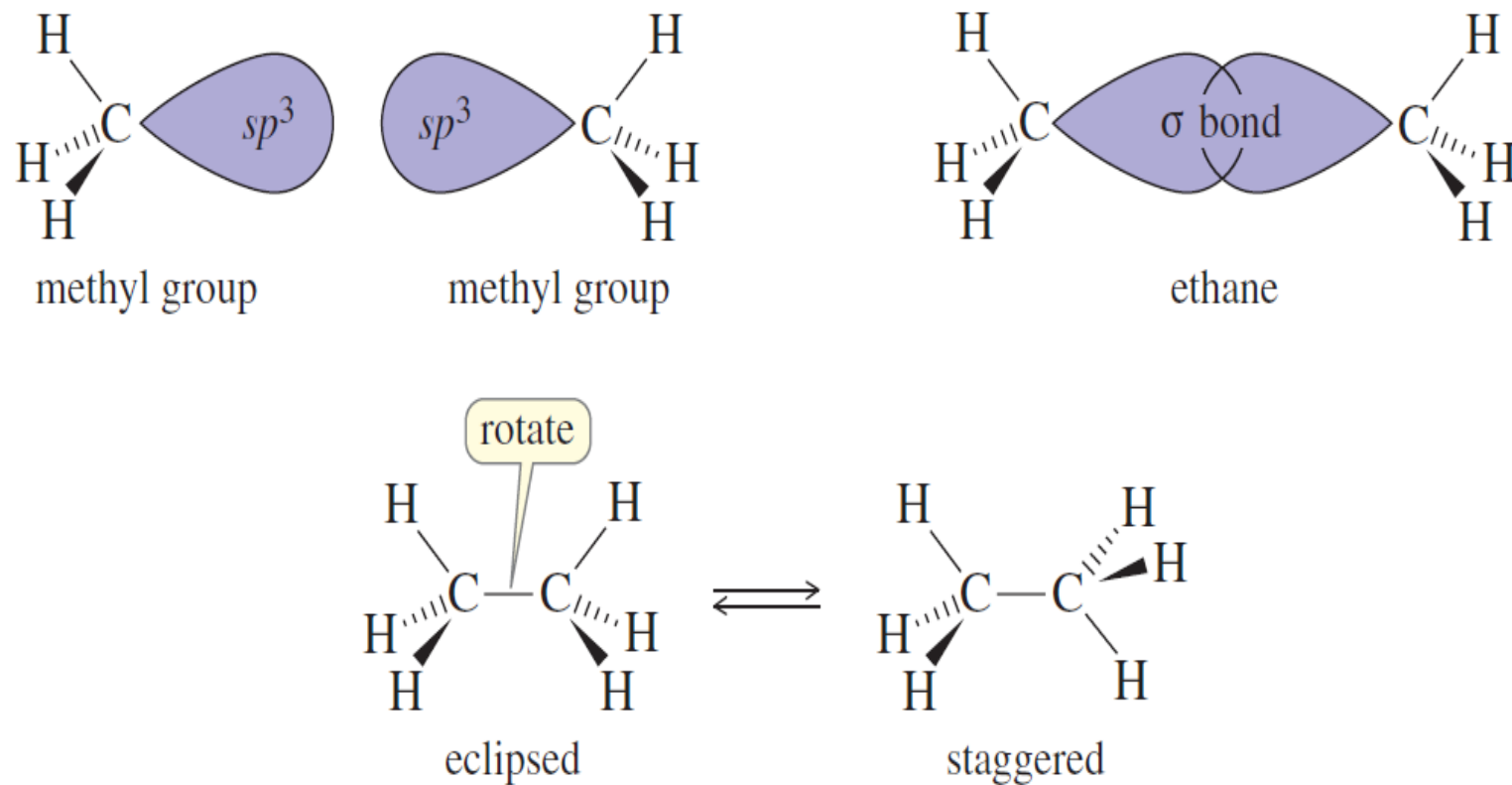
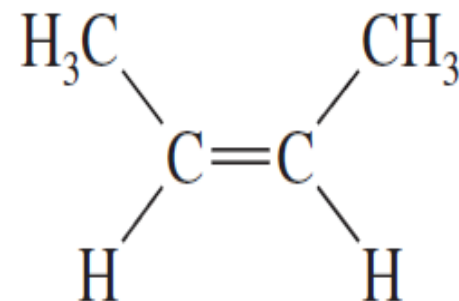
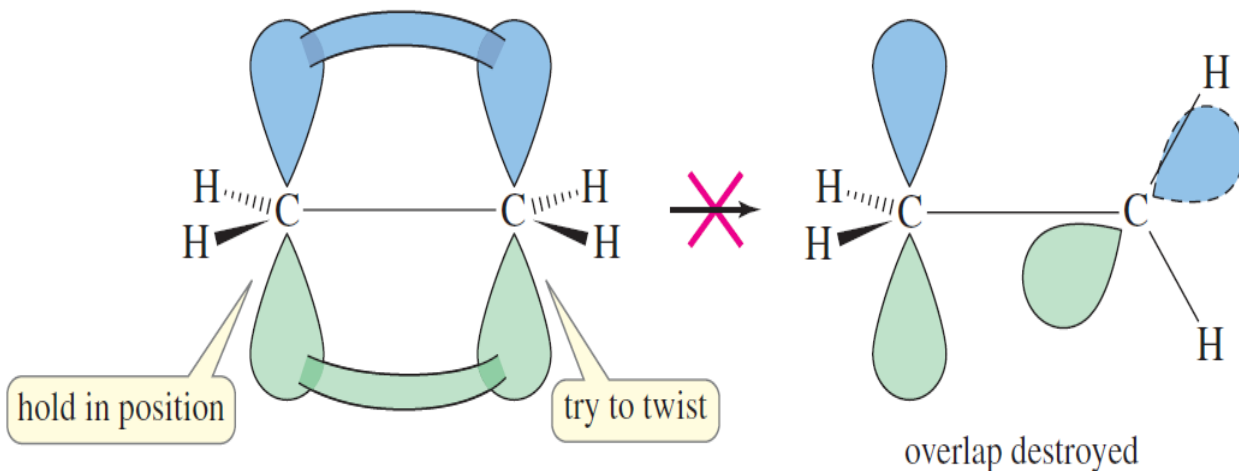


FIGURE 2-20

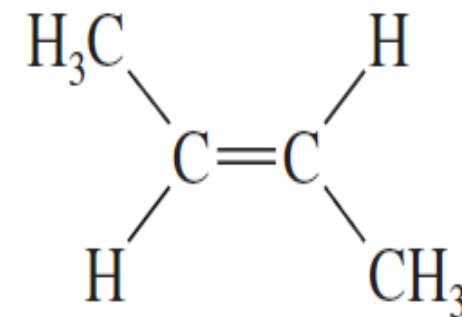
Rotation of single bonds. Ethane is composed of two methyl groups bonded by overlap of their sp^3 hybrid orbitals. These methyl groups may rotate with respect to each other.

2-7B Rigidity of Double Bonds



cis-but-2-ene

bp = 3.7 °C



trans-but-2-ene

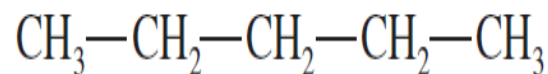
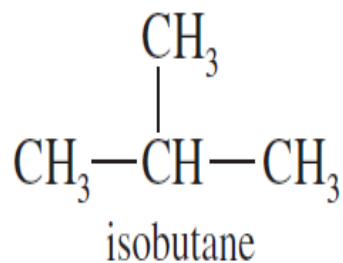
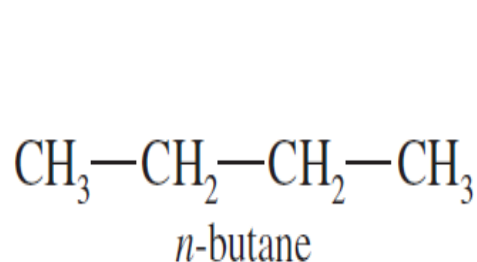
bp = 0.9 °C

Rotation about single bonds is allowed, but double bonds are rigid and cannot be twisted.

