Chapter 1
Bonding, Structure, and Physical Properties

1.1 Nature of Organic Chemistry

Organic molecules are molecules that contain carbon. Several million different organic molecules, both natural and synthetic, have been characterized, and they are found throughout both the living and the inanimate parts of our world.

How is carbon so special that so many compounds can be derived from it? Among the elements only carbon and hydrogen bond strongly to many types of atoms, including hydrogen, carbon, oxygen, nitrogen, and chlorine. Furthermore, carbon can form four bonds at a time, but

hydrogen only has a valence of one. Strong bonds among multivalent carbon atoms allow great versatility in the size and shape of stable carbon skeletons, the array of interconnected carbons. These skeletons can stretch as chains thousands of carbons long, or branch into intricate shapes, or encircle themselves in rings of any size. The organic molecule cellulose comprises thousands of rings! Superimposed on such stable backbones, both single and multiple bonds between carbon and other atoms confer a wide variety of functionality, that is, ability to react.

Calling the chemistry of these carbon-containing molecules organic is appropriate for several reasons. In the nineteenth century organic chemistry originally meant the chemistry of compounds in living organisms. Certainly, life in all organisms depends on chemical reactions, almost all of which involve organic molecules. Organic chemistry continues to provide a basis for studies in medicine, pharmacology, biochemistry, molecular biology, microbiology, biotechnology, and agriculture.

Also like an organism, organic chemistry in the last hundred years has grown into fields such as dyes, explosives, polymers, pharmaceuticals, food additives, and petroleum chemistry. Organic chemistry is not a static body of knowledge, but continues to grow with new discoveries, applications, theories, and, of course, controversies. Indeed, without expecting immediate applications to practical problems, many organic chemists study organic molecules and their reactions simply for their endless fascination.

Although reactions involving organic molecules are practically limitless, a frequent, simplifying theme of this book is the intimate connection between the structure and reactivity of organic molecules. By developing a keener sense of molecular structure, you will be able to not only rationalize organic reactions, but also predict them. Fundamental structural features examined in the first four chapters will frequently be invoked to explain and predict new reactions in later chapters. So organic chemistry is like the cohesive, interconnected, integrated tissues of organisms.

Also like a tissue in an organism, organic chemistry develops in conjunction with other branches of chemistry. For example, it grows out of general chemistry, where many of its essential concepts are first encountered. In fact, this first chapter mostly reviews material already learned in general chemistry. In addition, kinetic studies of physical chemistry and the instruments of analytical chemistry determine just how organic reactions proceed.

A final way that the chemistry of this book is organic is that it can and, if given a fair chance, will grow on you. Good luck!

1.2 Bonding

Atoms and ions are often closely and strongly associated with other atoms and ions. A strong, enduring association is called a **bond**. Accordingly, atoms and ions linked by bonds assemble in molecules and ionic compounds. Two types of associations result from two types of bonds: ionic and covalent.

1.2A Ionic Bonds

A cation is an ion with a positive charge. According to a fundamental law of physics, a cation strongly attracts a nearby anion, an ion with a negative charge. This strong attraction between adjacent, oppositely charged ions is called an **ionic bond.** For example, table salt (i.e., sodium chloride) comprises sodium cations and chloride anions ionically bonded:

$$\text{Na}^+ \ :\!\overset{..}{\underset{..}{\text{Cl}}}\!:^- \ \text{Na}^+ \ :\!\overset{..}{\underset{..}{\text{Cl}}}\!:^-$$

$$:\!\overset{..}{\underset{..}{\text{Cl}}}\!:^- \ \text{Na}^+ \ :\!\overset{..}{\underset{..}{\text{Cl}}}\!:^- \ \text{Na}^+$$

$$\text{Na}^+ \ :\!\overset{..}{\underset{..}{\text{Cl}}}\!:^- \ \text{Na}^+ \ :\!\overset{..}{\underset{..}{\text{Cl}}}\!:^-$$
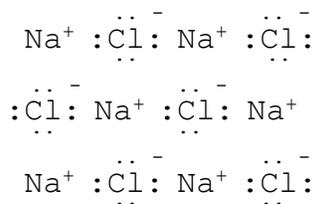
```
ions bonded along one layer of sodium chloride
```

The ionic bonds connect the ions in all three dimensions of the crystal lattice, although only two dimensions of one layer are shown above.

1.2B Covalent Bonds

A more common kind of bond in organic compounds is the **covalent bond.** A covalent bond links two atoms that share an electron pair. For example, in methane, CH_4, carbon shares two electrons of a covalent bond with each hydrogen:

$$\text{H} : \overset{..}{\underset{..}{\text{C}}} : \text{H}$$

with H above and below the C.
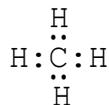
```
shared electron pairs in covalent bonds
```

In this way each hydrogen and carbon fill their outer shells with two and eight electrons, respectively. Covalent bonds generally result from the desire of atoms for filled outer shells, as discussed in Section 1.4B.

Each covalent bond above arises from the overlap of two atomic orbitals, one from each atom:
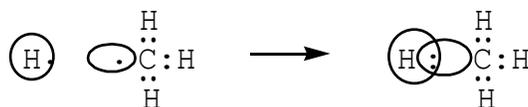

```
overlap of atomic orbitals in one σ bond
```

The greatest electron density or probability lies in the head-on overlap between the two nuclei along the internuclear axis. Such a bond is called a **σ (sigma)** bond. σ bonds are cylindrically symmetric about the internuclear axis. All single covalent bonds are σ bonds.

1.2C Multiple Bonds

Covalent bonds are not always single, with the sharing of only one pair of electrons. Less frequently two atoms share two or even three pairs of electrons, resulting in **double** or **triple bonds,** respectively. Double and triple bonds are called **multiple bonds.** For example, ethene has one double bond, as well as four single bonds:

```
H:C::C:H
 ..   ..
 H    H
```
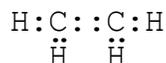
double and single bonds in ethene

A total of four bonds surround each carbon with eight electrons, which fill the outer shells of the carbons. The two carbon atoms share two pairs of electrons in their double bond. One bonding electron pair forms a σ bond between the two carbons in the head-on overlap of orbitals. The second bonding pair of the double bond resides in the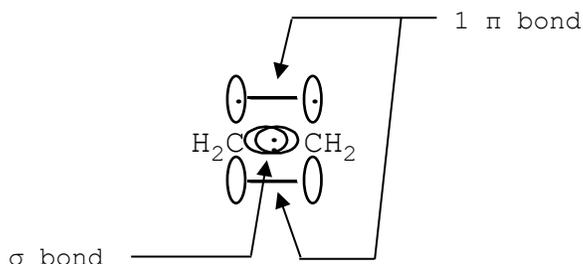 overlap of two parallel *2p* orbitals, one for each carbon. The greatest electron density or probability lies not along the internuclear axis, but extensively spread above and below this axis. This bond is called a **π (pi) bond.**

a σ bond and a π bond combining as a double bond

In contrast to the head-on overlap of a σ bond, a π bond arises from the sideways overlap of both lobes of the parallel *p* orbitals and is not cylindrically symmetric about the internuclear axis. Thus a double bond comprises one σ bond and one π bond.
Triple bonds are much less common than single or double bonds in organic molecules. Ethyne (i.e., acetylene) provides an example:

```
H:C:::C:H
```

triple and single bonds in ethyne

By sharing three pairs of electrons in a triple bond and another pair in a single bond to hydrogen, each carbon fills its outer shell with eight electrons. In a triple bond one bonding pair forms a σ bond between the two carbons, while two bonding pairs form two π bonds.
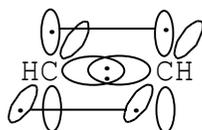
a triple bond comprising a σ bond and two π bonds.

Two parallel *2p* orbitals in the plane of the paper overlap for one π bond. Each carbon also supplies another *2p* orbital perpendicular to the plane of the paper. These two *p* orbitals are parallel to each other and consequently overlap for the second π bond. A σ bond and two π bonds compose a triple bond.

1.3 Structures of Organic Molecules

To discuss organic molecules and their reactions, organic chemists use not only words but also depictions of molecular structures. These representations can range from the very complete and explicit to shorthand sketches, which imply much. With such structures we can communicate about many types of organic molecules.

1.3A Types of Representations

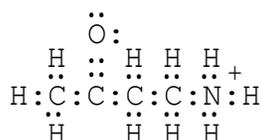The most explicit and painstaking type of representation is the **Lewis structure** (Gilbert N. Lewis, USA, 1875-1946). While omitting electrons from inner shells, this method shows all valence electrons with all atoms and any formal charge. For example:

```
              ..
              O:
       H  .. H H  H
       ..  ..  ..  ..  .. +
     H:C:C:C:C:N:H
       ..     ..  ..  ..
       H      H H  H
```

Lewis structure

Dots represent both bonding and nonbonding valence electrons. A simpler version of the Lewis structure symbolizes each bonding electron pair with a line:

```
     H  :Ö  H  H  H
      \   ‖   |   |   |+
     H–C–C–C–C–N–H
      |       |   |   |
      H       H  H  H
```
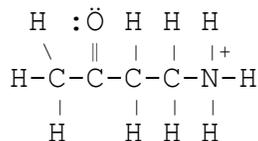
simpler Lewis structure

Dots still indicate the nonbonding electrons. The greater ease of writing lines instead of dots makes this a more common type of Lewis structure.

A **condensed structure** of the above Lewis structures is easier to draw but leaves more to the imagination.

$$O$$
$$\|$$
$$CH_3CCH_2CH_2NH_3{}^+$$

condensed structure

Here single bonds and nonbonding electrons are only implied and hydrogens bonded to the same atom are grouped together. Multiple bonds, however, are shown explicitly. We depend on our knowledge of the valences of carbon, nitrogen, and hydrogen to make sense of this condensed structure. For example, carbon's tendency to form four bonds and hydrogen's normal maximum of one bond suggest the actual arrangement of hydrogens around the carbons.

We can further simplify structures with a **line structure**, equivalent to the earlier structures:
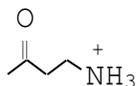
$$\underset{\text{line structure}}{\overset{\displaystyle O}{\|}} \quad \overset{+}{NH_3}$$

This method uses lines to represent bonds to carbons, while omitting symbols for carbons and their hydrogens. Enough hydrogens to satisfy the valence of carbon are implied. Atoms other than carbon and hydrogen are shown with any associated hydrogens. This method is especially convenient when drawing large organic molecules with lots of carbons and hydrogens that would be tedious to represent by even condensed structures.

Table 1.1 demonstrates how these three types of representations apply to some organic compounds. This chapter uses mostly Lewis structures, but as our sophistication and the size of organic molecules grow, we will use condensed and line structures increasingly.

Table 1.1 Three Kinds of Representations

Simple Lewis	Condensed	Line

```
   H H H H
   | | | |
 H-C-C-C-C-H        CH3CH2CH2CH3
   | | | |
   H H H H
```

```
   H H H
   | | |
 H-C-C-C-Ö-H        CH3CH2CH2OH
   | | | ··
   H H H
```

```
   H H    H
   | | .. |
 H-C-C-N-C-H        CH3CH2NHCH3
   | | | |
   H H H H
```

```
  H\ /H
    C                   CH2
   /\ ..               /\
 H-C-C-Cl:          H2C-CH-Cl
   | |  ··
   H H
```

Puzzle 1.1 ——

Draw condensed and line structures for the Lewis structure:

```
  H      H  H  H  H
  |   .. |  |  |  |
H-C-N=C-C-C-C-H
  |         |  |  |
  H         H  H  H
```
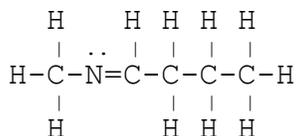
Puzzle 1.2 ———

Draw the condensed and Lewis structures for the line structure of proline, one of the 20 amino acids that compose proteins:
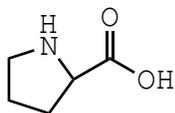
1.3B Types of Organic Molecules

Many different types of organic molecules exist. Usually they are classified by **functional group,** the group of atoms that confers reactivity to the molecule. Aside from **alkanes,** molecules containing only carbons and hydrogens with single bonds, all organic molecules have functional groups. More complex organic molecules have more than one functional group. Table 1.2 lists the common types of organic molecules by functional group. Become familiar with this table, and learn to recognize the functional groups by name and structure.

Table 1.2 Common Types of Organic Molecules

Name	Functional group	Name ending
alkane	$-\overset{\|}{\underset{\|}{C}}-$ or R-H	-ane
alkene	$-\overset{\|}{C}=\overset{\|}{C}-$	-ene
alkyne	$-C\equiv C-$	-yne
phenyl ring	$\langle\hexagon\rangle-$ or Ph- or C_6H_5-	-benzene
alkyl halide	R-Ẍ:	---
alcohol	R-ÖH	-ol
ether	R-Ö-R′	ether
amine	$R-\overset{..}{\underset{\|}{N}}-$	-amine
aldehyde	$-\overset{:O:}{\overset{\|\|}{C}}H$	-al
ketone	$R-\overset{:O:}{\overset{\|\|}{C}}-R′$	-one
carboxylic acid	$-\overset{:O:}{\overset{\|\|}{C}}-ÖH$	-oic acid
ester	$-\overset{:O:}{\overset{\|\|}{C}}-Ö-R$	-oate
acid anhydride	$-\overset{:O:}{\overset{\|\|}{C}}-Ö-\overset{:O:}{\overset{\|\|}{C}}-$	-oic anhydride
acid chloride	$-\overset{:O:}{\overset{\|\|}{C}}-\overset{..}{\underset{..}{C}}l:$	-oyl chloride
amide	$-\overset{:O:}{\overset{\|\|}{C}}-\overset{..}{N}\overset{\diagup}{}$	-amide
nitrile	$R-C\equiv N:$	-nitrile

This table features symbols used throughout the text. An open-ended bond, not ending at a specified atom, is a kind of generic bond to either hydrogen or a carbon group. Thus, the first structure of an alkane in the table stands for countless possible alkanes.

```
                                        H           H           H
                                        |           |           |
          —C—                        H-C-H       H-C-CH₃     H₃C-C-CH₂CH₃
                                        |           |           |
                                        H           H           CH₃

     generic alkane                              various alkanes
```
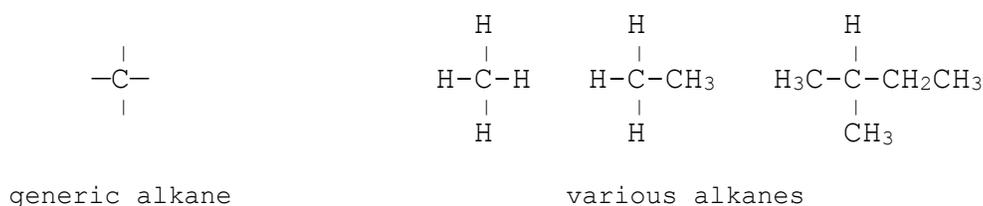
Do not confuse the open-ended bonds of generic structures with line segments of line structures. Context should clarify the meaning of these lines in a given structure.

