Chapter 1 – Structure and Bonding

Chapter Outline

I. Atomic Structure (Sections 1.1–1.3).
  A. Introduction to atomic structure (Section 1.1).
    1. An atom consists of a dense, positively charged nucleus surrounded by negatively charged electrons.
      a. The nucleus is made up of positively charged protons and uncharged neutrons.
      b. The nucleus contains most of the mass of the atom.
      c. Electrons move about the nucleus at a distance of about 2×10^{-10} m (200 pm).
    2. The atomic number (*Z*) gives the number of protons in the nucleus.
    3. The mass number (*A*) gives the total number of protons and neutrons.
    4. All atoms of a given element have the same value of *Z*.
      a. Atoms of a given element can have different values of *A*.
      b. Atoms of the same element with different values of *A* are called isotopes.
  B. Orbitals (Section 1.2).
    1. The distribution of electrons in an atom can be described by a wave equation.
      a. The solution to a wave equation is an orbital, represented by Ψ.
      b. Ψ^2 predicts the volume of space in which an electron is likely to be found.
    2. There are four different kinds of orbitals (*s*, *p*, *d*, *f*).
      a. The *s* orbitals are spherical.
      b. The *p* orbitals are dumbbell-shaped.
      c. Four of the five *d* orbitals are cloverleaf-shaped.
    3. An atom's electrons are organized into electron shells.
      a. The shells differ in the numbers and kinds of orbitals they contain.
      b. Electrons in different orbitals have different energies.
      c. Each orbital can hold up to a maximum of two electrons.
    4. The two lowest-energy electrons are in the 1*s* orbital.
      a. The 2*s* orbital is the next higher in energy.
      b. The next three orbitals are $2p_x$, $2p_y$ and $2p_z$, which have the same energy.
        i. Each *p* orbital has a region of zero density, called a node.
      c. The lobes of a *p* orbital have opposite algebraic signs.
  C. Electron Configuration (Section 1.3).
    1. The ground-state electron configuration of an atom is a listing of the orbitals occupied by the electrons of the atom in the lowest energy configuration.
    2. Rules for predicting the ground-state electron configuration of an atom:
      a. Orbitals with the lowest energy levels are filled first.
        i. The order of filling is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*.
      b. Only two electrons can occupy each orbital, and they must be of opposite spin.
      c. If two or more orbitals have the same energy, one electron occupies each until all are half-full (Hund's rule). Only then does a second electron occupy one of the orbitals.
        i. All of the electrons in half-filled shells have the same spin.

II. Chemical Bonding Theory (Sections 1.4–1.5).
  A. Development of chemical bonding theory (Section 1.4).
    1. Kekulé and Couper proposed that carbon has four "affinity units"; carbon is tetravalent.
    2. Kekulé suggested that carbon can form rings and chains.

3. Van't Hoff and Le Bel proposed that the 4 atoms to which carbon forms bonds sit at the corners of a regular tetrahedron.
4. In a drawing of a tetrahedral carbon, a wedged line represents a bond pointing toward the viewer, a dashed line points behind the plane of the page, and a solid line lies in the plane of the page..

B. Covalent bonds.
1. Atoms bond together because the resulting compound is more stable than the individual atoms.
   a. Atoms tend to achieve the electron configuration of the nearest noble gas.
   b. Atoms in groups 1A, 2A and 7A either lose electrons or gain electrons to form ionic compounds.
   c. Atoms in the middle of the periodic table share electrons by forming covalent bonds.
   d. The neutral collection of atoms held together by covalent bonds is a molecule.
2. Covalent bonds can be represented two ways.
   a. In electron-dot structures, bonds are represented as pairs of dots.
   b. In line-bond structures, bonds are represented as lines drawn between two bonded atoms.
3. The number of covalent bonds formed by an atom depends on the number of electrons it has and on the number it needs to achieve an octet.
4. Valence electrons not used for bonding are called lone-pair (nonbonding) electrons.
   a. Lone-pair electrons are often represented as dots.