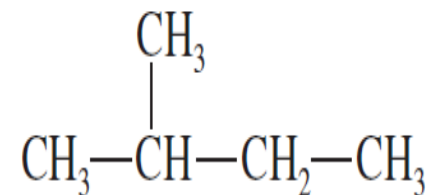
2-8 Isomerism

2-8A Constitutional Isomerism (or structural isomers):

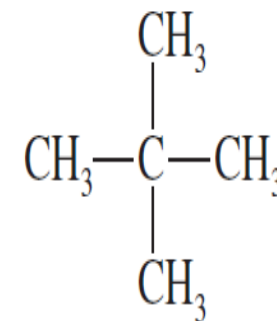
are isomers that differ in their bonding Sequence.



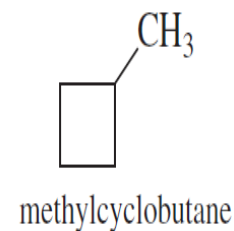
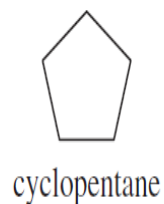
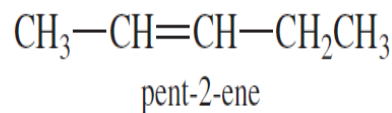
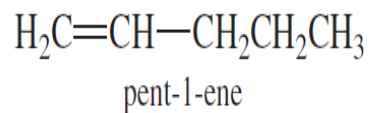
n-pentane



isopentane

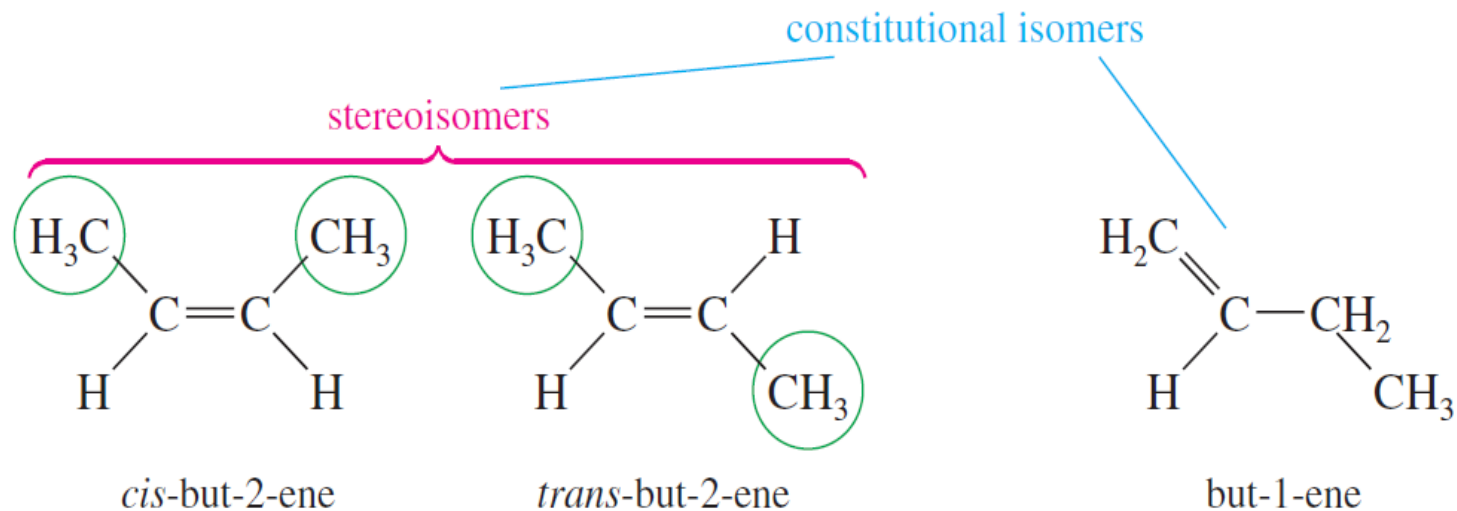


neopentane

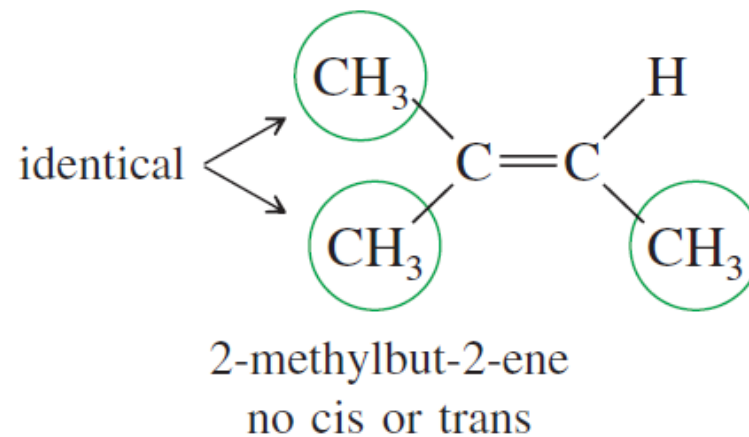
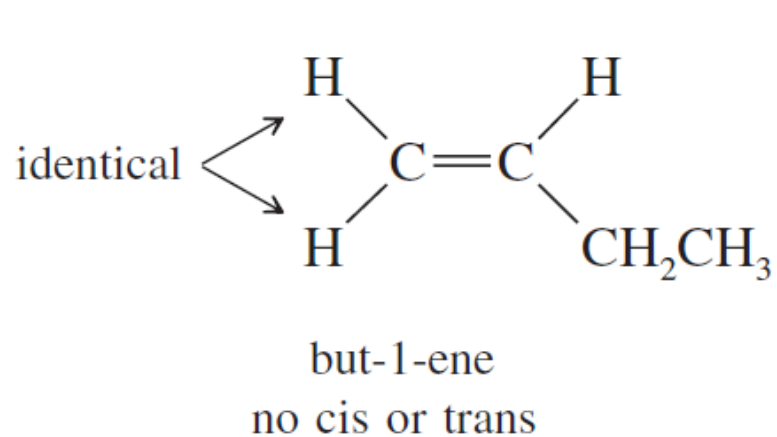