A slightly more specific symbol is *R*, which represents any carbon or **alkyl group**. An alkyl group (derived from *alkane*) is a molecular portion containing only singly bonded carbons and hydrogens.

```
                                           CH₃
                                           |
          —CH₃     —CH₂CH₂CH₃     —CH-CH₃

               various alkyl groups (R)
```
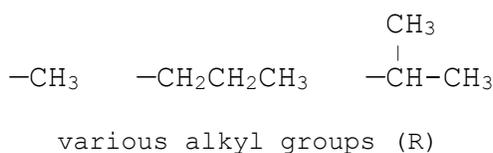
A specific symbol is *Ph*, which means a **phenyl ring**, that is, a benzene ring with a substituent. For example:

```
                                                         H       H
                                                          \     /
                                                           C — C
   C₆H₅-Cl  ≡  Ph-Cl  ≡   ⌬—Cl  ≡  H—C         C—Cl
                                                           C = C
                                                          /     \
                                                         H       H
```

four representations of chlorobenzene
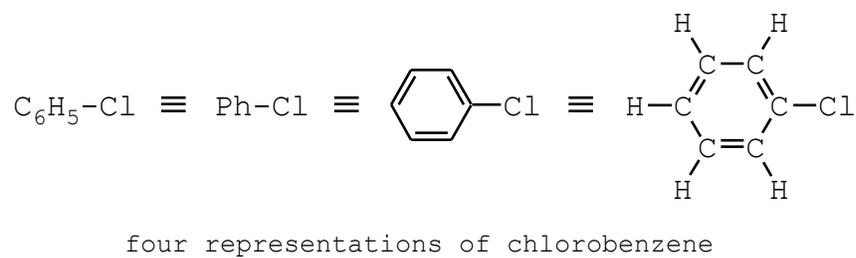
Another symbol found in the table and throughout the text is *X*. This indicates a halogen atom, that is, fluorine, chlorine, bromine, or iodine.

Generic symbols simplify analysis of molecular structures by focusing attention on essential structural features. They suggest an interchangeability frequently encountered in organic chemistry. An open-ended bond indicates that any carbon group or hydrogen bonded there influences the rest of the molecule similarly. Likewise, *R* or *X* suggests that various alkyl groups or various halogen atoms, respectively, behave similarly at that location.

Puzzle 1.3 ───

Name the functional group in each molecule:

```
              O                   O
              ‖                   ‖
(a)    CH₃CH        (b)    CH₃CCH₃       (c)    BrCH₂CH₃       (d)    HC≡CCH₃
```

(e) CH_3NH_2 (f) $H_2C=CH_2$ (g) $\overset{\overset{\textstyle O}{\parallel}}{HOCCH_3}$ (h) $Ph-CH_3$

(i)   ⬡—OH   (j) $CH_3NH\overset{\overset{\textstyle O}{\parallel}}{C}R$ (k) $CH_3OCH_2CH_3$ (l) $CH_3\overset{\overset{\textstyle O}{\parallel}}{C}OCH_3$
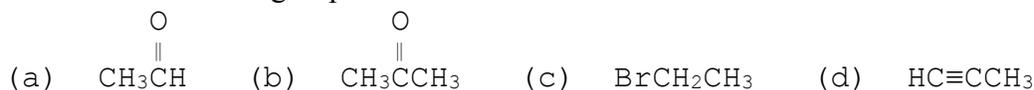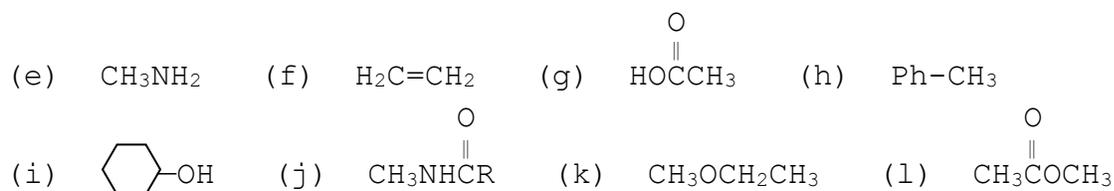
Puzzle 1.4 ───

Find all the functional groups in strychnine, both a poison and a stimulant of the central nervous system:

───
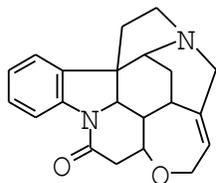
1.4 Electron Accounting

Because valence electrons determine chemical reactivity, chemists note the number of these electrons on atoms. Two methods of electron accounting are discussed here. A third method will be discussed in Section 1.6D.

1.4A Formal Charge

Formal charge roughly indicates any excess or deficiency of electrons on an atom compared with its nuclear charge. The importance of formal charge demands that all structures, even line structures, include any formal charge on an atom. Formal charge is always assessed because it strongly influences physical and chemical properties, as observed throughout this text. For example, uncharged copper is a reddish solid metal that does not dissolve in water, whereas dissolved copper(II) cations give water a blue color. We will find that charged atoms often seek to neutralize their charges by both physical and chemical processes.

Formal charge is determined by an artificial kind of ownership of electrons that reflects an excess or deficiency of electrons. Although electrons in covalent bonds are actually shared by atoms, for formal charges we artificially divide all valence electrons in a molecule among its atoms. An atom receives all of its nonbonding electrons and half of the electrons that it shares in covalent bonds. This assigned portion of electrons that an atom "owns" is then compared with the number of valence electrons that the isolated, uncharged atom would have. Because half the number of bonding electrons equals the number of covalent bonds, we have the formula:

formal charge = # of valence e's of uncharged atom

– (# of nonbonding e's + # of covalent bonds)

For example consider the structure from Section 1.3A:

```
H :Ö H H H
 \  ‖  |  |  |+
H-C-C-C-C-N-H
 |     |  |  |
 H     H  H  H
```
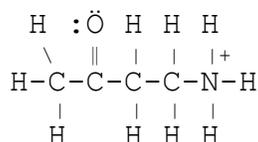
formal charge on a cation

Here each hydrogen owns one electron from one bond, each carbon owns four electrons from four bonds, and the oxygen owns six electrons from four nonbonding electrons and two bonds. Because these portions equal the number of valence electrons each of these atoms would have in the uncharged state, none of these atoms has a formal charge. Yet, nitrogen owns four electrons from four bonds. Because an uncharged nitrogen owns five valence electrons, the deficiency of one electron results in a +1 charge. Although some of this positive charge is shared with nearby atoms, we approximate the charge on this nitrogen as a full +1.

Puzzle 1.5 ───

Locate any formal charges missing from these structures:

(a)   H₃O: (b)   HNCH₃   (c)   :CH₃   (d)   :F-C-F: (e)   :F:

(f)   H₂CÖ: (g)   H₃C·   (h)   H₄N   (i)   HN=CH
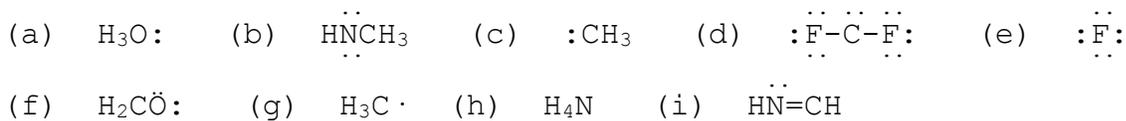
Puzzle 1.6 ───

The amino acid alanine, a component of proteins, changes form in water at different pH values. Show the nonbonding electrons for each form.

```
              H₃C   O                              H₃C   O
              + |   ‖                              + |   ‖
(a)  at pH 1: H₃N-CH-C-OH      (b)  at pH 7: H₃N-CH-C-O⁻
              H₃C   O
                |   ‖
(c)  at pH 13: H₂N-CH-C-O⁻
```
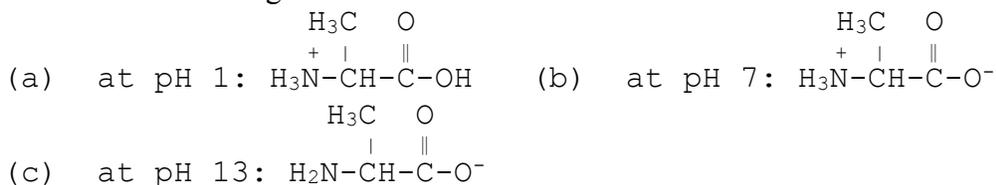
1.4B Octet Rule

A second method of electron accounting recognizes another kind of excess or deficiency of electrons. According to the **octet rule,** an atom seeks to fill its outer electron shell with nonbonding and covalently bonding electrons. Thus, atoms in the second row of the periodic table, such as carbon, nitrogen, and oxygen, so important in organic chemistry, desire an octet (eight) of nonbonding and bonding electrons. A second-row atom surrounded by fewer than eight electrons seeks enough electrons to fill its outer shell. On the other hand, more than eight electrons cannot surround a second-row atom under normal circumstances. Accordingly, carbons and nitrogens do not generally form five bonds because ten valence electrons would then surround these second-row atoms:

```
        :Ö                    H
        ‖ -                    |
    H-C  H              H-N  C-H
        |                    |  |
        H                    H  H
```

<p align="center">absurd molecules
5 bonds, 10 electrons surround second-row atoms</p>

Although the octet rule derives its name from these octet-seeking second-row atoms, other atoms also seek a filled outer shell. First-row hydrogens want to be surrounded by two electrons and normally do not tolerate more. Third-row atoms, such as phosphorus and sulfur, are stable with eight electrons, but their additional $3d$ orbitals permit a total of 10 or 12 electrons as well. Examples show five or six bonds around third-row atoms:

```
        :Ö                           :Ö
        ‖                            ‖
    HÖ-P-ÖH                      HÖ-S-ÖH
     ·· | ··                      ·· ‖ ··
       :OH                          :O
        ··                           ··
```

<p align="center">phosphoric acid   sulfuric acid
5 bonds, 10 electrons on P   6 bonds, 12 electrons on S</p>

Let us apply the octet rule to the Lewis structure from Section 1.4A:

```
    H :Ö H H H
     \ ‖ | | |+
    H-C-C-C-C-N-H
      |   | | |
      H   H H H
```

<p align="center">molecule with full octets</p>

One bond surrounds each hydrogen with the desired two electrons. Eight electrons in four bonds surround nitrogen and each carbon. Two bonds and four nonbonding electrons yield an octet for the oxygen. Thus, all atoms in this molecule have filled outer shells and some stability. Nitrogen's formal charge still makes it reactive, but the molecule will try to maintain filled outer shells while relieving its charge. Consider this reaction:

```
  H :Ö H H H                          H :Ö H H
   \ ‖ | | |+                          \ ‖ | | ··
  H-C-C-C-C-N-H   +  HÖ:⁻   ⟶   H-C-C-C-C-N-H   +   HÖ-H
    |   | | |          ··                |   | | |          ··
    H   H H H                            H   H H H
```

The product's nitrogen still has a full outer shell, but now it owns five electrons and so no formal charge. Note that the octet rule requires counting *all* electrons in covalent bonds as well as nonbonding electrons. In contrast, determination of formal charge counts only *half* the bonding electrons in addition to all nonbonding electrons.

An atom without a full outer shell of electrons tends to react to fill its outer shell. For example, because only six valence electrons surround the second-row boron of boron trichloride,

it seeks a covalent bond with two nonbonding electrons of ammonia:

```
        ..                  ..
      :Cl:        H       :Cl: H
      .. |        |        .. |- +/
    :Cl-B    +  :N-H  —>  :Cl-B-N-H
      .. |        |        .. |  \
      :Cl:        H       :Cl: H
        ..                  ..

   unfilled outer shell       full outer shells
```

In the product electron octets fill the outer shells of both the boron and the nitrogen, a strong incentive for the reaction. Note the positive and negative charges coexisting with full outer shells in the product.

Clearly, counting electrons for formal charge differs from counting for the octet rule. Carbon, nitrogen, oxygen, and hydrogen (the most common atoms in organic molecules) normally have full shells and no formal charge. Table 1.3 shows the typical numbers of covalent bonds and **lone pairs,** that is, pairs of nonbonding electrons, for these four atoms. Carbon typically has four covalent bonds and no lone pairs. Nitrogen usually has three bonds and one lone pair. Oxygen has two bonds and two lone pairs, whereas hydrogen typically has one bond and no lone pairs.

Table 1.3 Typical Numbers of Covalent Bonds and Lone Pairs for Some Uncharged Atoms

Atom	Number of bonds	Number of lone pairs	Example
carbon	4	0	CH_4
nitrogen	3	1	$:NH_3$
oxygen	2	2	$H_2\ddot{O}:$
hydrogen	1	0	H_2
halogen	1	3	$H\overset{..}{\underset{..}{Cl}}:$

One of these atoms without its typical electron arrangement would have a formal charge or violate the octet rule. Thus, a quick scan of a Lewis structure can detect structural features important for physical and chemical properties. In the following structure the oxygen on the right looks unusual with one bond and three lone pairs:

$$:\ddot{O}=\ddot{N}-\overset{..}{\underset{..}{O}}:^-$$

nitrite anion

So it is not surprising that this atom carries a formal charge: negative because it owns seven electrons.

Puzzle 1.7 ——

Which second-row atoms in Puzzle 1.5 (Section 1.4A) break the octet rule?

——

1.5 Resonance

Sometimes one Lewis structure cannot accurately express the physical reality of a molecule. Consider the nitrite anion of the last section:

$$:\ddot{O}=\dot{N}-\ddot{O}:^-$$

nitrite anion

This one Lewis structure by itself suggests that the bonds between nitrogen and the two oxygens have unequal length, because double bonds are generally shorter than single bonds. Experimental evidence, however, indicates *equal* bond lengths! Furthermore, both oxygens have charge densities that are equally negative.

How can we explain these data? Chemists often use the concept of **resonance** to explain and predict physical and chemical properties of molecules, inexplicable and unpredictable by a single structure. Nitrite anion has two **resonance forms,** that is, two different structures each inadequately depicting the real molecule:

$$:\ddot{O}=\dot{N}-\ddot{O}:^- \quad <-> \quad ^-:\ddot{O}-\dot{N}=\ddot{O}:$$
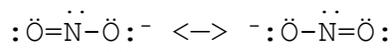
resonance forms of nitrite anion

The double-headed arrow indicates that the structures are resonance forms. Do not confuse this double-headed arrow with double arrows of an equilibrium, because *the two resonance forms do not exist as distinct molecules in equilibrium with each other*. The molecule is not one resonance form at one moment and later the other form. Instead, the molecule is simultaneously a kind of hybrid of the electronic properties of its resonance forms.

A blended structure more accurately depicts the nitrite anion hybrid:

$$^{-1/2}O\,\underset{=}{=}\,N\,\underset{=}{=}\,O^{-1/2}$$

nitrite anion as a hybrid

Here the formal -1 charge is averaged over the two oxygens that share it. The combination of a solid and dashed line represents a bond that is between a single and double bond, the average of the single and double bonds of the two resonance forms. Normally we will not draw the resonance hybrid as a single structure, which can be hard to draw and interpret, especially when blending more than two resonance forms. Instead, we will represent the molecule as a group of resonance forms. (Of course, a single structure suffices when resonance is not an issue.)