C. Valence bond theory (Section 1.5).
1. Covalent bonds are formed by the overlap of two atomic orbitals, each of which contains one electron. The two electrons have opposite spins.
2. Bonds formed by the head-on overlap of two atomic orbitals are cylindrically symmetrical and are called σ bonds.
3. Bond strength is the measure of the amount of energy needed to break a bond.
4. Bond length is the optimum distance between nuclei.
5. Every bond has a characteristic bond length and bond strength.

III. Hybridization (Sections 1.6–1.10).

A. sp^3 Orbitals (Sections 1.6, 1.7).
1. Structure of methane (Section 1.6).
   a. When carbon forms 4 bonds with hydrogen, one 2*s* orbital and three 2*p* orbitals combine to form four equivalent atomic orbitals (sp^3 hybrid orbitals).
   b. These orbitals are tetrahedrally oriented.
   c. Because these orbitals are unsymmetrical, they can form stronger bonds than unhybridized orbitals can.
   d. These bonds have a specific geometry and a bond angle of 109.5°.
2. Structure of ethane (Section 1.7).
   a. Ethane has the same type of hybridization as occurs in methane.
   b. The C–C bond is formed by overlap of two sp^3 orbitals.
   c. Bond lengths, strengths and angles are very close to those of methane.

B. sp^2 Orbitals (Section 1.8).
1. If one carbon 2*s* orbital combines with two carbon 2*p* orbitals, three hybrid sp^2 orbitals are formed, and one *p* orbital remains unchanged.
2. The three sp^2 orbitals lie in a plane at angles of 120°, and the unhybridized *p* orbital is perpendicular to them.
3. Two different types of bonds form between two carbons.
   a. A σ bond forms from the overlap of two sp^2 orbitals.
   b. A π bond forms by sideways overlap of two *p* orbitals.
   c. This combination is known as a carbon–carbon double bond.

4. Ethylene is composed of a carbon–carbon double bond and four σ bonds formed between the remaining four sp^2 orbitals of carbon and the 1*s* orbitals of hydrogen.
   a. The double bond of ethylene is both shorter and stronger than the C–C bond of ethane.

C. *sp* Orbitals (Section 1.10).
1. If one carbon 2*s* orbital combines with one carbon 2*p* orbital, two hybrid *sp* orbitals are formed, and two *p* orbitals are unchanged.
2. The two *sp* orbitals are 180° apart, and the two *p* orbitals are perpendicular to them and to each other.
3. Two different types of bonds form.
   a. A σ bond forms from the overlap of two *sp* orbitals.
   b. Two π bonds form by sideways overlap of four unhybridized *p* orbitals.
   c. This combination is known as a carbon–carbon triple bond.
4. Acetylene is composed of a carbon–carbon triple bond and two σ bonds formed between the remaining two *sp* orbitals of carbon and the 1*s* orbitals of hydrogen.
   a. The triple bond of acetylene is the strongest carbon–carbon bond.

D. Hybridization of nitrogen and oxygen (Section 1.10).
1. Covalent bonds between other elements can be described by using hybrid orbitals.
2. Both the nitrogen atom in ammonia and the oxygen atom in water form sp^3 hybrid orbitals.
   a. The lone-pair electrons in these compounds occupy sp^3 orbitals.
3. The bond angles between hydrogen and the central atom is often less than 109° because the lone-pair electrons take up more room than the σ bond.
4. Because of their positions in the third row, phosphorus and sulfur can form more than the typical number of covalent bonds.

IV. Molecular orbital theory (Section 1.11).

A. Molecular orbitals arise from a mathematical combination of atomic orbitals and belong to the entire molecule.
1. Two 1*s* orbitals can combine in two different ways.
   a. The additive combination is a bonding MO and is lower in energy than the two hydrogen 1*s* atomic orbitals.
   b. The subtractive combination is an antibonding MO and is higher in energy than the two hydrogen 1*s* atomic orbitals.
2. Two *p* orbitals in ethylene can combine to form two π MOs.
   a. The bonding MO has no node; the antibonding MO has one node.
3. A node is a region between nuclei where electrons aren't found.
   a. If a node occurs between two nuclei, the nuclei repel each other.

