

Organic Chemistry



Susan
McMurry
FIFTH EDITION

STUDY GUIDE AND SOLUTIONS MANUAL FOR McMURRY'S

**Study Guide and Solutions Manual
for McMurry's
Organic Chemistry**

Fifth Edition

Susan McMurry
Cornell University



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Preface

What enters your mind when you hear the words "organic chemistry?" Some of you may think, "the chemistry of life," or "the chemistry of carbon." Other responses might include "pre-med," "pressure," "difficult," or "memorization." Although formally the study of the compounds of carbon, organic chemistry encompasses many skills that are common to other areas of study. Organic chemistry is as much a liberal art as a science, and mastery of the concepts and techniques of organic chemistry can lead to an enhanced competence in other fields.

As you proceed to solve the problems that accompany the text, you will bring to the task many problem-solving techniques. For example, planning an organic synthesis requires the skills of a chess player; you must plan your moves while looking several steps ahead, and you must keep your plan flexible. Structure-determination problems are like detective problems, in which many clues must be assembled to yield the most likely solution. Naming organic compounds is similar to the systematic naming of biological specimens; in both cases, a set of rules must be learned and then applied to the specimen or compound under study.

The problems in the text fall into two categories: drill and complex. Drill problems, which appear throughout the text and at the end of each chapter, test your knowledge of one fact or technique at a time. You may need to rely on memorization to solve these problems, which you should work on first. More complicated problems require you to recall facts from several parts of the text and then use one or more of the problem-solving techniques mentioned above. As each major type of problem—synthesis, nomenclature, or structure determination—is introduced in the text, a solution is extensively worked out in this *Solutions Manual*.

Here are several suggestions that may help you with problem solving:

1. The text is organized into chapters that describe individual functional groups. As you study each functional group, *make sure that you understand the structure and reactivity of that group*. In case your memory of a specific reaction fails you, you can rely on your general knowledge of functional groups for help.
2. *Use molecular models*. It is difficult to visualize the three-dimensional structure of an organic molecule when looking at a two-dimensional drawing. Models will help you to appreciate the structural aspects of organic chemistry and are indispensable tools for understanding stereochemistry.
3. Every effort has been made to make this *Solutions Manual* as clear, attractive, and error-free as possible. Nevertheless, you should *use the Solutions Manual in moderation*. The principal use of this book should be to check answers to problems you have already worked out. The *Solutions Manual* should not be used as a substitute for effort; at times, struggling with a problem is the only way to teach yourself.
4. *Look through the appendices at the end of the Solutions Manual*. Some of these appendices contain tables that may help you in working problems; others present information related to the history of organic chemistry.

This edition of the *Solutions Manual* is almost completely new. All but a few of the structures and drawings have been revised, and much new material has been added. Each chapter of the *Solutions Manual* begins with an outline of the text that can be used for a concise review of the text material and can also serve as a reference. After every few chapters a Review Unit has been inserted. In most cases, the chapters covered in the Review Units are related to each other, and the units are planned to appear at approximately the place in the textbook where a test might be given. Each unit lists the vocabulary for the chapters covered, the skills needed to solve problems, and several important points that might need reinforcing or that restate material in the text from a slightly different point of view. Finally, the small self-test that has been included allows you to test yourself on the material from more than one chapter.

I have tried to include many types of study aids in this *Solutions Manual*. Nevertheless, this book can only serve as an adjunct to the larger and more complete textbook. If *Organic*

Chemistry is the guidebook to your study of organic chemistry, then the *Solutions Manual* is the roadmap that shows you how to find what you need.