One must be able to generate reasonable resonance forms in order to predict resonance phenomena. We normally generate resonance forms by shifting only nonbonding electrons and electrons in π bonds, not electrons in σ bonds nor nuclei of atoms. These electron shifts represent

not actual physical shifts, but hypothetical shifts that generate hypothetical resonance forms. They are bookkeeping tools to help predict resonance forms. Resonance is a very useful concept, but not a process. In the case of nitrite anion, we can obtain the second resonance form from the first by shifting a lone pair from the negatively charged oxygen to a π bond with the nitrogen:

$$:\ddot{O}=N-\ddot{O}:^- \quad <-> \quad {}^-:\ddot{O}-N=\ddot{O}:$$

electron delocalization in nitrite ion

Able to tolerate at most eight electrons around it, nitrogen releases the π electrons of its original double bond onto oxygen. The two electron pairs involved in resonance are delocalized over both an oxygen and a π bond, not confined to one place or the other. For ease of delocalization, the nonbonding and π electrons move among overlapping, parallel *p* orbitals. (Atoms below the second row may use *d* orbitals.) In the example of nitrite ion:
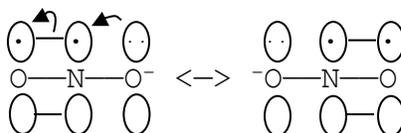
parallel *p* orbitals for resonance in nitrite ion

To help generate resonance forms organic chemists use **electron arrows**, also called curved arrows. These show the fictional flow of electron pairs as bonds are made and broken from one hypothetical resonance form to another. Three rules of electron arrows apply to resonance:
1. *An electron arrow always begins at an electron pair*, either nonbonding or in a π bond. Note that the electron arrows above obey this rule.
2. *An electron arrow always ends at an atom*, not at a bond. Again note that the electron arrows above do end at atoms.
3. In a series, *a succeeding arrow begins by the atom where the preceding arrow ends*. Successive arrows lie head-to-tail, never head-to-head nor tail-to-tail:

| head-to-tail | head-to-head | tail-to-tail |
| correct | wrong | wrong |
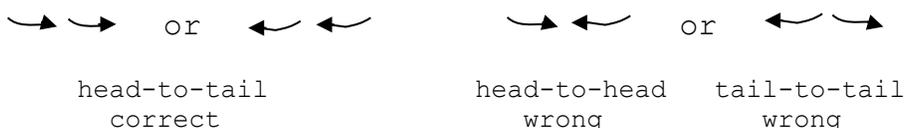
The earlier arrows do indeed lie properly. Similar electron arrows will be used later to show the course of reactions (Section 5.1). In the meantime, let us see how they generate other types of resonance forms.
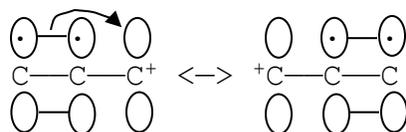
In another kind of resonance a π bond is adjacent to an atom with an unfilled outer shell. For example:
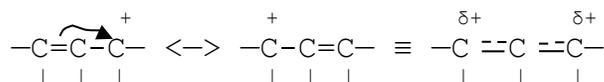
electron delocalization over 3 atoms of a cation

Pushing electrons from an electron-rich π bond to a positive charge on a carbon with an unfilled

outer shell generates a second, reasonable resonance form. In effect, the pair of π electrons is not confined to one π bond, but shared by two simultaneous, partial π bonds. Of course, parallel p orbitals allow ready delocalization of the π electrons:


parallel *p* orbitals for resonance

Another type of resonance arises when a lone pair is adjacent to an atom with an unfilled outer shell. For example:


electron delocalization over 2 atoms

To evoke the second form we move a lone pair toward the electron-poor carbon and form a π bond.
Whenever generating resonance forms, electrons flow from a region of high electron density, either a lone pair or a π bond. Note also that total charge is conserved among resonance forms because electrons are only shifted, not added or removed from the forms. Finally, note that the first resonance form can be obtained from the second by reversing the artificial electron flow:
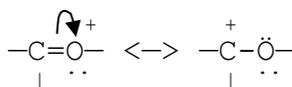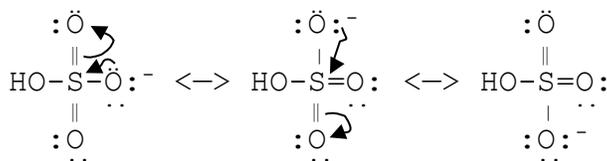

reversal of above electron delocalization

One property of resonance forms that is not averaged is energy. Because these forms are hypothetical structures of fictitious molecules, one can only estimate their energies. The hybrid nitrite anion achieves lower energy and greater stability than either resonance form alone:
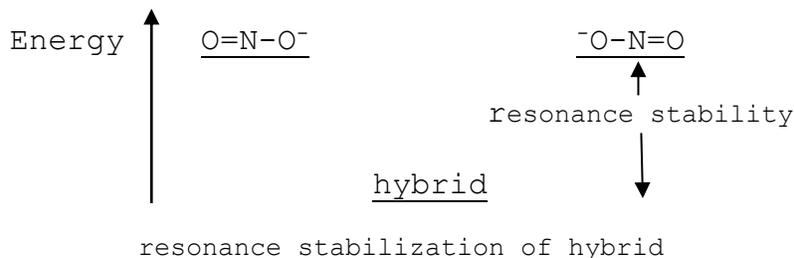
resonance stabilization of hybrid

Because molecules generally seek lower energy and greater stability, the anion exists as a hybrid, not as a resonance form of higher energy. The hypothetical energy difference between the most stable resonance form and the actual molecule is called the **resonance stability** or **resonance energy.** Resonance and its stabilizing effect can be used to explain many chemical phenomena.
By further delocalizing electrons, extra resonance forms increase resonance stability. For example, sulfuric acid is a strong acid. An important factor in its strength is the resonance stability of its conjugate base:

$$
\begin{array}{ccccc}
:\ddot{O} & & :\ddot{O}:^- & & :\ddot{O} \\
\| & & | & & \| \\
HO-S-\ddot{O}:^- & \longleftrightarrow & HO-S=O: & \longleftrightarrow & HO-S=O: \\
\| & & \| & & | \\
:\ddot{O} & & :\underset{..}{O} & & :\ddot{O}:^-
\end{array}
$$

conjugate base of sulfuric acid

Three resonance forms greatly stabilize and weaken the conjugate base. Consequently, sulfuric acid is a strong acid, very willing to surrender a proton to achieve the stability of its conjugate base.

By another property of resonance, a more stable resonance form contributes more to the nature of the hybrid than a less stable form. To use this property one must be able to estimate relative stabilities of resonance forms. The most important criterion for this estimate is the number of bonds. Because a valid bond (i.e., one that does not violate the octet rule) lowers the energy of the atoms involved, a resonance form with more valid bonds is more stable and contributes more to the hybrid than another form with fewer bonds. For example:

$$
\overset{+}{-}C-\ddot{O}- \quad \longleftrightarrow \quad -C=\overset{+}{O}-
$$

minor form   major form
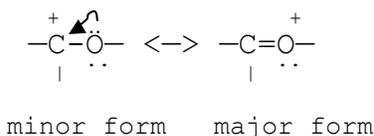
The major resonance form is the second one because it has an extra, stabilizing π bond. Thus, the bond between carbon and oxygen in the actual hybrid has more double than single bond character, and the oxygen holds more of the formal positive charge than the carbon. (The polarity of bonds further affects this charge distribution, however, as discussed in Section 1.9A.) Note also that the second form abides by the octet rule, whereas the carbon of the first form has an unfilled shell.

The following generalization pertains to the above resonance situation:
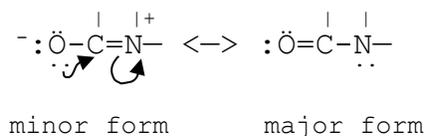
as attractions (e.g. bonds) ↑, energy ↓ & stability ↑

The additional bond must be valid, however. Consider the next situation, which superficially resembles the preceding one:

$$
\overset{+|}{-}N-\ddot{O}- \quad \longleftrightarrow\!\!/\!\!/\!\!\longrightarrow \quad -N=O
$$

only form   unfeasible
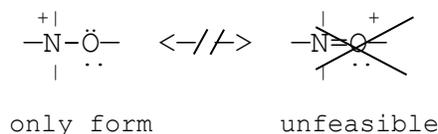
One might be tempted to regard the second form as the major resonance form because it shows an extra π bond. Yet with this extra bond 10 electrons in five bonds surround the second-row nitrogen and violate the octet rule. Unlike the previous example where the carbon of the first resonance form had an unfilled shell, the nitrogen of the first form here already has a full outer shell. Consequently, the second form is too unstable to be a feasible resonance form, and the first structure by itself properly describes the true molecule without any resonance.
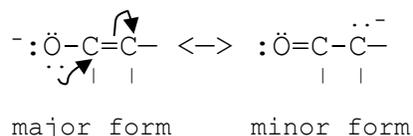
A second, less important criterion for judging the relative stabilities of resonance forms is the position of charges. According to a fundamental law of physics, opposite charges attract whereas like charges repel. Therefore, a resonance form with closer opposite charges or more

separate like charges will have lower energy and more stability. Consider the example:
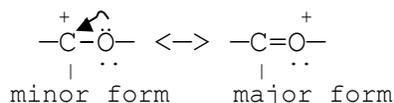
$$^-:\overset{\displaystyle|}{\underset{\displaystyle\cdot\cdot}{\ddot{O}}}-\overset{\displaystyle|}{C}=\overset{\displaystyle|+}{N}-\quad<->\quad:\ddot{O}=\overset{\displaystyle|}{C}-\overset{\displaystyle|}{\underset{\displaystyle\cdot\cdot}{N}}-$$

```
        minor form        major form
```

The separate opposite charges on the first form draw together and coincide in the second form. Thus, the second form is the major form, and the actual molecule has more double bond character between the carbon and oxygen than between the carbon and nitrogen.

Electronegativity (reviewed in Section 1.9A) also affects the stability of charges. Extra electrons and a negative charge are more stable on a more electronegative atom, whereas a positive charge prefers a less electronegative atom. For example:

$$^-:\overset{\displaystyle}{\underset{\displaystyle\cdot\cdot}{\ddot{O}}}-C=\overset{\displaystyle}{\underset{\displaystyle|\ \ |}{C}}-\quad<->\quad:\ddot{O}=C-\overset{\displaystyle\cdot\cdot^-}{\underset{\displaystyle|\ \ |}{C}}-$$
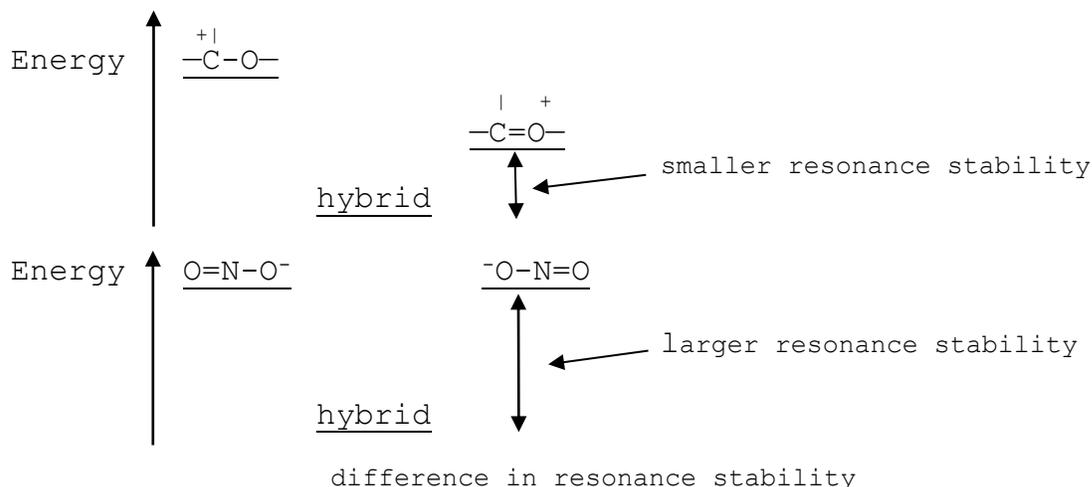
```
        major form        minor form
```

Because oxygen is more electronegative than carbon, the first form with the negative charge on the oxygen is more stable than the second form. The real molecule has more partial negative charge on the oxygen than on the carbon.

Aware of the factor of charge position, let us reexamine an earlier example of resonance:

$$\overset{+}{-C}-\overset{\displaystyle}{\underset{\displaystyle\cdot\cdot}{\ddot{O}}}-\quad<->\quad-\overset{\displaystyle|}{C}=\overset{+}{\underset{\displaystyle\cdot\cdot}{O}}-$$

```
   minor form     major form
```

The second form was judged to be stabler because it has an extra bond. On the other hand, this form also has the positive charge on the more electronegative atom, the oxygen. So by the second criterion of charge position, the first form is stabler. Yet, because extra bonding is generally more important than charge position, we estimate the second form to be the major one.

A final property of resonance indicates that a more stable resonance form stabilizes more than a less stable form. Two examples illustrate this principle.


```
                +|
Energy         —C-O—


                          |   +
                         —C=O—
                                        smaller resonance stability
              hybrid

Energy   O=N-O⁻             ⁻O-N=O

                                        larger resonance stability

         hybrid

              difference in resonance stability
```

A second major form stabilizes the anion more than the less stable, minor resonance form stabilizes the cation. Thus, a minor form contributes less to resonance stabilization, as well as to other electronic properties of the hybrid.

      Let us summarize the properties of resonance.

      1. *A molecule that cannot be accurately depicted by only one Lewis structure is a hybrid of more than one fictitious resonance form.* The actual molecule is not an equilibrium of the resonance forms, but a simultaneous blending of their electronic properties.

      2. *Resonance forms are generated by delocalizing nonbonding and π electrons in reversible patterns over overlapping parallel p (or d) orbitals.* Nuclei and σ electrons do not move. Total charge is conserved among a set of resonance forms.

      3. *Resonance lowers the energy of a molecule below that of its most stable resonance form.*

      4. *Resonance stabilization increases with the number of resonance forms.*

      5. *Stability of resonance forms can be estimated by two criteria: the number of valid bonds and the position of charges.* The first criterion is usually more important than the second.

      6. *A more stable resonance form contributes more to the identity and stability of the hybrid than a less stable form.*

      Of course, these many properties of resonance would be difficult to remember without working many examples and puzzles in this and later chapters. Fear not: both this text and organic chemistry as a whole offer plenty of examples.
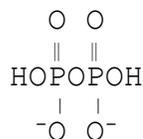
Puzzle 1.8 ———

With the help of electron arrows, draw all reasonable resonance forms for each molecule and decide major and minor forms:

```
        O                           O
        ‖                           ‖
(a)   HCO⁻     (b)   HOCHCH₃   (c)   ⁻ONO⁻    (d)   carbon monoxide
        +                                  +
(e)   O=N=O    (f)   N≡C-O⁻
```
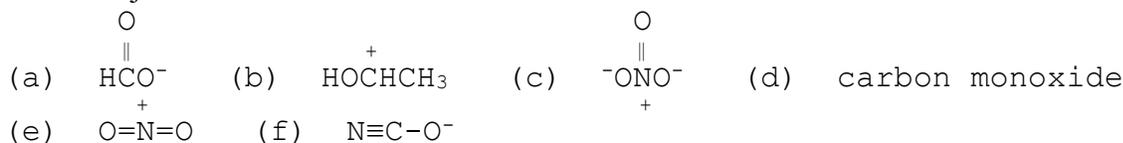
Puzzle 1.9 ———

Pyrophosphate ion and its derivatives are common biochemical metabolites.   At pH 4 pyrophosphate ion has the structure:

```
          O  O
          ‖  ‖
        HOPOPOH
          |  |
         ⁻O  O⁻
```

Draw all of its major resonance forms.

———

1.6 Molecular Geometry and Hybrid Orbitals

      Written structures, whether Lewis or condensed or line, normally do not indicate the true geometry of a molecule. These figures depict molecules on a planar surface, although many molecules are not planar. Molecular shape is important because many physical and chemical properties depend on it. Aided by the theory of hybrid orbitals, we will be able to predict molecular

shape. (Throughout this book molecular shape will reflect so-called electron-pair geometry, where lone pairs are an essential part of the shape.)
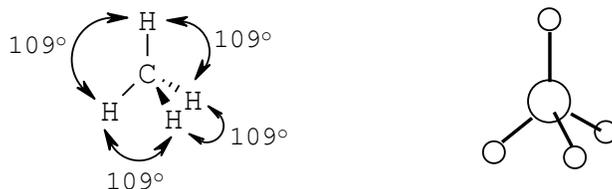
1.6A Molecular Geometry of Methane

Methane, CH_4, is the smallest, simplest alkane (Table 1.2) and the principal component of natural gas.

```
        H
        ..
    H:C:H
        ..
        H
```
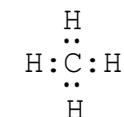
methane

One might infer from this two-dimensional representation that methane is a planar molecule with H-C-H bond angles of 90°. In fact, methane is a three-dimensional molecule with all H-C-H bond angles of 109°:

3-D structures of methane

To convey the three-dimensional nature of methane, three different symbols for bonds are used. The two solid lines indicate bonds in the plane of the paper. The wedge indicates a bond extending from the carbon outward to a hydrogen closer to the viewer. The dashed line represents a bond pointing inward from the carbon to a hydrogen farther from the viewer. One may also visualize the four hydrogens at the vertices of a tetrahedron surrounding the carbon:
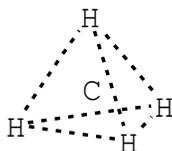

tetrahedral structure of methane

Accordingly, we say that this carbon has **tetrahedral geometry**. To better visualize this arrangement of bonds and atoms, a molecular model is very useful.