V. Chemical structures (Section 1.12).

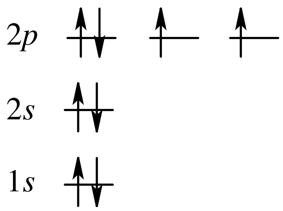
A. Drawing chemical structures.
1. Condensed structures don't show C–H bonds and don't show the bonds between CH_3, CH_2 and CH units.
2. Skeletal structures are simpler still.
   a. Carbon atoms aren't usually shown.
   b. Hydrogen atoms bonded to carbon aren't usually shown.
   c. Other atoms (O, N, Cl, etc.) are shown.

Solutions to Problems

1.1 (a) To find the ground-state electron configuration of an element, first locate its atomic number. For oxygen, the atomic number is 8; oxygen thus has 8 protons and 8 electrons. Next, assign the electrons to the proper energy levels, starting with the lowest level. Fill each level *completely* before assigning electrons to a higher energy level.

Notice that the $2p$ electrons are in different orbitals. According to *Hund's rule*, we must place one electron into each orbital of the same energy level until all orbitals are half-filled.

Oxygen

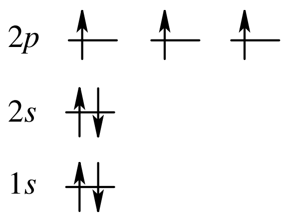


Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

A different way to represent the ground-state electron configuration is to simply write down the occupied orbitals and to indicate the number of electrons in each orbital. For example, the electron configuration for oxygen is $1s^2\ 2s^2\ 2p^4$.

(b) Nitrogen, with an atomic number of 7, has 7 electrons. Assigning these to energy levels:

Nitrogen

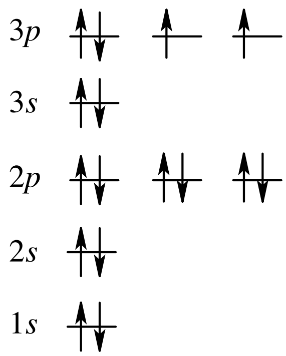


The more concise way to represent ground-state electron configuration for nitrogen: $1s^2\ 2s^2\ 2p^3$

(c) Sulfur has 16 electrons.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

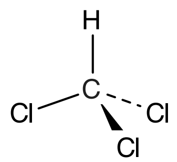
Sulfur



1.2 The elements of the periodic table are organized into groups that are based on the number of outer-shell electrons each element has. For example, an element in group 1A has one outer-shell electron, and an element in group 5A has five outer-shell electrons. To find the number of outer-shell electrons for a given element, use the periodic table to locate its group.

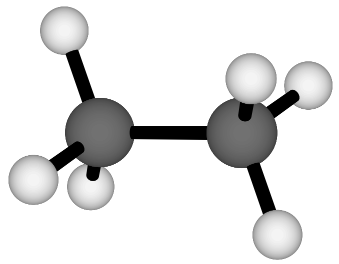
(a) Magnesium (group 2A) has two electrons in its outermost shell.
(b) Cobalt is a transition metal, which has two electrons in the 4*s* subshell, plus seven electrons in its 3*d* subshell.
(c) Selenium (group 6A) has six electrons in its outermost shell.

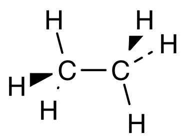
1.3 A solid line represents a bond lying in the plane of the page, a wedged bond represents a bond pointing out of the plane of the page toward the viewer, and a dashed bond represents a bond pointing behind the plane of the page.



Chloroform

1.4





Ethane

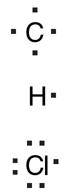
1.5 Identify the group of the central element to predict the number of covalent bonds the element can form.