Isomers are different compounds with the same molecular formula

2-8B Stereoisomers

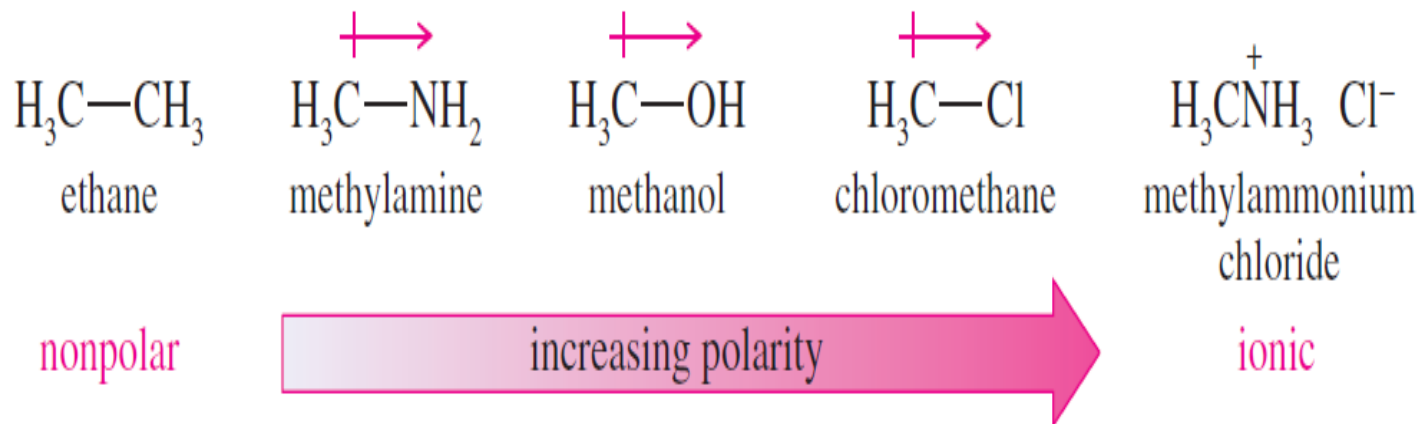


Cis-trans isomers are also called geometric isomers



2-9 Polarity of Bonds and Molecules

2-9A Bond Dipole Moments



The polarity of an individual bond is measured as its **bond dipole moment**, μ , defined as

$$\mu = \delta \times d$$

where δ is the amount of charge at either end of the dipole and d is the distance between the charges.

$$\mu = e \times d$$

e = charge (e.s.u)

d = distance (cm)

$$\mu_{\text{H-F}} = 1.7 \times 10^{-18} \text{ D}$$

Dipole moments are measured experimentally, and they can be used to calculate other information such as bond lengths and charge separations.

Bond dipole moments in organic compounds range from zero in symmetrical bonds to about 3.6 D for the strongly polar CN triple bond.

TABLE 2-1

Bond Dipole Moments (Debye) for Some Common Covalent Bonds

Bond	Dipole Moment, μ	Bond	Dipole Moment, μ
 C—N	0.22 D	 H—C	0.3 D
 C—O	0.86 D	 H—N	1.31 D
 C—F	1.51 D	 H—O	1.53 D
 C—Cl	1.56 D	 C=O	2.4 D
 C—Br	1.48 D	 C≡N	3.6 D
 C—I	1.29 D		

2-9B Molecular Dipole Moments

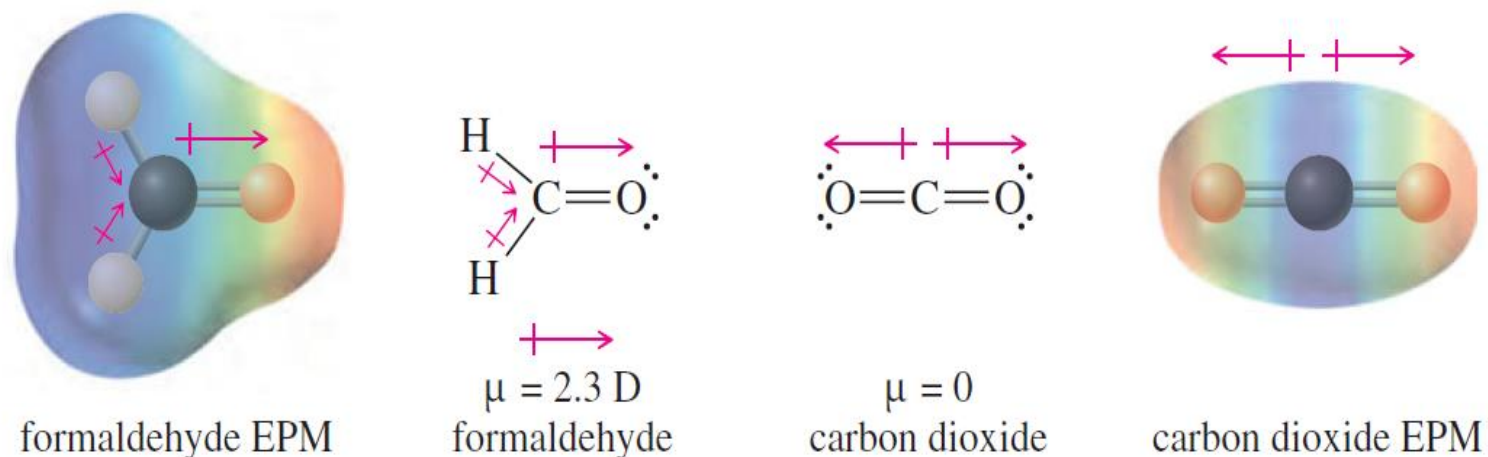
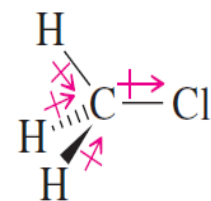


Figure 2-21 shows some examples of molecular dipole moments. Notice that the dipole moment of C—H bonds is small, so we often treat C—H bonds as nearly nonpolar. Also note that the tetrahedral symmetry of CCl_4 positions the four C—Cl dipole moments in directions so that they cancel. A partial canceling of the bond dipole moments explains why CHCl_3 , with three C—Cl bonds, has a smaller molecular dipole moment than CH_3Cl , with only one.

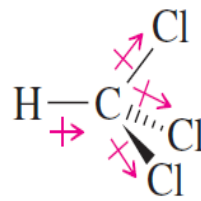
FIGURE 2-21

Molecular dipole moments.

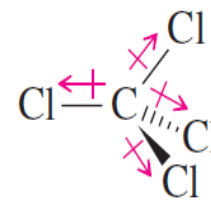
A molecular dipole moment is the vector sum of the individual bond dipole moments.



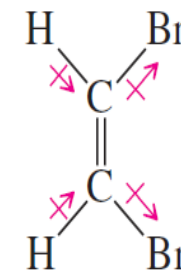
$\mu = 1.9 \text{ D}$
chloromethane



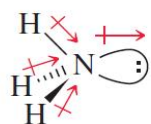
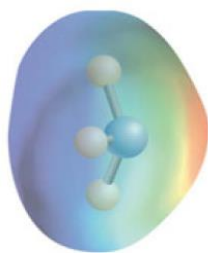
$\mu = 1.0 \text{ D}$
chloroform



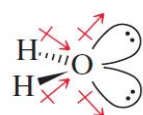
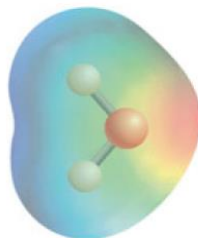
$\mu = 0$
carbon tetrachloride



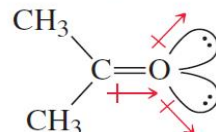
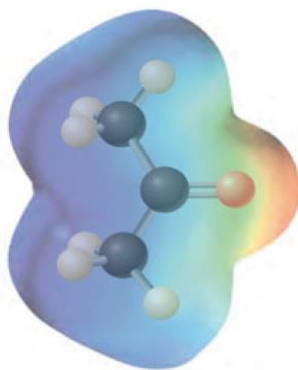
$\mu = 1.9 \text{ D}$
cis-1,2-dibromoethene



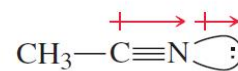
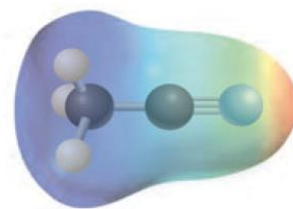
$\mu = 1.5 \text{ D}$
ammonia



$\mu = 1.9 \text{ D}$
water



$\mu = 2.9 \text{ D}$
acetone



$\mu = 3.9 \text{ D}$
acetonitrile

FIGURE 2-22

Effects of lone pairs on dipole moments. Lone pairs can make large contributions to molecular dipole moments.