Why does methane adopt this tetrahedral shape? It is a matter of physics and geometry. Four pairs of negatively charged electrons in four σ bonds surround the carbon. Because negative charges repel each other, the molecule has least energy and most stability if it arranges its four σ bonds as far apart as possible. Only a tetrahedral shape and 109° bond angles achieve this minimum repulsion. In molecular shape, as in resonance (Section 1.5):

as repulsions ↓, energy ↓ & stability ↑

How can we explain this geometry in terms of carbon's electron orbitals? The individual *s* and *p* orbitals of an isolated, unbonded carbon atom cannot explain the geometry of this bonded carbon. Instead, chemists invented the method of **orbital hybridization** to describe the orbital arrangement of carbon and other atoms in molecules. In this process *s* and *p* (and sometimes *d*) atomic orbitals are mathematically combined or **hybridized** to form **hybrid orbitals.** An important conservation rule applies to orbital hybridization: *the number of hybrid orbitals equals the number of atomic orbitals hybridized*. In methane, carbon extends hybrid orbitals, not *s* or *p* orbitals themselves, for its four σ bonds. The four outer-shell atomic orbitals, a 2*s* and three 2*p* orbitals, are hybridized to yield four *sp*³ hybrid orbitals:

front lobe—┘ └—back lobe

an *sp*³ hybrid orbital   4 tetrahedral *sp*³ orbitals minus back lobes
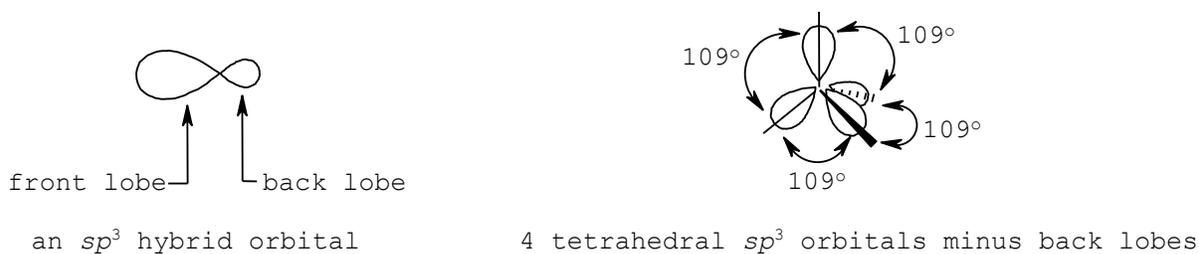
The *sp*³ designation indicates the number and kind of atomic orbitals that compose the hybrid orbitals: an *s* and three *p* orbitals. Note that an *sp*³ orbital resembles a *p* orbital in having two lobes. Yet, unlike *p* orbitals but typical of hybrid orbitals, the two lobes have different sizes, reflecting a much greater probability of finding an electron in the front lobe than in the smaller back lobe. In fact, for simplicity the back lobe is usually omitted from drawings, as in the assembly of four *sp*³ orbitals above. Here the hybrid orbitals define a tetrahedron with the axes of the orbitals separated by 109°.

In methane carbon's four valence electrons are evenly distributed among the four hybrid orbitals, identical in energy:

Energy

sp^3 ↑_ ↑_ ↑_ ↑_

$2p$ ↑_ ↑_ __

$2s$ ↑↓_

in methane   in isolated atom
electron configurations of carbon
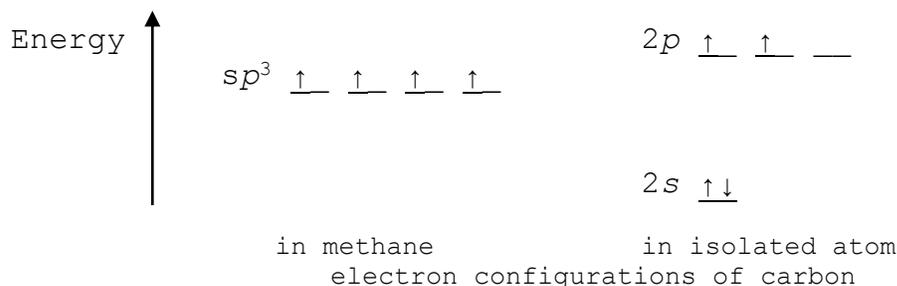
This distribution follows **Hund's rule:** place electrons in different orbitals of the same energy to minimize repulsion. The four unpaired electrons account for the four σ bonds in methane because each unpaired electron can form a bond with an unpaired electron from a hydrogen atom.

By comparison, the uncharged, isolated carbon atom distributes its four valence electrons in unhybridized 2*s* and 2*p* atomic orbitals. Two electrons are paired in the 2*s* orbital, and only two electrons are left unpaired and able to bond in 2*p* orbitals. Therefore, this electron configuration permits only two bonds. Because bonds tend to lower the energy of atoms, the four bonds allowed by hybridization are favored over the two bonds without hybridization.

It is no coincidence that the tetrahedral shape of the molecule perfectly reflects the geometry of the four *sp*³ orbitals. Carbon's hybrid orbitals, by overlapping head-on with the hydrogens' 1*s* orbitals, determine tetrahedral bond angles of 109°.
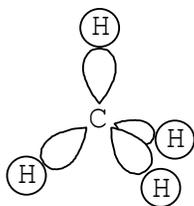
```
overlapping orbitals determining methane's shape
```

An advantage of hybridization becomes apparent. Because the more directed, front lobes of hybrid orbitals have greater electron density than either lobe of a p orbital, carbon can form stronger bonds with hybrid orbitals. Thus, the sp^3 hybridization of carbon explains the number, direction and strength of σ bonds in methane.

Puzzle 1.10 ───

(a) Draw the Lewis structure of ethane, CH_3CH_3.
(b) To minimize electron repulsion, what geometry should surround each carbon?
(c)   Using wedges and dashed lines, draw a three-dimensional structure showing the correct geometry at both carbons.

───

1.6B Molecular Geometry of Methyl Carbocation

Let us next explore the shape of the methyl **carbocation** (pronounced *car' bō cat' ī ən*), $^+CH_3$. In a carbocation a carbon carries a formal positive charge.

```
      H
      ..
   H:C +
      ..
      H
```
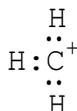
```
methyl carbocation
```

Again, we should not expect this Lewis structure to indicate the shape of the ion. To minimize repulsion among the three electron pairs, the molecule would not have two bond angles of 90° and one of 180°. Instead, the ion spreads its bonds to form three 120° bond angles, equally dividing the 360° field around carbon:
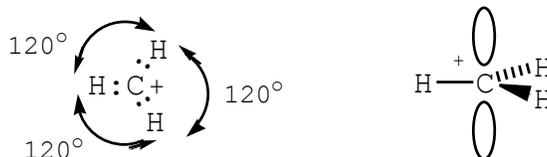


```
two views of methyl carbocation's geometry
```

Note in the second view above that all four atoms are in the same plane, perpendicular to an empty p orbital. Because the three hydrogens surrounding the carbon define a triangle, this shape is called

trigonal planar (i.e., triangular).

In accordance with this geometry, the carbon of the methyl carbocation hybridizes a $2s$ and two $2p$ orbitals to yield three sp^2 hybrid orbitals and leaves one $2p$ orbital unhybridized. The superscript in sp^2 specifies the number of p orbitals hybridized. Note that this hybridization properly conserves the number of orbitals.


front lobe— —back lobe

an sp^2 orbital   3 trigonal sp^2 orbitals minus back lobes
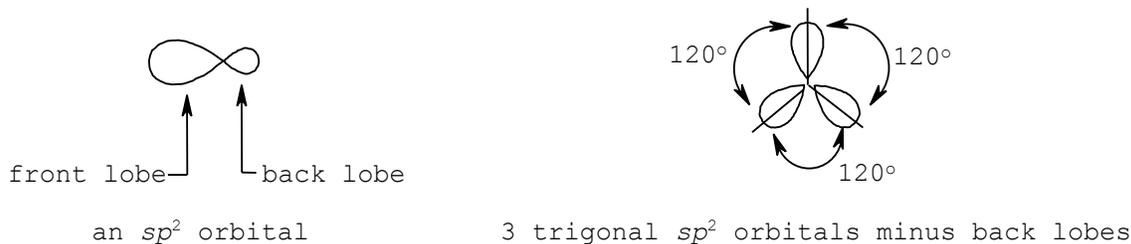
An sp^2 orbital resembles an sp^3 orbital with its small back lobe of low electron probability. Yet, the three sp^2 orbitals define a planar equilateral triangle, not the tetrahedron of sp^3 orbitals, and the axes of the sp^2 orbitals intersect at angles of $120°$.

Identical in energy, the three sp^2 orbitals share carbon's electrons in the methyl carbocation:
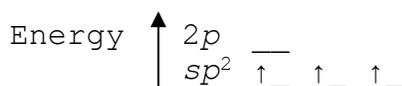
electron configuration of carbon in methyl carbocation

The three unpaired electrons seek three bonds with unpaired electrons, the correct number for the carbocation. Furthermore, overlap of one $1s$ orbital from hydrogen with each sp^2 orbital of carbon provides the desired trigonal planar orientation of bonds.
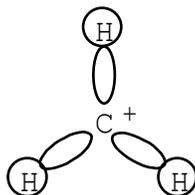
σ bonds of methyl carbocation.

Carbon's empty, unhybridized $2p$ orbital lies perpendicular to the plane of the three, bonding sp^2 orbitals. We see again that hybridization provides both the correct number and the correct orientation of bonds.
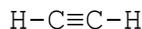
Puzzle 1.11 ————————————————————————————————————

Consider $^+CCl_3$.
(a) Draw its Lewis structure. (b) What Cl-C-Cl bond angle would you predict? Explain.
(c) Draw an accurate geometric structure for the cation.

1.6C Molecular Geometry of Ethyne

Ethyne, more commonly known as acetylene, is the smallest **alkyne,** a triply bonded hydrocarbon (Table 1.2).

$$H-C\equiv C-H$$

ethyne

For once, this linear representation does indicate the true shape of the molecule. The nuclei of all four atoms lie on one straight line with H-C-C bond angles of 180°. Evidently, this geometry minimizes electron repulsion, but a second look at the triple bond displayed in Section 1.2C helps us see this. Each carbon has two σ bonds (to a carbon and a hydrogen) and two π bonds (to a carbon). Each of the σ bonds has an electron pair most likely to be in a small region between the nuclei. In contrast, each of the π bonds has an electron pair likely to be in large regions above and below the internuclear axis. Because electrons in π bonds are so diffuse, they provide little consistent repulsion to other electron pairs. So for the most part, ethyne minimizes electron repulsion only among its σ bonds. By putting its atoms in a straight line, ethyne minimizes repulsion among its σ electron pairs, and consequently it minimizes its energy.

Once again orbital hybridization explains this optimum geometry as well as the number of bonds. Each carbon in ethyne hybridizes one 2*s* and one 2*p* orbital to provide two *sp* hybrid orbitals, while two 2*p* orbitals are left unhybridized. Of course, the number of hybrid orbitals equals the number of orbitals hybridized.

front lobe— —back lobe

an *sp* orbital

180°
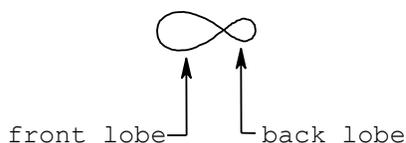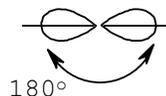
2 linear *sp* orbitals minus back lobes

Like all other hybrids of *s* and *p* orbitals, an *sp* orbital has two lobes, the front larger than the back.

The two *sp* hybrid orbitals are used for each carbon's two σ bonds and the two perpendicular, unhybridized 2*p* orbitals are used for each carbon's two π bonds.
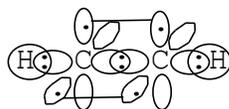
σ and π bonds of ethyne

The linear molecule results naturally from the orientation of the hybridized orbitals.

Puzzle 1.12 ───

Consider carbon dioxide.
(a) Draw its Lewis structure.   (b) What O-C-O bond angle would you predict? Explain.

(c) Draw an accurate geometric structure of the molecule.

1.6D General Rules of Molecular Geometry

So far, we have seen three examples where orbital hybridization was used to explain the molecular shape that minimizes electron repulsion. But how does one know which hybridization results from a particular shape? Indeed, how can one reliably predict the optimum shape? Let us formulate general rules that determine both molecular shape and hybridization of second-row atoms in molecules of all kinds.

First, *count the number of* **repelling electron pairs** *at a given second-row atom*. A repelling electron pair is one that resides mostly in a small region of the molecule and so fully repels other such electron pairs. As we have seen, any electron pair in a σ bond counts as a repelling electron pair. Also, a lone, nonbonding pair of electrons is a repelling electron pair because it lies in one orbital, a small region. In contrast, electron pairs in π bonds are too diffused over two p orbitals to fully repel (Section 1.6C). Thus, a double or triple bond contributes only one (σ) repelling electron pair to the count. Also, a single, unpaired electron, found in radicals, does not repel enough to count.

Second, *provide one hybrid orbital for each repelling electron pair*. This automatically minimizes electron repulsion. Remember that hybridization conserves the number of orbitals. Thus, if four repelling electron pairs surround a second-row atom, one $2s$ and three $2p$ orbitals must generate four sp^3 hybrid orbitals, separated by 109° angles in a tetrahedral shape. For example, the nitrogen in ammonia, NH_3, is surrounded by four repelling electron pairs: three σ pairs in bonds to hydrogen and one lone pair. Accordingly, the nitrogen is hybridized approximately sp^3 with approximately 109° bond angles:
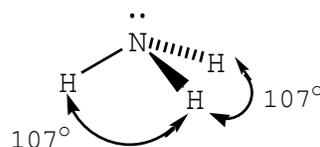
geometry of ammonia

The predicted hybridization and bond angles are only approximate because the repelling electron pairs are not all equivalent: the lone pair is more closely held by nitrogen and so more strongly repels the other shared electron pairs. Yet, for our purposes the rules generally give an accurate enough picture of molecular shape.