(a) Carbon (Group 4A) has four electrons in its valence shell and forms four bonds to achieve the noble-gas configuration of neon. A likely formula is CCl_4.

	Element	*Group*	*Likely Formula*
(b)	Al	3A	AlH_3
(c)	C	4A	CH_2Cl_2
(d)	Si	4A	SiF_4
(e)	N	5A	CH_3NH_2

1.6 Start by drawing the electron-dot structure of the molecule.

(1) Determine the number of valence, or outer-shell electrons for each atom in the molecule. For chloroform, we know that carbon has four valence electrons, hydrogen has one valence electron, and each chlorine has seven valence electrons.



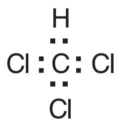
$4 \times 1 = 4$

$1 \times 1 = 1$

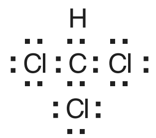
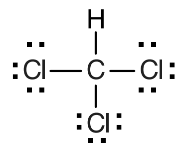
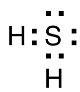
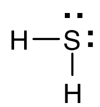
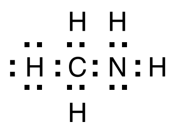
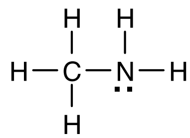
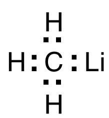
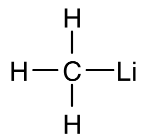
$7 \times 3 = \underline{21}$

26 total valence electrons

(2) Next, use two electrons for each single bond.

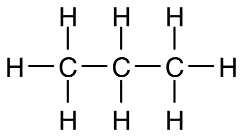


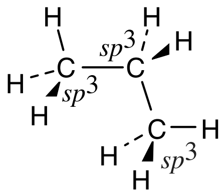
(3) Finally, use the remaining electrons to achieve an noble gas configuration for all atoms. For a line-bond structure, replace the electron dots between two atoms with a line.

	Molecule	*Electron-dot structure*	*Line-bond structure*
(a)	$CHCl_3$		
(b)	H_2S 8 valence electrons		
(c)	CH_3NH_2 14 valence electrons		
(d)	CH_3Li 8 valence electrons		

1.7 Each of the two carbons has 4 valence electrons. Two electrons are used to form the carbon–carbon bond, and the 6 electrons that remain can form bonds with a maximum of 6 hydrogens. Thus, the formula C_2H_7 is not possible.

1.8 Connect the carbons and add hydrogens so that all carbons are bonded to four different atoms.

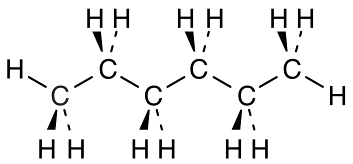


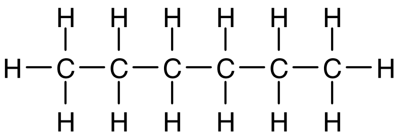


Propane

The geometry around all carbon atoms is tetrahedral, and all bond angles are approximately 109°.

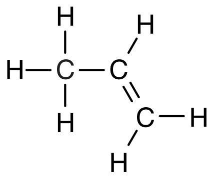
1.9

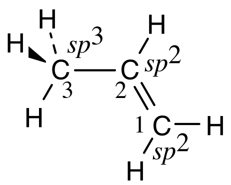




Hexane

1.10





Propene

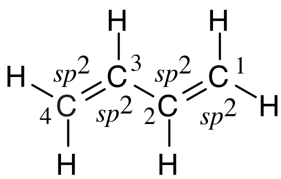
The C3–H bonds are σ bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen.

The C2–H and C1–H bonds are σ bonds formed by overlap of an sp^2 orbital of carbon with an *s* orbital of hydrogen.

The C2–C3 bond is a σ bond formed by overlap of an sp^3 orbital of carbon 3 with an sp^2 orbital of carbon 2.