2-10 Intermolecular Forces

1. the dipole–dipole forces of polar molecules;
2. the London dispersion forces that affect all molecules;
3. the “hydrogen bonds” that link molecules having –OH or –NH groups.

2-10A Dipole–Dipole Forces

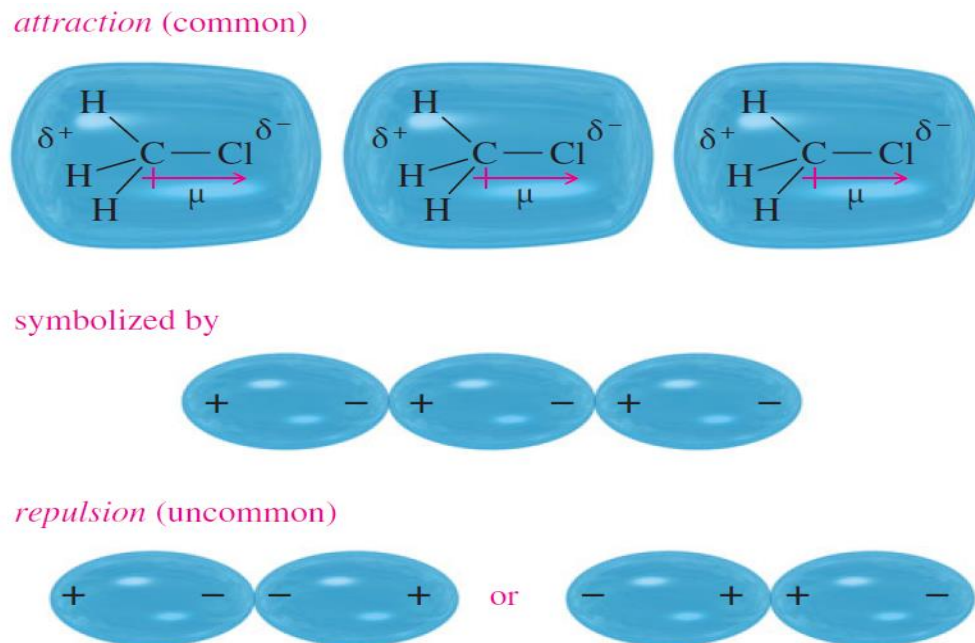
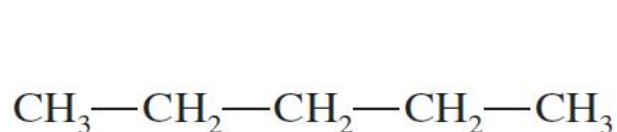


FIGURE 2-23

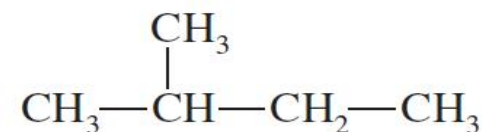
Dipole—dipole interactions. Dipole—dipole interactions result from the approach of two polar molecules. If their positive and negative ends approach, the interaction is attractive. If two negative ends or two positive ends approach, the interaction is repulsive. In a liquid or a solid, the molecules mostly orient with their positive and negative ends together, and the net force is attractive.

2-10B The London Dispersion Force

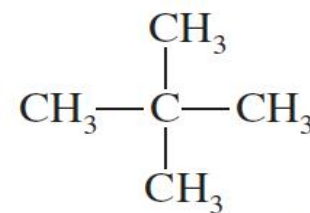
London dispersion force, one of the **van der Waals forces** (Figure 2-24).



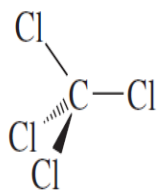
n-pentane, bp = 36 °C



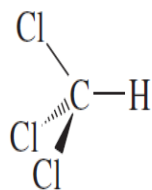
isopentane, bp = 28 °C



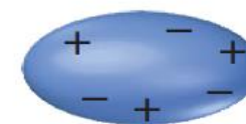
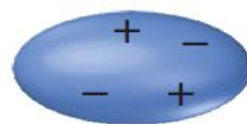
neopentane, bp = 10 °C



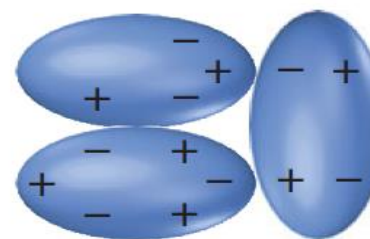
$\mu = 0$
carbon tetrachloride, bp = 77 °C



$\mu = 1.0 \text{ D}$
chloroform, bp = 62 °C



random temporary dipoles when separated



correlated temporary dipoles when in contact

FIGURE 2-24

London dispersion forces. London dispersion forces result from the attraction of correlated temporary dipoles.

2-10C Hydrogen Bonding

Breaking a hydrogen bond requires about 20 kJ mol (5 kcal mol), compared with about 400 kJ mol (about 100 kcal mol) required to break a C-H, O-H or N-H bond.

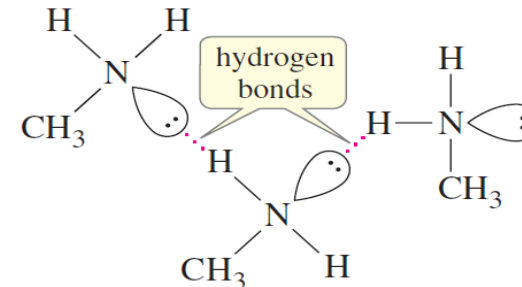
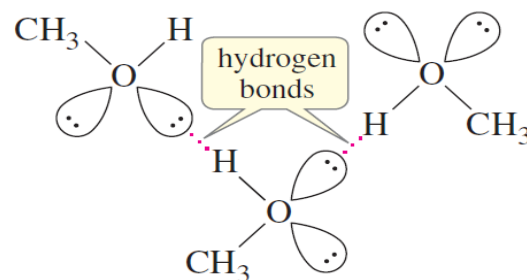
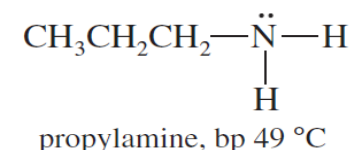
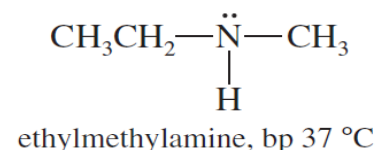
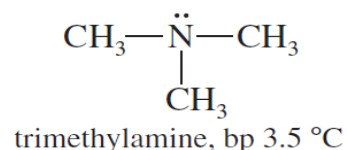
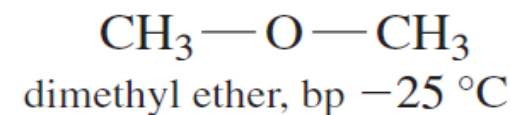
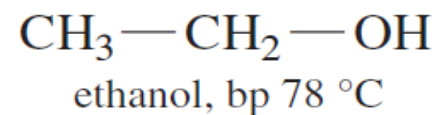
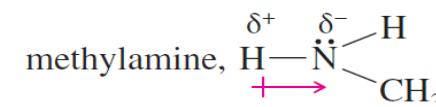
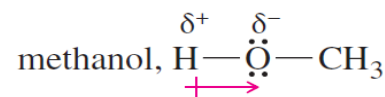


FIGURE 2-25

Hydrogen bonding. Hydrogen bonding is a strong attraction between an electrophilic O—H or N—H hydrogen atom and a pair of nonbonding electrons.