If a second-row atom has three repelling electron pairs, one $2s$ and two $2p$ orbitals provide three sp^2 hybrid orbitals, separated by 120° angles in a trigonal, planar fashion. One $2p$ orbital, perpendicular to the plane of the sp^2 orbitals, remains unhybridized. For example, each carbon in ethene, $H_2C=CH_2$, has three repelling electron pairs in three σ bonds (the π bond does not count). So each carbon is hybridized approximately sp^2 with approximately 120° bond angles:
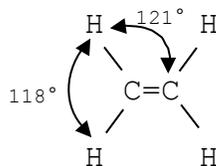
geometry of ethene

Bond angles deviate from 120° because of unequal repelling electron pairs

If two repelling electron pairs surround a second-row atom, two atomic orbitals, one 2*s* and one 2*p* orbital, hybridize into two *sp* orbitals at a 180° angle. Two 2*p* orbitals, perpendicular to each other and to the *sp* orbitals, remain unhybridized. For example, both carbon and nitrogen in cyanide anion, :N≡C:⁻, are *sp* hybridized because each second-row atom has two repelling electron pairs in a lone pair and a σ bond. Although a diatomic molecule has no bond angle, both lone pairs are in line with the atoms:
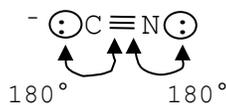
geometry of cyanide anion

Table 1.4 generalizes these rules. Except for instances of resonance (Section 1.6E) and ring strain (Section 2.8), these rules are general for second-row atoms. Even third-row atoms usually obey these rules. For example, the silicon in silane, SiH_4, has four repelling electron pairs in four σ bonds. So it is hybridized sp^3 with tetrahedral geometry. A third-row atom involves *d* orbitals only for more than four repelling pairs. A hydrogen, having only one repelling electron pair in a normal molecule, does not hybridize its 1*s* orbital.

Table 1.4 Rules of Hybridization and Geometry for Second-Row Atoms

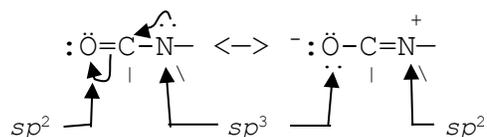| # of repelling electron pairs	Hybridization	Bond angle	Shape
4	4 x sp^3	109°	tetrahedral
3	3 x sp^2 & 2*p*	120°	trigonal planar
2	2 x sp & 2 x 2*p*	180°	linear
1	none	none	---

Puzzle 1.13 ——

Give the hybridization and geometry for each second- or third-row atom in these molecules:
(a) H_2O (b) H_3O^+ (c) ⁻CH_3 (d) ·CH_3 (e) N_2 (f) HO^- (g) $H_2C=N-CH_3$ (h) H_2SO_4

(i) PCl_3

1.6E Resonance and Hybridization

Let us see how resonance can affect hybridization. Consider two resonance forms that suggest ambiguous hybridizations for a molecule:

$$:\ddot{O}=C-N- \quad <-> \quad {}^-:\ddot{O}-C=N-$$

sp² �   sp³   sp

apparent hybridizations in different resonance forms

In the first form the oxygen with three repelling electron pairs is hybridized sp^2. Yet, in the second form four repelling electron pairs give this same oxygen sp^3 hybridization. Likewise, the nitrogen is hybridized sp^3 and sp^2 in the first and second forms, respectively.

What is the true hybridization of these two atoms in the actual molecule, the resonance hybrid? It is best to consider them hybridized sp^2, not sp^3 or some combination of sp^2 and sp^3. Resonance requires ready delocalization of π and nonbonding electrons in parallel p orbitals of second-row atoms (Section 1.5).

O—C—N <-> ⁻O—C—N⁺
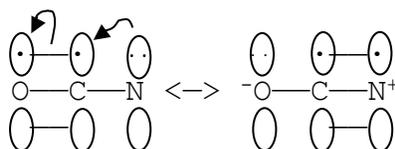
parallel p orbitals for resonance

Consequently, to provide p orbitals needed for resonance, second-row atoms must be hybridized sp^2 or sp, not sp^3.

Resonance's demand for p orbitals can affect the geometry of a molecule. Consider methanamide (i.e., formamide):

$$\ddot{O}: \qquad :\ddot{O}:^-$$
$$HC-NH_2 \quad <-> \quad HC=NH_2$$
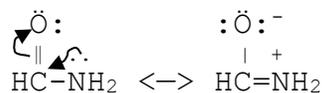
major form   minor form
methanamide

In the major resonance form the nitrogen appears to be sp^3 hybridized with bond angles at the nitrogen of about 109°. Yet, nitrogen's true hybridization in the actual molecule is about sp^2 to allow for resonance. Consequently, the bond angles at nitrogen are about 120° with trigonal planar geometry:
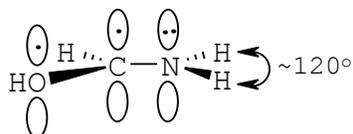
planar geometry of methanamide

Puzzle 1.14 ───

Give the hybridization and geometry for each second-row atom in the molecules of Puzzle 1.8 (Section 1.5)

Puzzle 1.15 ───

Aspartame is a popular artificial sweetener, 200 times sweeter than sucrose, table sugar. Aspartame has this structure:

```
      O      H₂N   O PhCH₂  O
      ‖       |    ‖    \    ‖
HO–C–CH₂–CH–C–NH–CH–C–O–CH₃
```
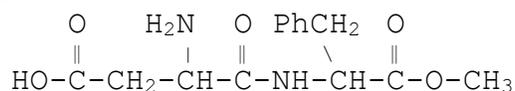
Which atoms must be in one plane to permit resonance in the amide functional group? (Table 1.2, Section 1.3B, shows an amide group.)

1.7 Bond Lengths

The length of a bond depends on the lengths and the number of overlapping orbitals. The length of a σ bond increases with longer overlapping orbitals. Also, the more overlapping orbitals in multiple bonds bind atoms more closely than do the fewer orbitals in single bonds. Let us examine the bond lengths in three organic molecules.

1.7A Bond Lengths in 1-Butene

1-Butene is an **alkene,** a hydrocarbon with a carbon-carbon double bond (Table 1.2).

```
        H  H
        |  |
      H–C–C–C=C–H
        |  |  |  |
        H  H  H  H
```
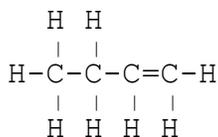
1-butene

Table 1.5 shows the bonding orbitals and the bond lengths in 1-butene. We see in the table that the carbon-carbon double bond is 134 pm long, shorter than the carbon-carbon single bonds of 153 and 150 pm (1 pm = 1 picometer = 10^{-12} m; pico- is pronounced $p\bar{e}'$ $k\bar{o}$). This difference results from the double bond's four overlapping orbitals bonding their atoms more closely. Why are the carbon-hydrogen bonds shorter (110, 108 pm) than the carbon-carbon single bonds? The smallness of hydrogen's 1s orbital shortens its part of the bond, and so the whole bond length

diminishes.

Table 1.5 Bonding Orbitals and Bond Lengths in 1-Butene and
Propyne

Molecule	Bond	Bonding orbitals	Bond length/pm
H H | | H-C-C-C=C-H | | | | H H H H	-**C-C**-	sp^3-sp^3	153
	C-C=	sp^3-sp^2	150
	C=C	sp^2-sp^2, $2p$-$2p$	134
	-**C-H**	sp^3-$1s$	110
	=**C-H**	sp^2-$1s$	108
H | H-C-C≡C-H | H	**C-C**	sp^3-sp	147
	C≡C	sp-sp, $(2p$-$2p)$x2	120
	-**C-H**	sp^3-$1s$	110
	≡**C-H**	sp-$1s$	106

   Why are the alkene's carbon-carbon single bonds of different lengths: 153 versus 150 pm? Again we consider the overlapping orbitals. The difference in the two bonds is the second sp^3 orbital used in the sp^3-sp^3 bond versus the sp^2 orbital in the sp^3-sp^2 bond. Evidently, the sp^3 orbital is longer than the sp^2 orbital. Why is this? The sp^3 orbital, derived from three $2p$ orbitals and one $2s$ orbital, has 75% p character and 25% s character. In contrast, the sp^2 orbital has less (67%) p character and more (33%) s character. Because a $2p$ orbital is longer than a $2s$ orbital, the greater length of the sp^3 orbital with more p character is reasonable. Consequently, the sp^3-sp^3 bond is longer than the sp^3-sp^2 bond. In summary:

    as p character ↑, hybrid orbital length ↑ and bond length ↑

Puzzle 1.16 ──

Explain the difference in carbon-hydrogen bond lengths for 1-butene.
──

1.7B Bond Lengths in Propyne

Let us next analyze the bond lengths in propyne, a three-carbon alkyne, that is, a hydrocarbon with a carbon-carbon triple bond (Table 1.2).
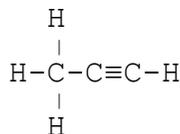
```
            H
            |
       H-C-C≡C-H
            |
            H

         propyne
```

In Table 1.5 (Section 1.7A) it is no surprise that the carbon-carbon triple bond is shorter (120 pm) than an analogous single (153 pm) or double bond (134 pm), because the triple bond has more (six) overlapping orbitals holding its atoms together. The very short carbon-hydrogen bond for the triply bonded carbon (106 pm) results from the relatively short *sp* orbital, which overlaps hydrogen's 1*s* orbital. This orbital, hybridized from one 2*p* and one 2*s* orbital, has only 50% *p* character, making it the shortest of hybrid orbitals.

Puzzle 1.17 ───

(a) Determine the hybridization of each second-row atom in $H_2C=C=CH-CH=CH_2$.
(b) Rank the carbon-carbon bonds in $H_2C=C=CH-CH=CH_2$ by length.

───

1.7C Bond Lengths in Benzene

Benzene is a hydrocarbon with double and single bonds apparently alternating around a ring:
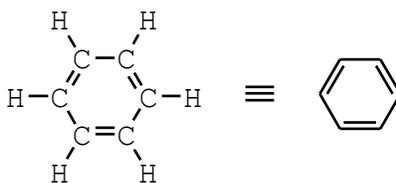
```
        H      H
         \    /
          C—C
         //    \\
    H—C        C—H    ≡    ⬡
         \    //
          C=C
         /    \
        H      H

      2 representations of benzene
```

The alternation of double and single bonds is misleading, however, because all of the carbon-carbon bonds in benzene have the same length, 139 pm. How can we explain this equality of bond lengths? When one structure does not represent reality, we consider resonance possibilities. In this case, we can construct a second resonance form by shifting π electrons around the ring:

major form   major form
        resonance in benzene
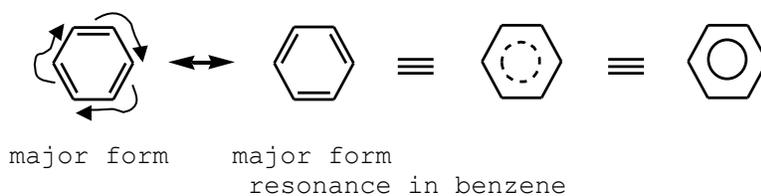
Being equally stable, these two forms contribute equally to the actual molecule. Therefore, all carbon-carbon bonds in the actual molecule should have equal length, between the lengths of a single and double bond. The measured bond lengths confirm this: the 139 pm length here is longer than a typical carbon-carbon double bond (134 pm, Table 1.5), and shorter than a typical carbon-carbon single bond (153 pm). The two resonance forms can be combined into the third blended form above, showing equal, partial double bonds all around the ring. More often the benzene ring is shown as the fourth depiction with a circle in the middle to suggest equal bonding around the ring.

        The two major resonance forms also affect benzene by stabilizing it. (Section 17.4A presents a second stabilizing factor.) As a result, a "double bond" in benzene is much less reactive than a normal carbon-carbon double bond of an alkene. In fact, reactions for alkenes in Chapter 8 do not apply to benzene rings.

Puzzle 1.18 ——

Benzene can cause leukemia. This toxicity might result from molecules of benzene sliding between consecutive bases of DNA, which stack in parallel planes along DNA's double helix. Are all 12 atoms of benzene in one plane, allowing benzene to slide between DNA's bases? Explain in terms of hybridization and bond angles. A molecular model might help.

——

1.8 Bond Energies

        Decreasing potential energy helps physical processes occur spontaneously, that is, without outside intervention. For example, a stretched spring has more potential energy than an unstretched spring. Work must be done on the spring to stretch it and this work energy increases the potential energy. The stretched spring then can spontaneously recoil because it thereby loses potential energy.

        The internal potential energy of a molecule is its **enthalpy, *H*.** So a decrease in enthalpy promotes a spontaneous chemical reaction. Let us reconsider forming the covalent bond between two hydrogen atoms (Section 1.2B):

$$H\cdot \;\; + \;\; H\cdot \;\; \longrightarrow \;\; H\!:\!H$$

This process is favorable and spontaneous because molecular hydrogen has less enthalpy and more stability than the two separate hydrogen atoms. Therefore, the change in enthalpy, ΔH, is negative and favorable:

$$
\begin{aligned}
\Delta H \;\; &= \;\; H(\text{product}) \, - \, \Sigma \, H(\text{reactants}) \\
&= \;\; -436 \text{ kJ/mol}
\end{aligned}
$$

(1 kilojoule (kJ) = 0.239 kilocalorie)   The 74-pm bond length in the hydrogen molecule corresponds to the separation of hydrogen atoms at minimum enthalpy and maximum stability.

enthalpy versus separation of hydrogen atoms
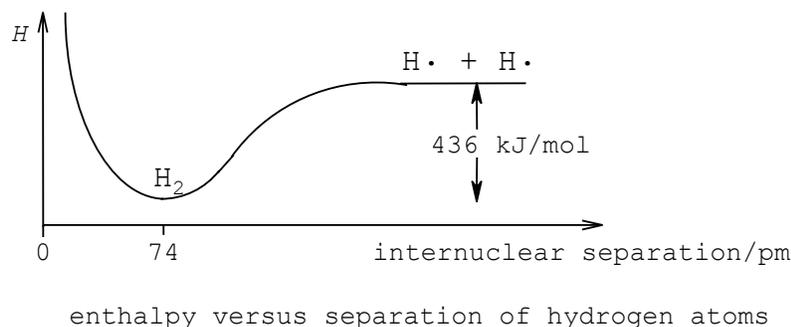
If the hydrogen nuclei are forced closer together than the bond length, increasing repulsion between the positively charged nuclei unfavorably increases the enthalpy. Pulling the nuclei farther apart than the bond length stretches the bond, lessens orbital overlap, and increases enthalpy. Likewise, a spring's potential energy increases by either compression or stretching beyond its resting state.

      Bond energy is the energy needed to completely separate bonded atoms. (In this text, bond energies result from homolytic cleavage of a bond to form two radicals.) It is always a positive number because energy is always needed to break a bond. Breaking the bond in molecular hydrogen reverses the process of bond formation:

$$H\text{-}H \quad \longrightarrow \quad 2\ H\cdot \qquad \Delta H = 436\ \text{kJ/mol}$$

The bond energy for H-H, then, is ΔH for this bond breaking, 436 kJ/mol, the opposite of ΔH for bond formation.

      Table 1.6 compiles bond energies for representative bonds. As bond strength increases, so does bond energy. So, it is reasonable that the triple bond of HC≡CH and the double bond of $H_2C=CH_2$ have greater bond energies than the carbon-carbon single bond of $H_3C\text{-}CH_3$ (962, 682, 368 kJ/mol, respectively). The nitrogen-nitrogen bond of hydrazine, $H_2N\text{-}NH_2$ (297 kJ/mol), the oxygen-oxygen bond of hydrogen peroxide, HO-OH (214 kJ/mol), and the chlorine-chlorine bond of molecular chlorine (243 kJ/mol) are relatively weak. By comparison, a bond between carbon and hydrogen, carbon, nitrogen, oxygen, or chlorine is strong: about 431, 368, 331, 377, or 339 kJ/mol, respectively. Such strong bonds to carbon explain the enormous ability of carbon to form stable organic compounds with a variety of atoms (Section 1.1). The stronger a bond, the stabler and less reactive it is. Ironically, then, *strong* bonds can mean a *weak*, unreactive molecule.

as bond strength ↑, bond energy ↑ & molecular energy ↓ & molecular reactivity ↓

Table 1.6 Bond Energies for Representative Bonds

Bond	Bond energy/ kJ/mol	Bond	Bond energy/ kJ/mol
H–H	436	H_3C–F	452
H–CH_3	431	H_3C–Cl	339
H–CH_2CH_3	410	H_3C–Br	284
H–NH_2	435	H_3C–I	232
H–OH	499	$H_2C=CH_2$	682
H–F	569	$HC≡CH$	962
H–Cl	432	H_2N–NH_2	297
H–Br	366	HO–OH	214
H–I	299	F–F	158
H_3C–CH_3	368	Cl–Cl	243
H_3C–NH_2	331	Br–Br	194
H_3C–OH	377	I–I	153

Puzzle 1.19 ——

(a) Which bonds are broken and made in this reaction?

$$H_2 + Cl_2 \longrightarrow 2\ HCl$$

(b) Aided by Table 1.6, calculate the ΔH.
(c) Does this ΔH favor the forward reaction?