There are two C1–C2 bonds. One is a σ bond formed by overlap of an sp^2 orbital of carbon 1 with an sp^2 orbital of carbon 2. The other is a π bond formed by overlap of a *p* orbital of carbon 1 with a *p* orbital of carbon 2. All four atoms connected to the carbon–carbon double bond lie in the same plane, and all bond angles between these atoms are 120°. The bond angle between hydrogen and the sp^3-hybridized carbon is 109°.

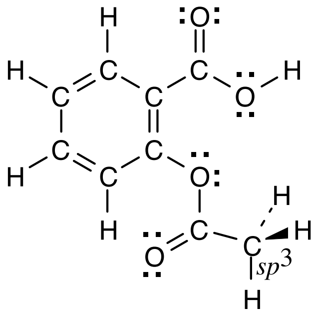
1.11



All atoms lie in the same plane, and all bond angles are approximately 120°.

1,3-Butadiene

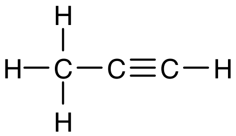
1.12

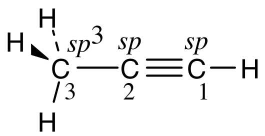


Aspirin.

All carbons are sp^2 hybridized, with the exception of the indicated carbon. All oxygen atoms have two lone pairs of electrons.

1.13





Propyne

The C3-H bonds are σ bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen.

The C1-H bond is a σ bond formed by overlap of an *sp* orbital of carbon 1 with an *s* orbital of hydrogen.

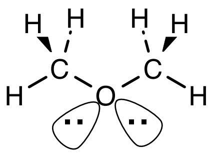
The C2-C3 bond is a σ bond formed by overlap of an *sp* orbital of carbon 2 with an sp^3 orbital of carbon 3.

There are three C1-C2 bonds. One is a σ bond formed by overlap of an *sp* orbital of carbon 1 with an *sp* orbital of carbon 2. The other two bonds are π bonds formed by overlap of two *p* orbitals of carbon 1 with two *p* orbitals of carbon 2.

The three carbon atoms of propyne lie in a straight line: the bond angle is 180°. The $H–C_1{\equiv}C_2$ bond angle is also 180°. The bond angle between hydrogen and the sp^3-hybridized carbon is 109°.

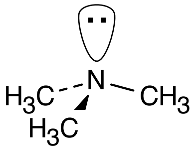
1.14

(a)



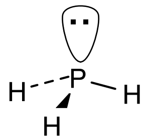
The sp^3-hybridized oxygen atom has tetrahedral geometry.

(b)



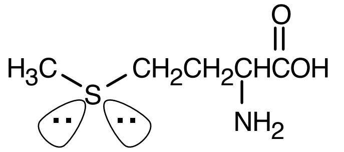
Tetrahedral geometry at nitrogen and carbon.

(c)



Like nitrogen, phosphorus has five outer-shell electrons. PH_3 has tetrahedral geometry.

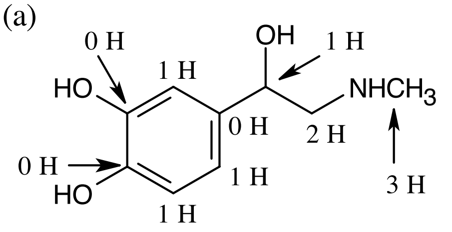
(d)



The sp^3-hybridized sulfur atom has tetrahedral geometry.

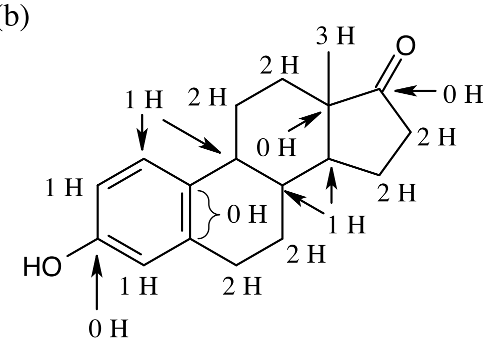
1.15 Remember that the end of a line represents a carbon atom with 3 hydrogens, a two-way intersection represents a carbon atom with 2 hydrogens, a three-way intersection represents a carbon with 1 hydrogen and a four-way intersection represents a carbon with no hydrogens.