2-11 Polarity Effects on Solubilities

- The general rule is that “*like dissolves like*.” Polar substances dissolve in polar solvents, and nonpolar substances dissolve in nonpolar solvents.
- We should consider four different cases: (1) a polar solute with a polar solvent, (2) a polar solute with a nonpolar solvent, (3) a nonpolar solute with a nonpolar solvent, and (4) a nonpolar solute with a polar solvent.
- **Polar Solute in a Polar Solvent (Dissolves)** When you think about sodium chloride dissolving in water, it seems remarkable that the oppositely charged ions can be separated from each other. A great deal of energy is required to separate these ions. A polar solvent (such as water) can separate the ions because it *solvates* them (Figure 2-26). If water is the solvent, the solvation process is called *hydration*.
- **Polar Solute in a Nonpolar Solvent (Does Not Dissolve)** If you stir sodium chloride with a nonpolar solvent such as turpentine or gasoline, you will find that the salt does not dissolve (Figure 2-27).

FIGURE 2-26

Polar solute in water (a polar solvent). The hydration of sodium and chloride ions by water molecules overcomes the lattice energy of sodium chloride. The salt dissolves.

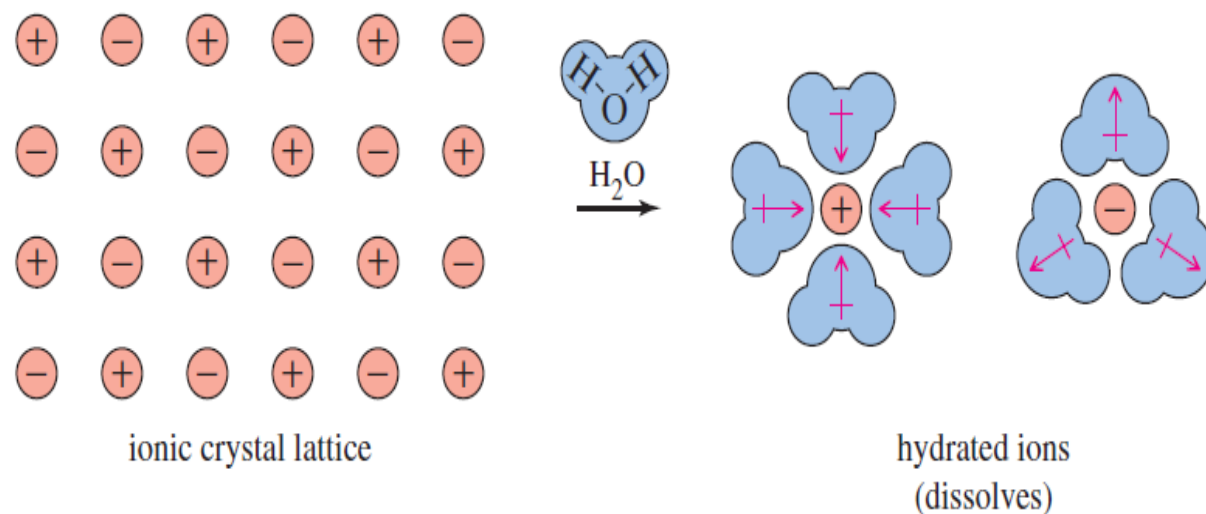
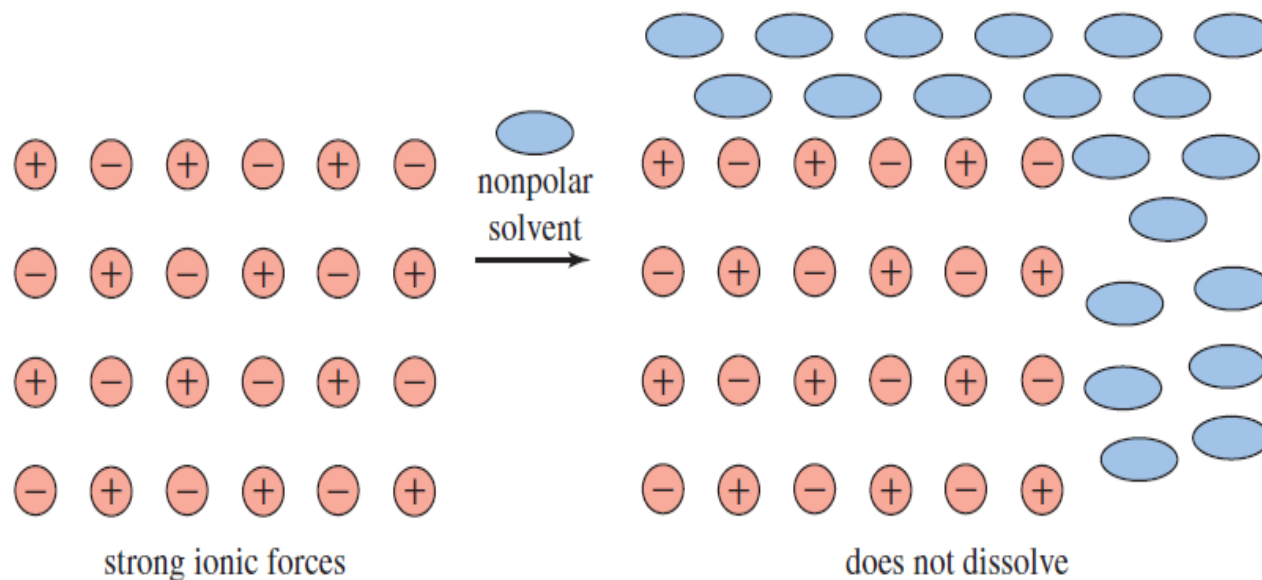


FIGURE 2-27

Polar solute in a nonpolar solvent. The intermolecular attractions of polar substances are stronger than their attractions for nonpolar solvent molecules. Thus, a polar substance does not dissolve in a nonpolar solvent.



Nonpolar Solute in a Nonpolar Solvent (Dissolves) Paraffin “wax” dissolves in gasoline. Both paraffin and gasoline are mixtures of nonpolar hydrocarbons (Figure 2-28).

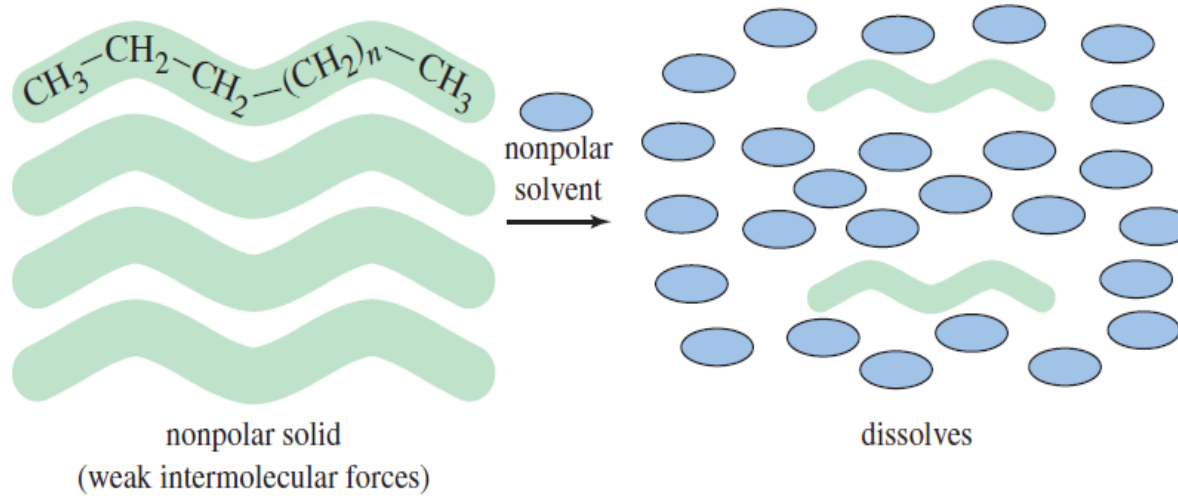


FIGURE 2-28

Nonpolar solute in a nonpolar solvent. The weak intermolecular attractions of a nonpolar substance are overcome by the weak attractions for a nonpolar solvent. The nonpolar substance dissolves.