——

1.9 Polarity

Another aspect of molecular structure that affects physical and chemical properties is **polarity.** Polarity indicates a separation of opposite charges in a bond or molecule, in other words, two poles of charge. The charges are usually not formal, but **partial charges** of fractional amount, less than a full formal charge. Partial positive and negative charges are symbolized $\delta+$ and $\delta-$, respectively (δ is pronounced *del′ tə*).

1.9A Bond Polarity

Two atoms share a pair of electrons in a covalent bond (Section 1.2B), but that sharing can be equal or unequal. An equal sharing results in a **nonpolar covalent bond.** For example, the covalent bond in the hydrogen molecule is nonpolar because the two hydrogen atoms share the

bonding pair equally. In contrast, by sharing the bonding electron pair unequally, hydrogen and chlorine form a **polar covalent bond** in hydrogen chloride:

```
      δ+   ..δ-
      H-Cl:
           ..
```
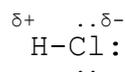
polar covalent bond in hydrogen chloride

Because the chlorine has a greater share of the negatively charged bonding electrons, it carries the partial negative charge, while the electron-deficient hydrogen has the partial positive charge. Having two poles of charge, this bond is polar.

Why does chlorine have a greater share of the bonding pair than hydrogen? It is a matter of **electronegativity,** the ability of an atom in a molecule to attract electrons. Table 1.7 displays the electronegativities of some elements important in organic chemistry. Within a row of the periodic table, electronegativity increases dramatically with atomic number. Within a column, however, increasing atomic number generally reduces electronegativity. Thus, the metals are less electronegative than the nonmetals and fluorine is the most electronegative atom. Because chlorine's electronegativity (3.1) exceeds hydrogen's (2.3), chlorine attracts more of their bonding pair.

Table 1.7 Electronegativities of Some Elements

H 2.3						

Li 1.0	Be 1.5		B 1.9	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.1
K 0.8							Br 2.9
							I 2.6

The degree of bond polarity depends on the difference in electronegativities between bonding atoms.

as Δ electronegativity ↑, bond polarity ↑

A very large electronegativity difference of at least 2 units can give the more electronegative atom almost complete control of the bonding pair. The sharing is so unequal that the bond is more ionic than covalent. This situation often arises when a metal of low electronegativity bonds to a non-metal of high electronegativity. An example is sodium amide, $NaNH_2$, whose sodium-nitrogen bond is ionic because the electronegativities (0.9 and 3.0, respectively) differ by 2.1.

$$Na^{+-}:\overset{..}{N}-H$$
$$|$$
$$H$$
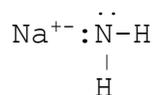
```
ionic bond in sodium amide
```

The nitrogen derives its full, formal negative charge from its ionic bond and the resulting six electrons allotted to it (four nonbonding and two σ bonding).

     If the bonding atoms differ little in electronegativity, their covalent bond is practically nonpolar. One very important example is a bond between carbon and hydrogen, whose small electronegativity difference (2.5 - 2.3) is usually neglected. *We generally consider carbon-hydrogen bonds nonpolar.*

     Bond polarity and partial charges strongly influence chemical reactivity of the bond and atoms involved, as discussed in later chapters.

Puzzle 1.20 ───

Locate full charges and partial charges in these molecules:
```
(a)   CCl₄     (b)   CH₃Cl    (c)   HOLi   (d)   HOF    (e)   CH₃NH₂
      H\   /H             H\   /F
(f)    C=C        (g)     C=C
      F/   \F            F/    \H
```

───
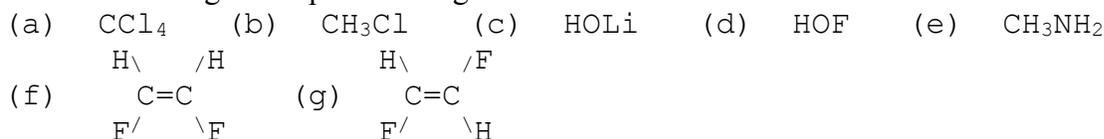
1.9B Molecular Polarity

     Not only individual bonds, but also molecules as a whole can be polar with two poles of opposite charge. A molecule is polar if its center (i.e., pole) of positive charge is separated from its center (i.e., pole) of negative charge. The charges can be full or partial. Let us inspect four molecules for molecular polarity:

```
                                                                    H
       δ+   ..δ-          δ+      δ-         δ-   δ+δ+   δ-           |
       H——F:            H——Ö:δ-        :Ö═══C═══Ö:         H——C——H
       ┼───▶             ↖╱▶                                         |
                          |                                         H
                         Hδ+

     hydrogen fluoride        water        carbon dioxide        methane
          polar               polar           nonpolar           nonpolar
```
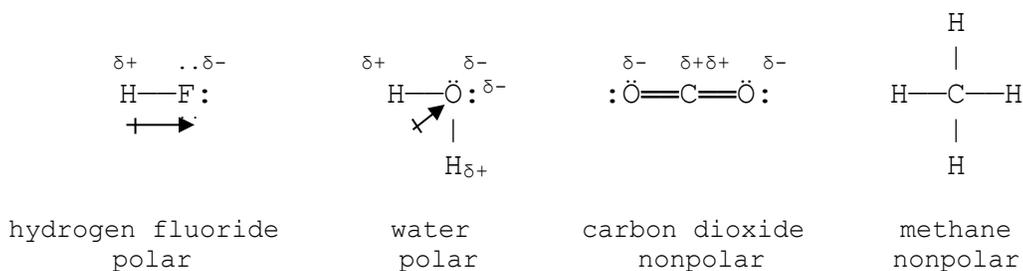
Hydrogen fluoride has one partial positive charge and one partial negative charge. Thus, its center

of positive charge at hydrogen does not coincide with its center of negative charge at fluorine, and so hydrogen fluoride is a polar molecule. We can indicate this molecular polarity with a crossed arrow (   ) pointing from the center of positive charge to the center of negative charge.

Water with two polar bonds is more complex. *When a molecule has more than one polar bond, the geometry of the polar bonds determines any molecular polarity.* The *sp³* hybridization of water's oxygen provides an H-O-H bond angle of about 109°. The center of negative charge is the oxygen, whereas the positive center lies half way between the hydrogens. In other words, the polarities of these two bonds do not cancel each other. The crossed arrow marks the polarity of the molecule by connecting the two centers of charge.

Another molecule with two polar bonds is carbon dioxide, but its geometry differs from water's. The *sp* hybridization of its carbon yields an O-C-O bond angle of 180°. Consequently, the negative center coincides with the positive center on the carbon. Carbon dioxide is nonpolar despite its polar bonds. In effect, the opposing polarities of these polar bonds cancel each other.

Methane, the fourth molecule, has no polar bonds (carbon and hydrogen have similar electronegativities), no charges (partial or formal), and so no poles of charge. Thus it is nonpolar.

Polar molecules differ in their degrees of polarity. Molecular polarity can be measured as the **dipole moment,** the arithmetic product of the amount of separated charge and the distance between charge centers. Polarity increases as the dipole moment increases. Hydrogen fluoride with a dipole moment of 1.98 D (debyes) is more polar than water with a dipole moment of 1.84 D. Molecular polarity greatly affects various physical properties, as discussed in Section 1.11.

Puzzle 1.21 ───

Locate the polarity in the polar molecules of Puzzle 1.20 (Section 1.9A).

Puzzle 1.22 ───

Octadecanoic acid, also known as stearic acid, is a common fatty acid, a component of fats. Like other fatty acids it is large:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}OH$$
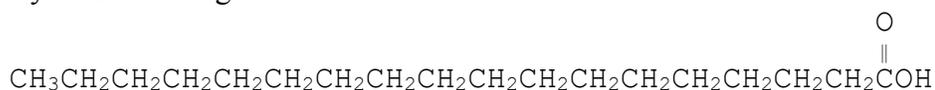
(a) Which are its polar bonds?
(b) Is it a very polar molecule? Explain.

1.10 Intermolecular Forces

Intramolecular forces, that is, forces *within* a molecule, include bonds and some weaker repulsions and attractions among atoms and electrons within one molecule. **Intermolecular forces** are generally attractive forces *between* molecules. Let us include forces involving ions as intermolecular forces, although some chemists do not classify even complex ions as molecules. Intermolecular forces vary greatly in type and strength and will now be examined.

1.10A Ionic bonds

As discussed in Section 1.2A, ionic bonds are very strong attractions between adjacent anions and cations. Consider sodium methoxide:

$$Na^{+-}:\ddot{O}CH_3$$
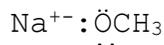
```
ionic bond in sodium methoxide
```

The bond between the metallic sodium (electronegativity 0.9) and the nonmetallic oxygen (electronegativity 3.5) is ionic. Because of the attraction between full, formal charges, ionic bonds are the strongest intermolecular forces (defined broadly).

Puzzle 1.23 ──

Locate any ionic bonds in these compounds:
(a) BeF_2 (b) CF_4 (c) KBr (d) H_2NLi

───

1.10B Dipole-Dipole Forces

With its two distinct centers, or poles, of charge, a polar molecule is a dipole (*di-* means two). Polar molecules minimize their potential energy by orienting positive centers close to negative centers on nearby molecules. An example is dimethyl ether in the solid or liquid state:

```
      δ+CH3        δ+CH3
       /            /
  δ-O◄+  ──δ-O◄+
   δ- \         δ- \
     δ+CH3       δ+CH3
```
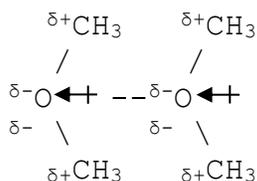
```
dipole-dipole force between two polar molecules
```

The broken line connecting the molecules indicates an association weaker than an intramolecular bond. The attraction between centers of opposite charge in nearby polar molecules is called a **dipole-dipole force.** Because it involves partial instead of formal charges, a dipole-dipole force is much weaker than an ionic bond.

Puzzle 1.24 ──

Indicate which of these compounds have dipole-dipole forces:
(a) CO_2 (b) SCl_2 (c) H_2O (d) $SiCl_4$ (e) CF_2Cl_2

───

1.10C Hydrogen Bonds

When a hydrogen atom is bonded to a much more electronegative atom, usually nitrogen, oxygen, or fluorine, the polar bond places a significant partial positive charge on the hydrogen. Because the hydrogen is so small, this partial positive charge is very dense and strongly attracts a partial or formal negative charge on a nearby molecule. This normally *intermolecular* attraction between a partial positive charge on a hydrogen and a partial or formal negative charge on another molecule is called a **hydrogen "bond"**. Ethanol illustrates a hydrogen "bond":

$$\overset{\delta-}{}\quad\overset{\delta+}{}$$
$$CH_3CH_2-O--H-O-CH_2CH_3$$
$$\underset{H}{|}$$

hydrogen "bond" ————⌐   ⌐———— not a hydrogen "bond"

A hydrogen "bond" involving an anion is also possible:

$$\overset{-}{}\quad\overset{\delta+}{}$$
$$Cl--H-O-CH_2CH_3$$

hydrogen "bond" ————⌐   ⌐——not a hydrogen "bond"

Despite its name, *a hydrogen "bond" is not a bond*, either ionic or covalent, but a much weaker force between molecules, about 20-40 kJ/mol. Nonetheless, hydrogen bonds tend to be stronger than dipole-dipole forces. (From now on, we will omit the quotation marks from hydrogen bonds.)

Although usually an intermolecular force, a hydrogen bond can occur within molecules of suitable structure:

intramolecular hydrogen bond

Such intramolecular hydrogen bonds are especially important in proteins (Section 21.5).

Puzzle 1.25 ——

Which compounds have hydrogen bonds among its molecules in the solid or liquid state?
(a) H_2O (b) NH_3 (c) HF (d) CH_4 (e) CH_3OCH_3 (f) $N(CH_3)_3$ (g) $HN(CH_3)_2$
(h) CH_3F

Puzzle 1.26 ——

Proteins are polymers of amino acids. A partial structure of a protein follows:

```
            Z   O      Z' O
            |   ‖      |   ‖
     ...NH-CH-C-NH-CH-C...
```
where Z and Z' are various groups of atoms.
(a) Show an intermolecular hydrogen bond for this protein.
(b) Show an intramolecular hydrogen bond for this protein.

1.10D Dispersion Forces

The three types of intermolecular forces so far considered all depend on permanent charges, formal or partial, on the molecules. A fourth type, **dispersion force,** occurs between nearby molecules with or without polarity. Dispersion (i.e., London, one type of van der Waals forces) forces attract molecules by momentary polarities. Moving electrons can momentarily distribute themselves unsymmetrically throughout even a nonpolar molecule to generate a temporary dipole. The momentary centers of positive and negative charge can induce momentary centers of opposite charge in a neighboring molecule, which in turn attract the charge centers in the first molecule.

```
        ⎛δ+⎞ -- ⎛δ-⎞
        ⎝δ-⎠ -- ⎝δ+⎠
                    ↑        ↑
momentary dipole ──┘        └── induced dipole
```
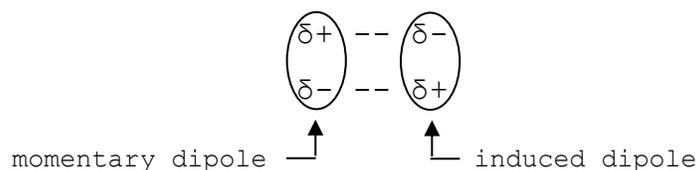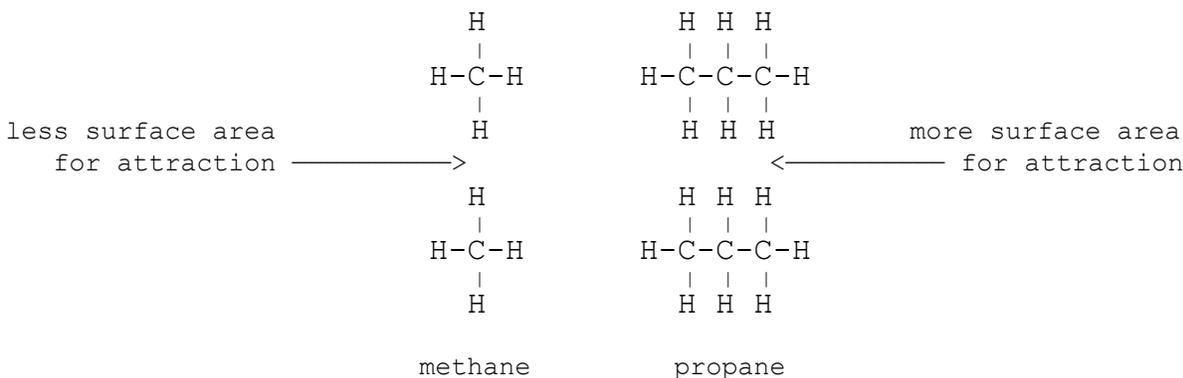
Polar, as well as nonpolar, molecules experience these momentary but frequent attractions, supplementing attractions due to permanent charges.