(a)



Adrenaline – $C_9H_{13}NO_3$

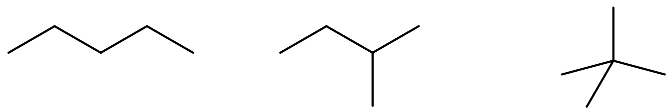
(b)



Estrone – $C_{18}H_{22}O_2$

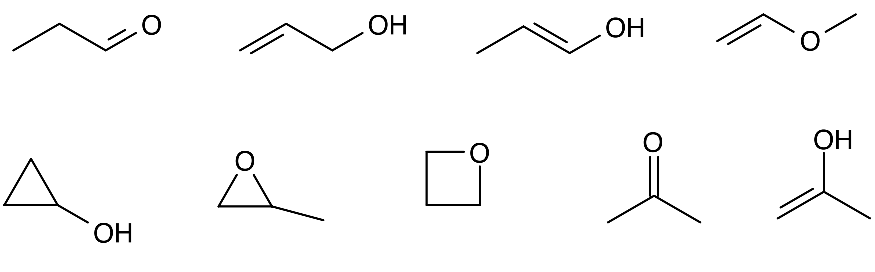
1.16 Several possible skeletal structures can satisfy each molecular formula.

(a) C_5H_{12}

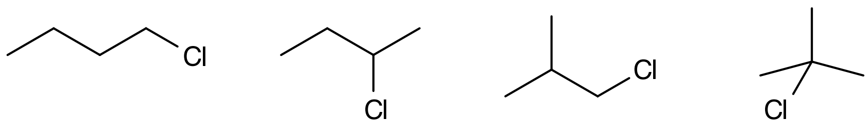


(b) C_2H_7N

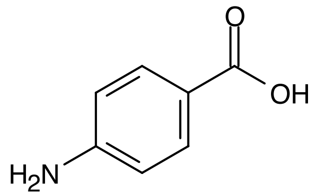
(c) C_3H_6O



(d) C_4H_9Cl



1.17

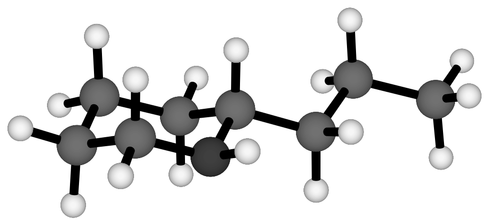


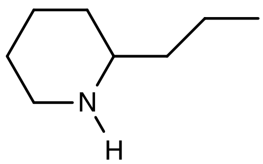
PABA

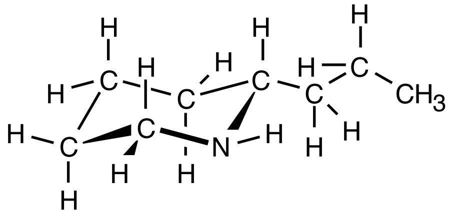
Visualizing Chemistry

1.18

(a)

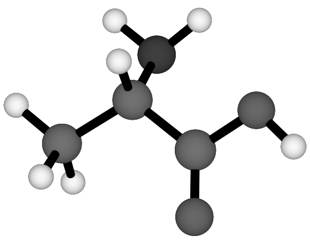


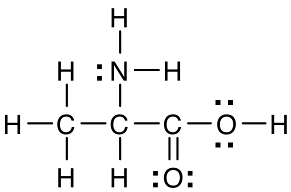


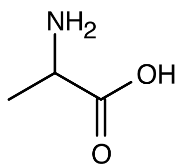


$C_8H_{17}N$

(b)