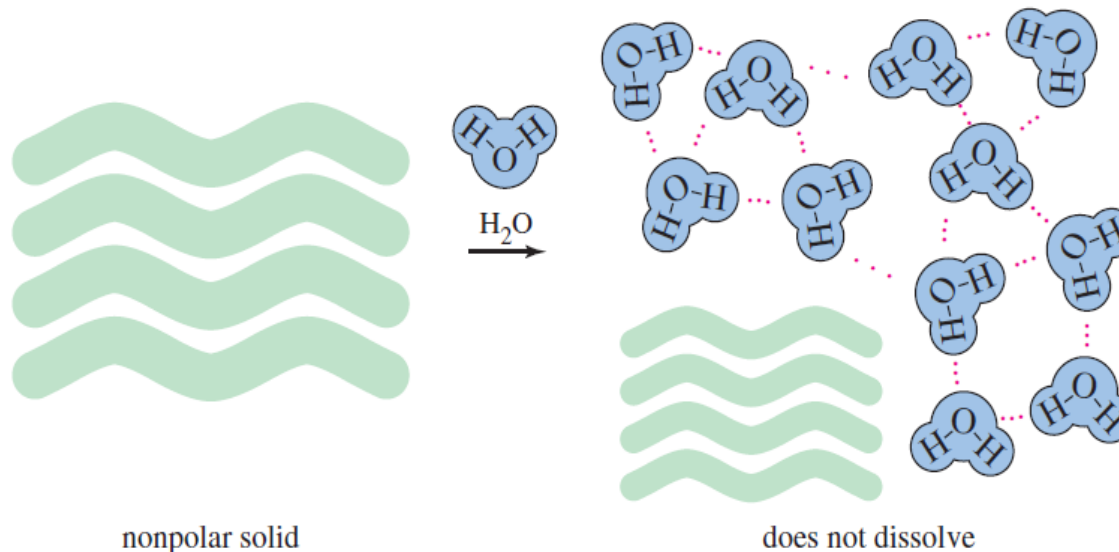
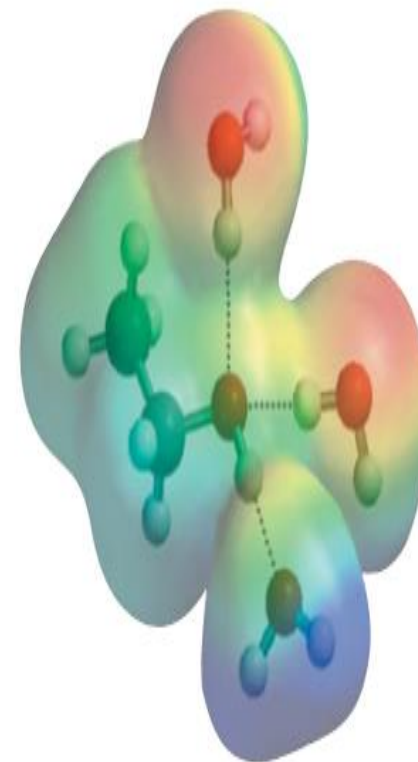
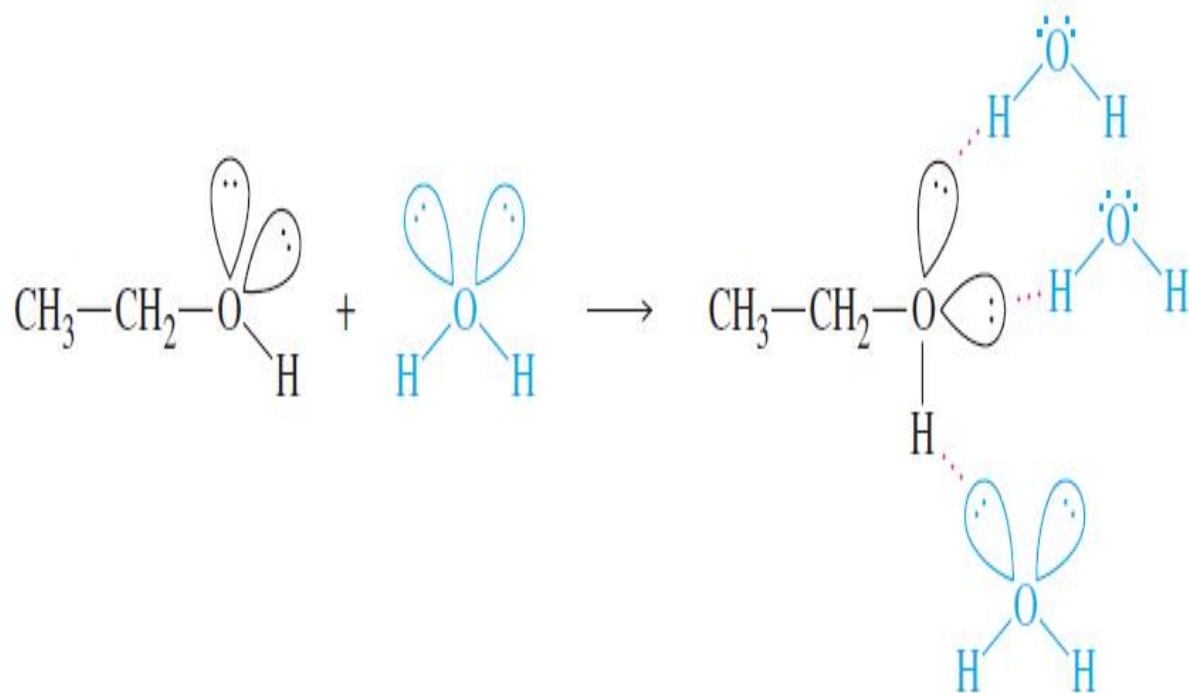


FIGURE 2-29

Nonpolar solute in a polar solvent (water). Nonpolar substances do not dissolve in water because of the unfavorable entropy effects associated with forming a hydrogen-bonded shell of water molecules around a nonpolar molecule.



Motor oil and water do not mix because the nonpolar oil molecules cannot displace the strong intermolecular attractions between water molecules.



2-12 Hydrocarbons

The **hydrocarbons** are compounds composed entirely of carbon and hydrogen.

2-12A Alkanes

-ane suffix

TABLE 2-2 Correspondence of Prefixes and Numbers of Carbon Atoms

Alkane Name	Number of Carbons	Alkane Name	Number of Carbons
<i>methane</i>	1	<i>hexane</i>	6
<i>ethane</i>	2	<i>heptane</i>	7
<i>propane</i>	3	<i>octane</i>	8
<i>butane</i>	4	<i>nonane</i>	9
<i>pentane</i>	5	<i>decane</i>	10

CH_4 methane	$\text{CH}_3\text{—CH}_3$ ethane	$\text{CH}_3\text{—CH}_2\text{—CH}_3$ propane	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$ butane	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH—CH}_3 \\ \text{isobutane} \end{array} $
--------------------------	-------------------------------------	--	---	--

Alkanes are hydrocarbons that contain only single bonds

The **cycloalkanes** are a special class of alkanes in the form of a ring. Alkanes undergo few reactions because they have no **functional group**, the part of the molecule where reactions usually occur. An **alkyl group** is an alkane portion of a molecule, with one hydrogen atom removed to allow bonding to the rest of the molecule.