The size of a molecule affects the strength of its dispersion forces. Because more surface area with more electrons more readily allows an unbalanced electron distribution:

as surface area of molecule ↑, dispersion forces ↑

Therefore, propane, $CH_3CH_2CH_3$, has greater dispersion forces than methane:

```
                        H              H  H  H
                        |              |  |  |
                     H-C-H          H-C-C-C-H
                        |              |  |  |
less surface area       H              H  H  H        more surface area
   for attraction ───────────>            <─────────── for attraction
                        H              H  H  H
                        |              |  |  |
                     H-C-H          H-C-C-C-H
                        |              |  |  |
                        H              H  H  H

                     methane         propane
```

Puzzle 1.27 ───

(a) Hexadecanoic acid, also known as palmitic acid, has the structure $CH_3(CH_2)_{14}CO_2H$ and is

obtained from palm oil. Octadecanoic acid, or stearic acid, is $CH_3(CH_2)_{16}CO_2H$ and can be derived from tallow. Both are fatty acids, components of fats. Which has greater dispersion forces? Explain.

(b) Which has greater dispersion forces, $CH_3(CH_2)_3CH_3$ or $C(CH_3)_4$? Explain with structures.

1.11 Physical Properties

Physical properties are properties of bulk material, whereas **chemical properties** concern the reactivity of individual molecules. Let us explore the influence of molecular polarity and intermolecular forces on three physical properties: boiling point, melting point, and solubility.

1.11A Boiling Points

Boiling point is the temperature at which the vapor pressure of a liquid equals atmospheric pressure, normally 1 atmosphere. Molecules closely associated with each other in a liquid must break intermolecular forces to become widely separated in a gas. Therefore:

as intermolecular forces ↑, vaporization ↓ and bp ↑

It is important to remember that *boiling does not involve separating atoms within a molecule, but separating molecules from each other*. During boiling, only intermolecular forces are overcome, not covalent bonds. So the strength of covalent bonds does not affect boiling point.

Let us analyze the relative boiling points of four compounds examined in Sections 1.10 A-D:

	$Na^{+-}OCH_3$	CH_3OCH_3	CH_3CH_2OH	$CH_3CH_2CH_3$
	sodium methoxide	dimethyl ether	ethanol	propane
bp:	> 1000°C	-25°C	78°C	-42°C

Sodium methoxide, $NaOCH_3$, is ionic, so that very strong ionic bonds must be broken to vaporize the liquid. A very high boiling point greater than 1000°C results. Ionic compounds generally have very high boiling points.

Dimethyl ether, CH_3OCH_3, has no ionic bonds between its molecules, so its boiling point is –25°C, much lower than sodium methoxide's. Thus it is a gas at room temperature and atmospheric pressure. As a polar molecule, it has dipole-dipole forces along with the usual dispersion forces (Section 1.10B).

Another nonionic molecule is ethanol. Why is its boiling point, 78°C, much higher than dimethyl ether's? A large difference in some intermolecular force must explain this fact. Being similarly polar, the two compounds have similar dipole-dipole forces. Being of similar size and surface area, they have similar dispersion forces. The key difference is hydrogen bonding, which only ethanol has, and its higher boiling point results.

Of the four compounds propane, $CH_3CH_2CH_3$, has the lowest boiling point, -42°C. Because it is nonpolar, it has no dipole-dipole forces. Also, without a hydrogen bonded to a very electronegative atom, it has no hydrogen bonds. Like all molecules it has dispersion forces, but these forces are similar for all four compounds with similar surface areas. Thus, propane has the least total intermolecular forces and the lowest boiling point.

These four compounds illustrate a general trend for boiling points. Here is the order of boiling points for molecular types *of similar surface area*:

ionic > polar & H bonds > polar, no H bonds > nonpolar

ranking of bp by molecular type

The above stipulation of similar surface area is important. Despite their amorphous, temporary nature, dispersion forces can be great for large molecules. So large nonpolar compounds can have relatively high boiling points. For example, heptane, $CH_3(CH_2)_5CH_3$, which is a large nonpolar hydrocarbon, boils at 98°C. This surpasses the 78°C boiling point for ethanol, which is polar with hydrogen bonds. Evidently, the combined multitude of dispersion forces for the much larger heptane are great enough to more than compensate for its lack of hydrogen bonds and dipole-dipole forces.

Puzzle 1.28 ──

In each pair determine the compound with the higher boiling point. Explain.
(a) H_2O or $LiCl$ (b) $H_2NCH_2CH_2CH_3$ or $N(CH_3)_3$
(c) $CH_3CH_2CH_3$ or CH_3CH_2F (d) CH_3OH or CH_3CH_2OH

```
        H\   /H          H\    /Cl
(e)       C=C      or      C=C
       Cl/   \Cl        Cl/    \H
```

Puzzle 1.29 ──

Frying involves cooking in oil, composed mostly of hydrocarbons with high molecular weight.
(a) Which takes more time, cooking a potato in boiling water or cooking it in hot oil?
(b) Which has a higher boiling point, water or cooking oil?
(c) Explain the difference in boiling point.
(d) Identify the chemical that bubbles up during the frying of a potato.
──
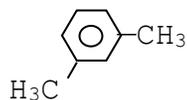
1.11B Melting Points

During melting of a molecular or ionic solid, the molecules or ions lose the order of their crystal lattice and become free to move through the liquid. Atoms within the molecules are not loosened, but molecules from one another are. Thus, like boiling points melting points are affected by intermolecular forces. Melting points increase as intermolecular forces increase.

The five compounds whose boiling points were compared in Section 1.11A have these melting points:

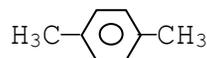|	$Na^{+-}OCH_3$	CH_3OCH_3	CH_3CH_2OH	$CH_3CH_2CH_3$	$CH_3(CH_2)_5CH_3$
	sodium methoxide	dimethyl ether	ethanol	propane	heptane
mp:	> 300°C	-138°C	-117°C	-190°C	-91°C
bp:	> 1000°C	-25°C	78°C	-42°C	98°C

Note that each compound has a lower melting point than boiling point because loosening molecules from each other is generally easier than completely separating the molecules. Furthermore, because intermolecular forces affect both physical properties similarly, their orders of melting point and boiling point match.

An additional factor, symmetry, affects melting point more than boiling point. A molecule that is more symmetric fits into a crystal lattice more readily than a less symmetric molecule does. Because more energy would be needed to dislodge the more symmetric molecule from its crystal lattice, symmetry can increase the melting point without directly affecting the boiling point. Consider these two molecules:

	1,3-dimethylbenzene	1,4-dimethylbenzene
mp:	-48°C	13°C
bp:	139°C	138°C

The more symmetric molecule on the right has a much higher melting point but a slightly lower boiling point!

mp ↑ as intermolecular forces ↑ and as symmetry ↑

Puzzle 1.30 ───

For each pair in Puzzle 1.28 (Section 1.11A), determine the compound with the higher melting point. Explain.

Puzzle 1.31 ───

Which has the higher melting point, hexadecanoic acid or octadecanoic acid (see Puzzle 1.27a, Section 1.10D)? Explain.

───

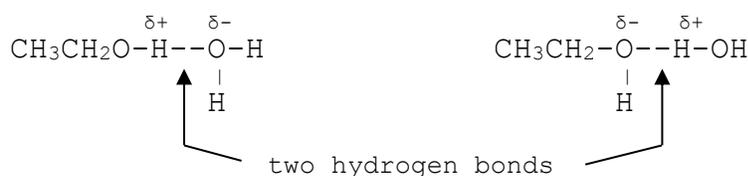## 1.11C Solubilities

The last, important physical property to be discussed in Chapter 1 is solubility.   The familiar adage, "like dissolves like," serves us well here. Polar solvents dissolve polar solutes and nonpolar solvents dissolve nonpolar solutes, whereas a solvent does not dissolve a solute of very different polarity. Consider tetrachloromethane (i.e., carbon tetrachloride, CCl_4):

$$Cl_{\delta-}$$

$$\delta+ \quad \delta+$$
$$\delta- \quad Cl^{\delta+} C^{\delta+}$$
$$Cl^{} \quad \delta+$$
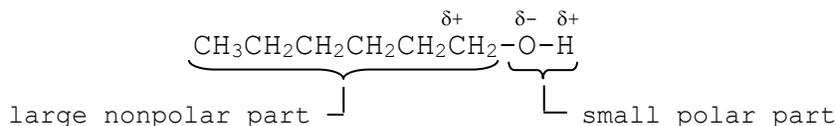$$\delta- \quad Cl \qquad Cl^{\delta-}$$
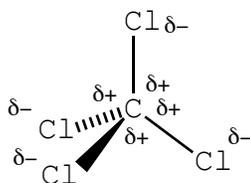
tetrachloromethane

Its polar bonds symmetrically disposed around the tetrahedral carbon make this a nonpolar solvent. Until it was found to be carcinogenic, it was used as a dry cleaner because it dissolves oils and grease, which are mostly nonpolar hydrocarbons. On the other hand, oil does not dissolve water because water is very polar.
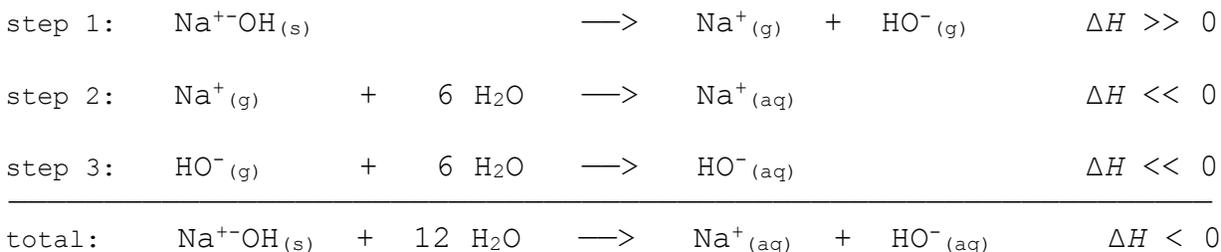
Two liquids that dissolve in each other in all proportions are **miscible.** The small alcohol ethanol and water are miscible because they are both very polar. The strongest attraction between the two molecules is a hydrogen bond in one of two forms:

$$CH_3CH_2O-\overset{\delta+}{H}--\overset{\delta-}{O}-H \qquad\qquad CH_3CH_2-\overset{\delta-}{O}--\overset{\delta+}{H}-OH$$
$$\quad\quad\quad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$\quad\quad\quad\quad H \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H$$

two hydrogen bonds

Either ethanol or water can donate the hydrogen for this bond. As the size of an alcohol increases, its two polar bonds become a smaller portion of the molecule, and the overall polarity of the molecule decreases. Consequently, the solubility in water decreases. For example, only 0.6 g of 1-hexanol, $CH_3(CH_2)_5OH$, dissolve in 100 mL of water because this large alcohol is only slightly polar.

$$CH_3CH_2CH_2CH_2CH_2CH_2\overset{\delta+}{}-\overset{\delta-}{O}-\overset{\delta+}{H}$$

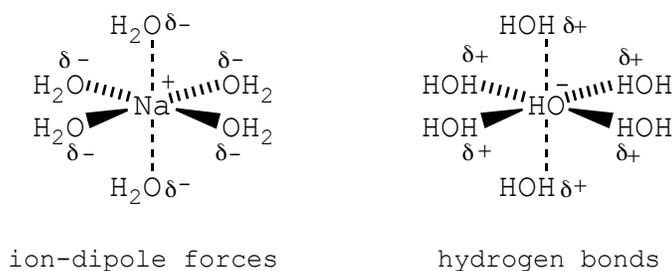large nonpolar part ⌐   ⌐ small polar part

Very polar with formal charges, many ionic compounds dissolve in water and other very polar solvents. For example, if pellets of sodium hydroxide are shaken with water, not only do the pellets dissolve, but also heat evolves, a sign of a favorable exothermic reaction. We can explain the dissolving process by artificially dividing it into three steps:

step 1:	$Na^{+-}OH_{(s)}$			$\longrightarrow$	$Na^+_{(g)}$	$+$	$HO^-_{(g)}$	$\Delta H \gg 0$
step 2:	$Na^+_{(g)}$	$+$	$6\ H_2O$	$\longrightarrow$	$Na^+_{(aq)}$			$\Delta H \ll 0$
step 3:	$HO^-_{(g)}$	$+$	$6\ H_2O$	$\longrightarrow$	$HO^-_{(aq)}$			$\Delta H \ll 0$
total:	$Na^{+-}OH_{(s)}$	$+$	$12\ H_2O$	$\longrightarrow$	$Na^+_{(aq)}$	$+$	$HO^-_{(aq)}$	$\Delta H < 0$

The first step is very endothermic because it breaks a strong ionic bond to separate the ions into an imaginary gas state. The last two steps must be very exothermic to compensate for this endothermic step and achieve an overall exothermic reaction. These last two steps **solvate** each

separate ion with water solvent. **Solvation** is the association of solvent and solute molecules, whereas solvation by water solvent is called **hydration.** Here an inner core of six water molecules surrounds each hydrated ion on all six sides:

$$
\begin{array}{cc}
\text{H}_2\text{O}\,\delta- & \text{HOH}\,\delta+ \\
\delta-\quad\quad\delta- & \delta+\quad\quad\delta+ \\
\text{H}_2\text{O}\cdots\text{Na}^+\cdots\text{OH}_2 & \text{HOH}\cdots\text{HO}^-\cdots\text{HOH} \\
\text{H}_2\text{O}\quad\quad\text{OH}_2 & \text{HOH}\quad\quad\text{HOH} \\
\delta-\quad\quad\delta- & \delta+\quad\quad\delta+ \\
\text{H}_2\text{O}\,\delta- & \text{HOH}\,\delta+ \\
\text{ion-dipole forces} & \text{hydrogen bonds}
\end{array}
$$

Actually an outer-core of water molecules also hydrates the ions but more weakly because of its remoteness. The sodium cation attracts the partial negative charge on the water's oxygen with an ion-dipole force, while the anionic hydroxide associates with the partial positive charge on the solvent's hydrogen in a hydrogen bond. Although each individual association is much weaker than the ionic bond to be broken, the large number of these favorable, exothermic solvations more than compensates for the endothermic bond breaking. *The breaking of any valid bond or association is endothermic, whereas the making of any valid bond or association is exothermic.* The importance of solvation is next discussed in Section 6.6.

In addition to the enthalpies of intermolecular forces, another essential factor in successful or unsuccessful dissolving is **entropy (S),** the measure of disorder in a system. Increasing entropy (i.e., $\Delta S > 0$) favors a process, just as decreasing enthalpy (i.e., $\Delta H < 0$) does. Even if enthalpy unfavorably increases, dissolving succeeds if entropy increases enough to compensate. Yet, when discussing solubilities, we will not directly consider entropy, but focus on polarities and the "like dissolves like" adage (which vaguely incorporates the entropy factor) because they are easier to apply and generally suffice in organic systems.

We have observed an important fact about boiling points, melting points, and solubilities: *these physical properties do not depend on the stability of individual molecules and their bond strengths, but on intermolecular forces*.

Puzzle 1.32 ——————————————————————————————————————

In each pair determine the compound more soluble in water. Explain.
(a) CH_3Br or $NaBr$ (b) CH_3Br or CH_3F (c) CH_3OH or CH_3SH
(d) $CH_3CH_2CH_2NH_2$ or $H_2NCH_2CH_2CH_2NH_2$ (e) CH_3Cl or CH_3CH_2Cl

Puzzle 1.33 ——————————————————————————————————————

Gasoline comprises mostly hydrocarbons. Does gasoline dissolve well in water? Explain.