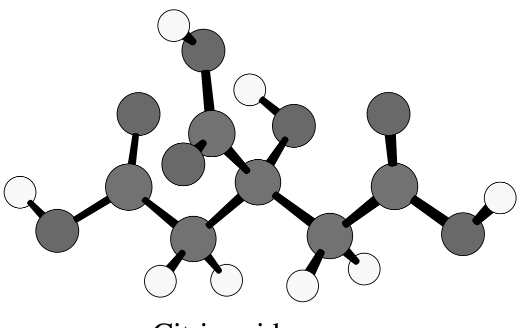




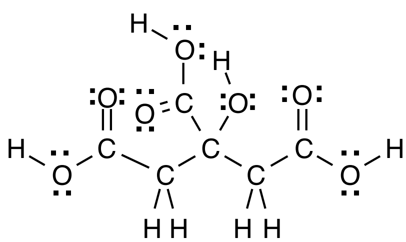


$C_3H_7NO_2$

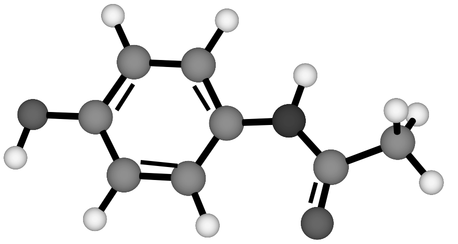
1.19 Citric acid ($C_6H_8O_7$) contains seven oxygen atoms, each of which has two electron lone pairs. Three of the oxygens form double bonds with carbon.



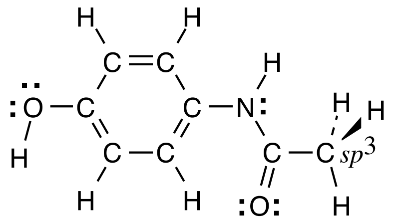
Citric acid



1.20

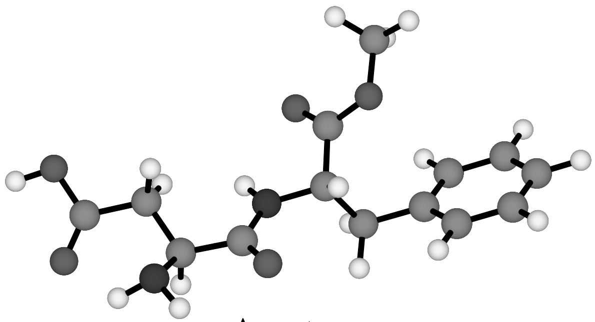


Acetaminophen

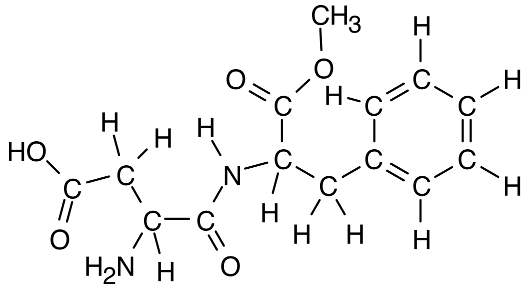


All carbons are sp^2 hybridized, except for the carbon indicated as sp^3. The two oxygen atoms and the nitrogen atom have lone pair electrons, as shown.

1.21



Aspartame



Additional Problems

Electron Configuration

1.22

Element	Atomic Number	Number of valence electrons
(a) Zinc	30	2
(b) Iodine	53	7
(c) Silicon	14	4
(d) Iron	26	2 (in 4*s* subshell), 6 (in 3*d* subshell)

1.23

Element	Atomic Number	Ground-state electron configuration
(a) Potassium	19	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$
(b) Arsenic	33	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^3$
(c) Aluminum	13	$1s^2\,2s^2\,2p^6\,3s^2\,3p^1$
(d) Germanium	32	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^2$

Electron-Dot and Line-Bond Structures

1.24 (a) NH_2OH (b) $AlCl_3$ (c) CF_2Cl_2 (d) CH_2O