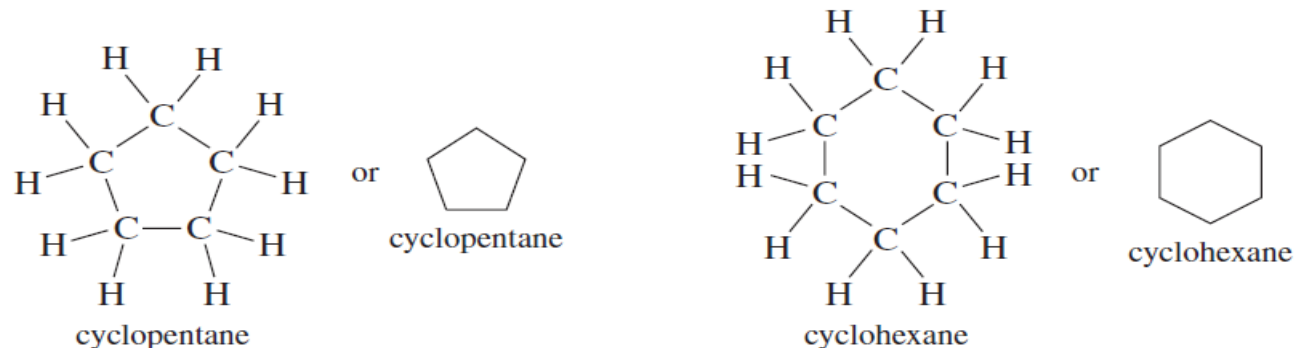
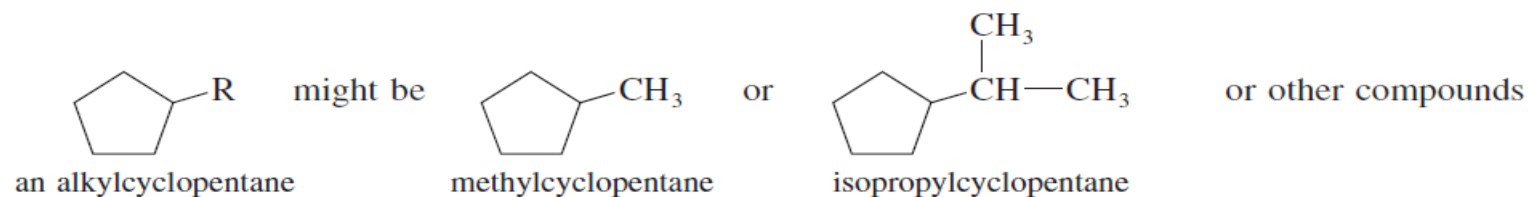


FIGURE 2-30

Cycloalkanes. Cycloalkanes are alkanes in the form of a ring.

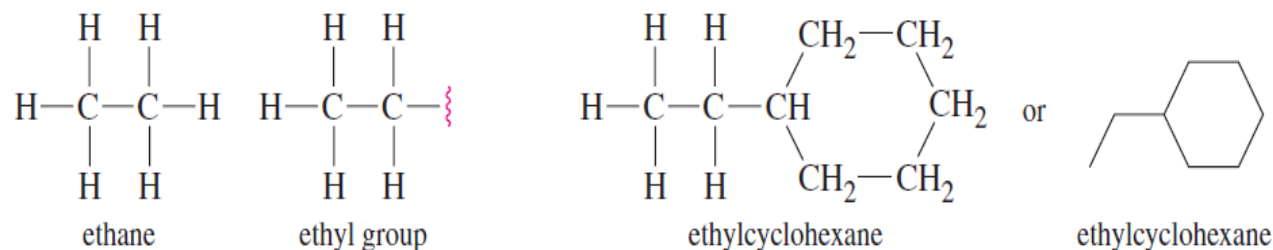
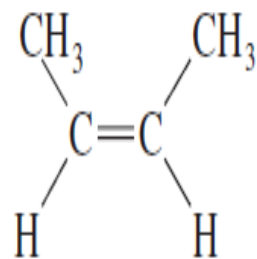
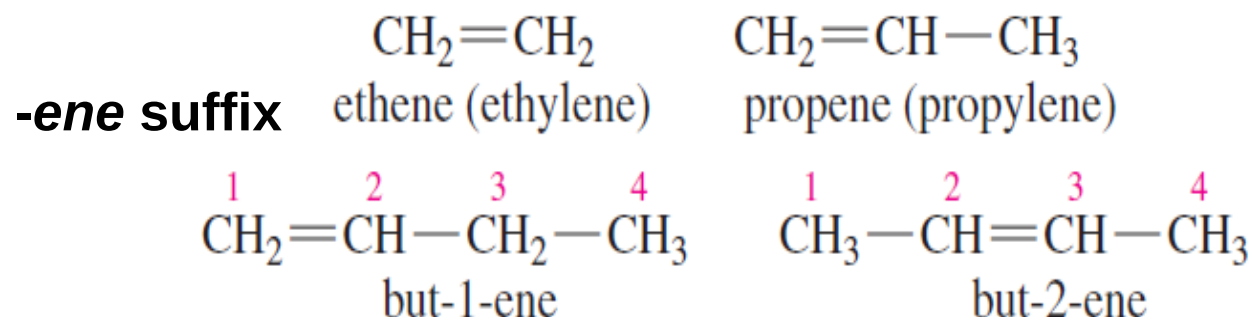


FIGURE 2-31

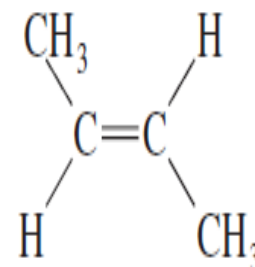
Naming alkyl groups. Alkyl groups are named like the alkanes they are derived from, with a -yl suffix.

2-12B Alkenes

Alkenes are hydrocarbons that contain carbon–carbon double bonds. A carbon–carbon double bond is the most reactive part of an alkene, so we say that the double bond is the *functional group* of the alkene.



cis-but-2-ene



trans-but-2-ene



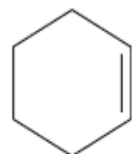
cis-hex-2-ene



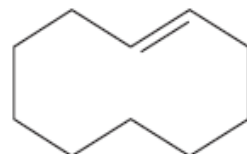
trans-hex-2-ene



cyclopentene



cyclohexene

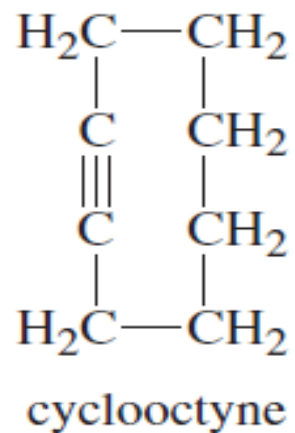
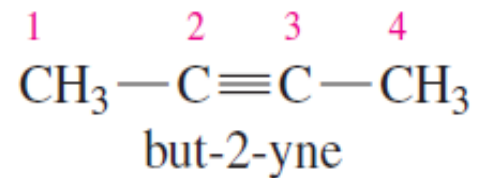
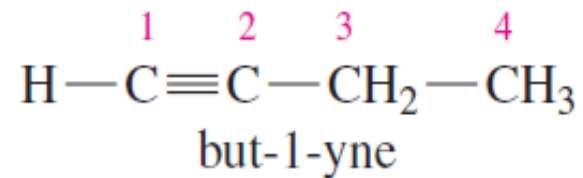
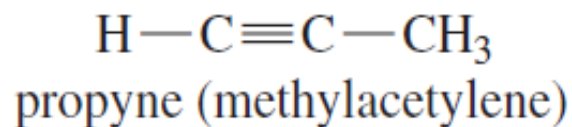
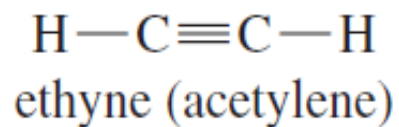


trans-cyclodecene

2-12C Alkynes

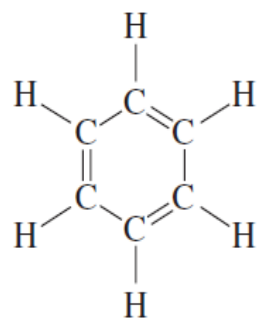
Alkynes are hydrocarbons with carbon–carbon triple bonds as their functional group.