Chapter Summary

1. Organic molecules contain carbon.
2. Ionic bonds attach anions to cations.
3. In a covalent bond two atoms share an electron pair. A covalent bond resulting from head-on overlap of orbitals is a σ bond. A π bond is a covalent bond resulting from sideways overlap of parallel p orbitals.
4. A double bond comprises two electron pairs shared in a σ bond and a π bond. Three electron pairs are shared in a triple bond, comprising a σ bond and two π bonds.
5. Organic molecules can be represented by a variety of types of structures, from very explicit Lewis structures to faster drawn line structures.
6. A functional group is a reactive site in an organic molecule.
7. Formal charge, based on an artificial ownership of electrons, indicates an excess or deficiency of electrons on an atom. It strongly affects physical and chemical properties of molecules.
8. The octet rule states than an atom seeks to fill its outer electron shell with nonbonding and covalently bonding electrons. The outer shell of a second-row atom accommodates a maximum of eight electrons.
9. Resonance blends fictitious resonance forms into a hybrid that reflects reality. While averaging the electronic properties of resonance forms, resonance lowers the energy of the molecule below that of any single resonance form.
10. Second- and third-row atoms hybridize their outer-shell orbitals to minimize repulsion among surrounding electron pairs. Four repelling electron pairs require sp^3 hybridization and tetrahedral geometry. Three repelling electron pairs require sp^2 hybridization and trigonal planar geometry. Two repelling electron pairs require sp hybridization and linear geometry.
11. Bond lengths depend on the number and length of overlapping orbitals. As the number of overlapping orbitals increases, the bond length decreases. For a given element the lengths of the front lobes of hybridized orbitals are ranked according to the percentage of p character:
$$sp^3 > sp^2 > sp$$
12. Benzene is a stable resonance hybrid of a six-carbon cyclic hydrocarbon.
13. Bond energy is the energy needed to break a bond. Energy is required to break any bond or intermolecular association. Stronger bonds are harder to react and easier to form.
14. The internal potential energy of a molecule is its enthalpy. Decreasing enthalpy promotes a spontaneous reaction.
15. A difference in electronegativity between bonding atoms results in a polar bond with partial charges on the atoms. These partial charges affect chemical reactivity.
16. A polar molecule has separate centers of positive and negative charge. Molecular polarity affects physical properties.
17. Intermolecular forces are generally attractive forces between molecules (and ions). They include ionic bonds, dipole-dipole forces, hydrogen bonds, and dispersion forces. A hydrogen bond is an attraction (not a bond) between a hydrogen with a partial positive charge and a partial or formal negative charge on an atom not bonded to it. Dipole-dipole forces attract permanent centers of positive and negative charges on neighboring polar molecules. Dispersion forces attract momentary centers of positive and negative charges on neighboring molecules.
18. Physical properties depend on intermolecular forces, not on the stability of individual molecules.
19. Boiling points and melting points increase with increasing intermolecular forces. Melting points increase with increasing symmetry. Solvents dissolve solutes of similar polarity and do not
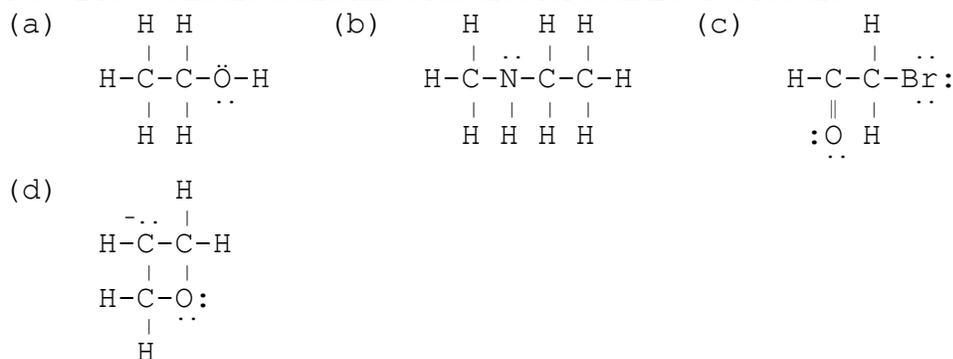
dissolve solutes of very different polarity.

Additional Puzzles

1.34 Indicate whether the bonds in these compounds are ionic or covalent. Also note any multiple bonds.
(a) CS_2 (b) KCl (c) LiOH (d) CF_4 (e) NaCN

1.35 Draw condensed and line structures for each Lewis structure:

```
(a)      H  H              (b)       H     H  H          (c)            H
         |  |                        |  .. |  |                         |    ..
       H-C-C-Ö-H                  H-C-N-C-C-H                       H-C-C-Br:
         |  |  ..                    |  |  |  |                         ‖  |   ..
         H  H                        H  H  H  H                       :O  H
                                                                       ..
(d)         H
         -.. |
       H-C-C-H
         |  |
       H-C-O:
         |   ..
         H
```

1.36 Draw condensed and Lewis structures for each molecule:

```
(a)    ∧∧∧∧+     (b)   ＼–N̄–    (c)  +OH     (d)   Cl+
                                         △            △
```

(e) C_6H_5-Cl
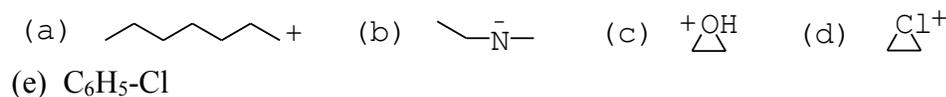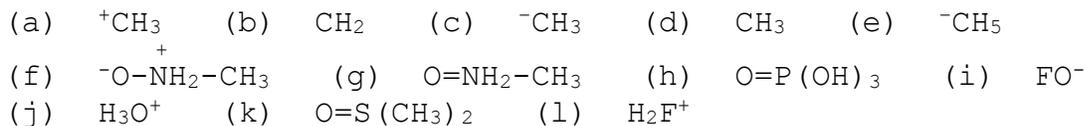
1.37 Draw a typical molecule with each of these functional groups and molecular formulas:
(a) ether, $C_4H_{10}O$ (b) alcohol, $C_4H_{10}O$ (c) aldehyde, C_3H_6O (d) ketone, C_3H_6O
(e) amine, C_2H_7N (f) carboxylic acid, $C_3H_6O_2$ (g) ester, $C_3H_6O_2$ (h) alkyne, C_4H_6
(i) cyclic alkene, C_4H_6 (j) benzene, C_6H_6 (k) doubly cyclic, double alkene (i.e., diene), C_6H_6
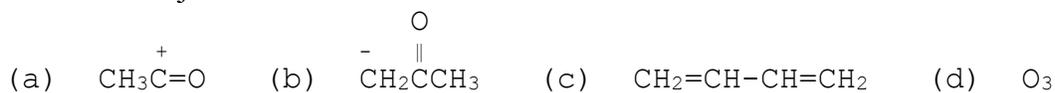
1.38 Draw a Lewis structure with appropriate nonbonding electrons for each chemical:
(a) $^+CH_3$ (b) $^+NH_4$ (c) $^+OH_3$ (d) CH_3 (e) NH_3 (f) OH_2 (g) HF (h) $^-CH_3$ (i) $^-NH_2$
(j) HO^- (k) Cl^- (l) CH_2 (m) NH_2 (n) HO (o) Br

1.39 Indicate which atoms violate the octet rule:
```
(a)    +CH3      (b)    CH2     (c)    -CH3      (d)    CH3      (e)     -CH5
                +
(f)    -O-NH2-CH3      (g)    O=NH2-CH3      (h)    O=P(OH)3      (i)    FO-
(j)    H3O+      (k)    O=S(CH3)2      (l)    H2F+
```

1.40 With the help of electron arrows, draw all reasonable resonance forms for each molecule and decide the major and minor forms:
```
                          O
         +          -    ‖
(a)    CH3C=O     (b)    CH2CCH3      (c)    CH2=CH-CH=CH2      (d)    O3
```

(e) $\overset{-}{C}H_2CH=CH\overset{+}{N}H_3$

1.41   Indicate the hybridization and bond angles of second- and third-row atoms in these molecules:
(a) CF_4 (b) $^+NH_4$ (c) BCl_3 (d) benzene (e) BeH_2 (f) CS_2 (g) $^-NH_2$ (h) H_2SO_3

1.42 Draw each molecule with correct geometry at each second-row atom:

(a)   HOCl   (b) CH_3 (c) H_2F^+ (d) $O=\overset{+}{N}=O$
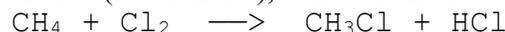
1.43 Indicate the hybridization and bond angles of second-row atoms in the molecules of Puzzle 1.40.

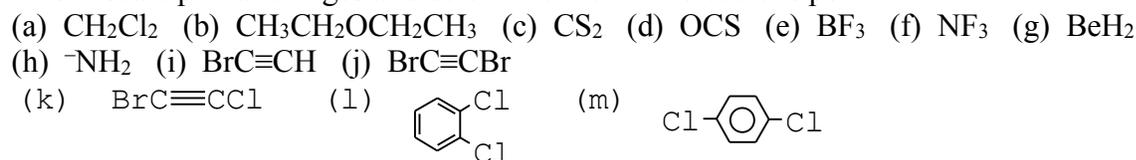1.44 Rank the carbon-carbon bond lengths in each molecule:
(a) ⬠   (b) $CH_3CH=CH-C\equiv CH$ (c) $C_6H_5-CH_2-CH=CH_2$
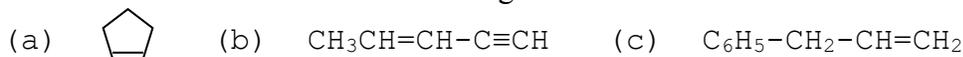
1.45 With the help of Table 1.6 (Section 1.8), consider the reaction:
$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$
(a) Of the bonds broken, which is the hardest to break?
(b) Of the bonds made, which is the strongest?
(c) Calculate ΔH for this reaction. Does this ΔH favor the forward reaction?

1.46 Locate partial charges and determine if each molecule is polar:
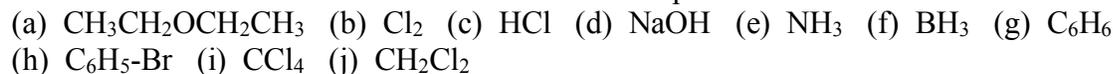(a) CH_2Cl_2 (b) $CH_3CH_2OCH_2CH_3$ (c) CS_2 (d) OCS (e) BF_3 (f) NF_3 (g) BeH_2
(h) $^-NH_2$ (i) $BrC\equiv CH$ (j) $BrC\equiv CBr$
(k) $BrC\equiv CCl$ (l) [benzene ring with two Cl substituents, ortho]   (m) $Cl-⟨O⟩-Cl$

1.47 For each compound that can hydrogen bond among its molecules, draw such a hydrogen bond:
(a) CH_2F_2 (b) HF (c) HCl (d) CH_3OH (e) CH_3SH (f) H_2NCH_3 (g) $(CH_3)_2C=O$

1.48 For each compound that can hydrogen bond with water, draw such a hydrogen bond:
(a) CH_3F (b) HF (c) CH_3OH (d) H_2NCH_3 (e) $(CH_3)_2C=O$ (f) $^-C\equiv N$ (g) $^+NH_4$

1.49 List all the intermolecular forces for each compound:
(a) $CH_3CH_2OCH_2CH_3$ (b) Cl_2 (c) HCl (d) NaOH (e) NH_3 (f) BH_3 (g) C_6H_6
(h) C_6H_5-Br (i) CCl_4 (j) CH_2Cl_2

1.50 In each pair determine the compound with the higher boiling point. Explain each choice.
(a) CH_3NH_2 or $CH_3CH_2NH_2$ (b) $CH_3CH_2CH_2OH$ or $CH_3OCH_2CH_3$
(c) CH_3Cl or CH_3CH_3 (d) $NaNH_2$ or CH_3NH_2 (e) $CH_3(CH_2)_3CH_3$ or $(CH_3)_4C$
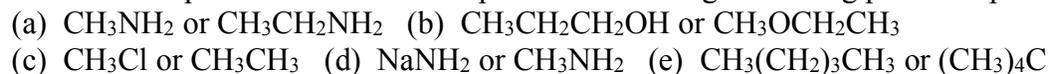
1.51 In each pair of Puzzle 1.50, determine the compound with the higher melting point. Explain each choice.

1.52 Like most inorganic salts ammonium chloride, H_4NCl, is insoluble in chloroform, $CHCl_3$. Yet, tetraethylammonium chloride, $(CH_3CH_2)_4NCl$, is fairly soluble in chloroform.
(a) How do you account for the contrasting solubilities?
(b) What kind of ammonium chloride salt would be even more soluble in chloroform than $(CH_3CH_2)_4NCl$?

1.53 Which is longer, the oxygen-hydrogen bond within a water molecule or the oxygen-hydrogen hydrogen bond between water molecules? Explain.

1.54 (a) According to Table 1.6 (Section 1.8), the carbon-carbon double bond of $H_2C=CH_2$ is stronger than the carbon-carbon single bond of H_3C-CH_3, but is it twice as strong?
(b) Which is apparently stronger, a carbon-carbon σ bond or a carbon-carbon π bond? Explain.

1.55 Why does carbon monoxide have a surprisingly low boiling point of -192°C, only slightly higher than that of nonpolar molecular nitrogen, -196°C? Hint: consider resonance forms.

1.56 In which solvent, ethanol (CH_3CH_2OH) or propanone ($(CH_3)_2C=O$), is an anion more reactive? Explain.

1.57 Three molecules containing only nitrogen atoms have been isolated: N_2, $^-N_3$ anion, and the recently discovered $^+N_5$ cation. These molecules are neither branched nor cyclic. For each of them draw the most stable resonance form(s) and show the approximate bond angles.
(a) N_2 (b) $^-N_3$ (c) $^+N_5$

1.58 In the 1990s it was discovered that children's latent (invisible) fingerprints generally disappear faster than those of adults. The oil in an adult's fingerprint has much higher concentrations of chemicals similar to $CH_3(CH_2)_{14}CO_2(CH_2)_{15}CH_3$. In contrast, a child's fingerprint has more compounds like $CH_3(CH_2)_{11}CO_2H$.
(a) Name the functional groups in the two chemicals specified above.
(b) List all the intermolecular forces for each of the two chemicals.
(c) Explain why children's fingerprints evaporate faster than those of adults.

1.59 According to Table 1.7, Cl is slightly more electronegative than N. Yet the Cl in H_3CCl forms at most a very weak hydrogen bond with water, whereas the N in $(H_3C)_3N$ forms a strong hydrogen bond with water. Explain why. Hint: consider the amounts of partial charge on Cl and N.

1.60 Base pairing stabilizes the double helix of DNA. Consider the adenine-thymine base pairing with its two hydrogen bonds:
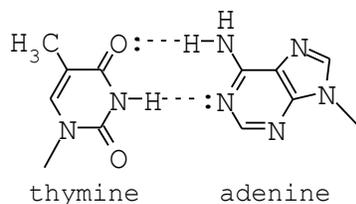
A hydrogen bond is strongest when the hydrogen is in line with its two electronegative atoms.
(a) Does the hybridization of thymine's hydrogen bonded oxygen above put one of its lone pairs

in position to allow a strong, linear hydrogen bond? Explain.
(b) Does the hybridization of adenine's hydrogen bonded ring nitrogen put its lone pair in position to allow a strong, linear hydrogen bond? Explain.

1.61 Geckos are lizards with a remarkable ability to defy gravity by sticking to vertical surfaces. Recently they were found to adhere equally well to polar and nonpolar surfaces. What kind of intermolecular force is mostly responsible for the gecko's adhesion? Explain.

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