-Yne suffix

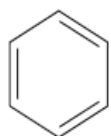


2-12D Aromatic Hydrocarbons

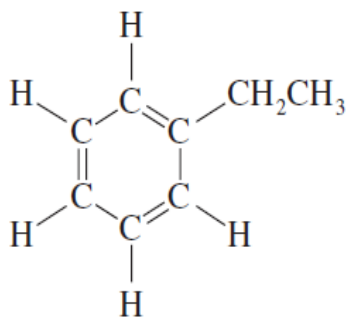
The following compounds may look like cycloalkenes, but their properties are different from those of simple alkenes. These **aromatic hydrocarbons** (also called **arenes**) are all derivatives of *benzene*, represented by a six-membered ring with three double bonds.



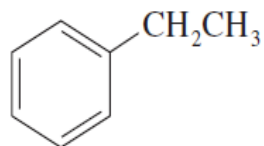
or



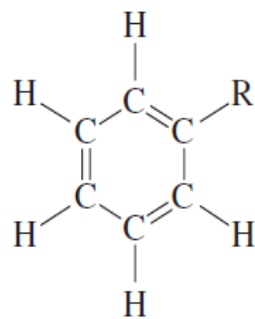
benzene



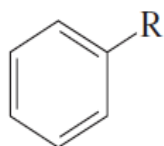
or



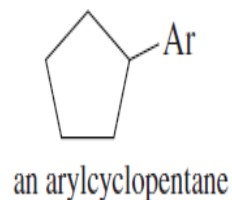
ethylbenzene



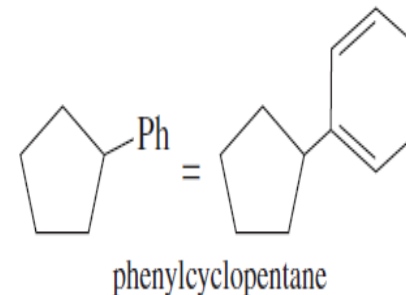
or



an alkylbenzene



might be



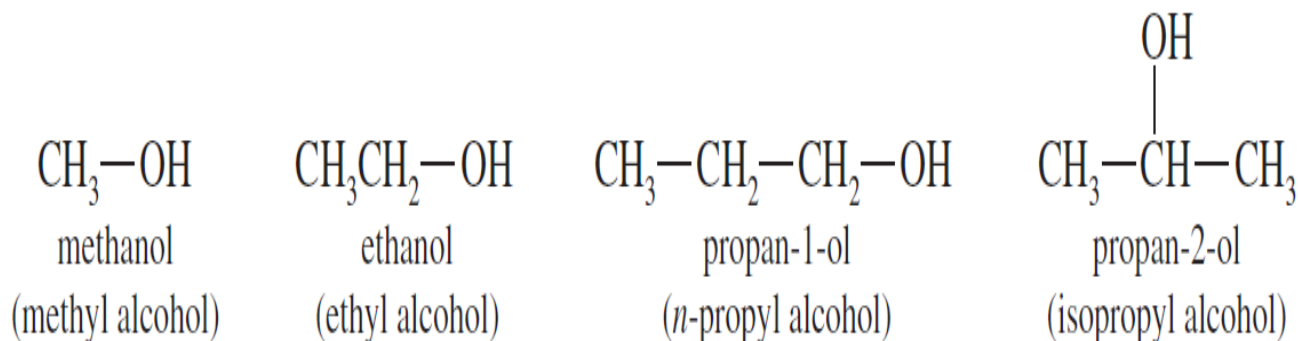
phenylcyclopentane

or other compounds

2-13 Organic Compounds Containing Oxygen

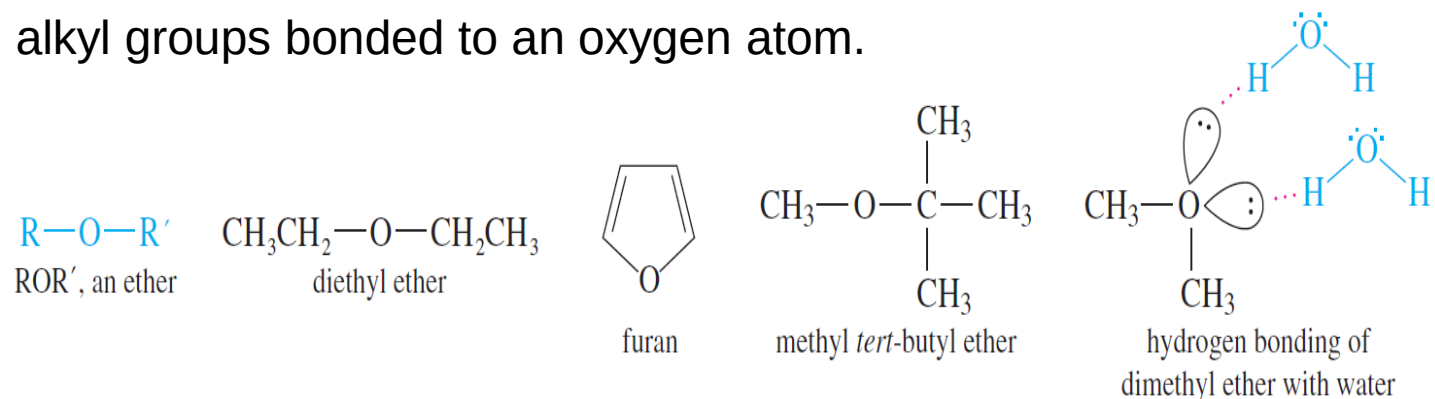
2-13A Alcohols

Alcohols are organic compounds that contain the **hydroxyl group (-OH)** as their functional group.



2-13B Ethers

Ethers are composed of two alkyl groups bonded to an oxygen atom.



- Chemical bonds
- Atoms, electrons, orbitals
- Element: characterized by atomic number (Z) = number of protons in its nucleus
- Neutral atom has equal number of protons with positive charge and electrons with negative charge
- Electrons were believed to be particles from 1897-1924
- Electrons have wave-like properties (Louis de Broglie)
- Erwin Schrodinger calculated the energy of electron in hydrogen atom by using equation for electron with wave-like property (2 years later)
- Erwin Schrodinger obtained a series of energy level instead of a single energy, each of which corresponded to a different Mathematical description of the electron wave.
- These Mathematical descriptions are called **Wave functions (Ψ)**
- According to Heisenberg uncertainty principle, we can't tell where exactly an electron is but we can tell where it is most likely to be.
- The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function (**Ψ**) at that point.
- The probability of finding an electron at various point in the lowest energy (most stable) state of hydrogen atom.
- **Wave functions** are called **orbitals**.
- Orbitals are described by specifying their size, shape and directional properties. Spherically symmetrical ones are called **S Orbital**.