Acknowledgments I would like to thank my husband, John McMurry, for offering me the opportunity to write this book many years ago and for supporting my efforts while this edition was being prepared. I am indebted to C. Peter Lillya, University of Massachusetts, Amherst, and Eric Simanek, Texas A & M University, for combing this manuscript for errors and for improving the clarity of my writing. Many people at Brooks/Cole Publishing company have given me encouragement during this project; special thanks are due to Jennifer Huber, Melissa Henderson, and Beth Wilbur. Finally, I would like to thank our eleven-year-old son Paul McMurry, who helped in many small ways and who patiently watched me work on this book, hoping that his turn to use the computer would come soon.

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Chapter 1 – Structure and Bonding

Chapter Outline

I. Atomic Structure (Sections 1.1 – 1.3).

A. Introduction to atomic structure (Section 1.1).

1. Atoms consist 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 10^{-10} m.
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 shells.
 - a. The shells differ in the numbers and kinds of orbitals they have.
 - b. Electrons in different orbitals have different energies.
 - c. Each orbital can hold two electrons.
4. The two lowest-energy electrons are in the 1*s* orbital.
 - a. The 2*s* orbital is the next in energy.
Each *p* orbital has a region of zero density, called a node.
 - b. The next three orbitals are 2*p_x*, 2*p_y* and 2*p_z*.

C. Electron Configuration (Section 1.3).

1. The ground-state electron configuration of an atom is a listing of the orbitals occupied by the atom.
2. Rules for predicting the ground-state electron configuration of an atom:
 - a. Orbitals with the lowest energy levels are filled first.
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.

All of the electrons in a half-filled shell have the same spin.

II. Chemical Bonding Theory (Sections 1.4 – 1.6).

A. Development of chemical binding theory (Section 1.4).

1. Kekulé and Couper proposed that carbon has four "affinity units" – carbon is tetravalent.
2. Other scientists suggested that carbon can form double bonds, triple bonds and rings.

2 Chapter 1

3. Van't Hoff 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, and a dashed line points behind the plane of the page.

B. Covalent bonds (Section 1.5).

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.
2. 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.
3. Covalent bonds can be represented two ways.
 - a. In Lewis structures, bonds are represented as pairs of dots.
 - b. In line-bond structures, bonds are represented as lines drawn between two atoms.
4. Valence electrons not used for bonding are called lone-pair electrons.
Lone-pair electrons are represented as dots.

C. Theories of covalent bond formation (Section 1.6).

1. Valence bond theory.
 - a. Covalent bonds are formed by the overlap of two atomic orbitals, each of which contains one electron. The two electrons have opposite spins.
 - b. Each of the bonded atoms retains its atomic orbitals, but the electron pair of the overlapping orbitals is shared by both atoms.
 - c. The greater the orbital overlap, the stronger the bond.
 - d. Bonds formed by the head-on overlap of two atomic orbitals are cylindrically symmetrical and are called σ bonds.
 - e. Bond strength is the measure of the amount of energy needed to break a bond.
 - f. Bond length is the optimum distance between nuclei.
 - g. Every bond has a characteristic bond length and bond strength.
2. Molecular orbital theory.
 - a. Molecular orbitals arise from a mathematical combination of atomic orbitals and belong to the entire molecule.
 - b. Two 1s orbitals can combine in two different ways.
 - i. The additive combination is a bonding MO and is lower in energy than the two hydrogen 1s atomic orbitals.
 - ii. The subtractive combination is an antibonding MO and is higher in energy than the two hydrogen 1s atomic orbitals.
 - c. A node is a region between nuclei where electrons aren't found.
If a node occurs between two nuclei, the nuclei repel each other.
 - d. The number of MOs in a molecule is the same as the number of atomic orbitals combined.

III. Hybridization (Sections 1.7 – 1.11).

A. sp^3 Orbitals (Sections 1.7, 1.8).

1. Structure of methane (Section 1.7).
 - a. When carbon forms 4 bonds with hydrogen, one 2s orbital and three 2p 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 1.8).
 - 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 1.9).
 1. If one carbon $2s$ orbital combines with two carbon $2p$ 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 p orbital is perpendicular to them.
 3. Two different types of bond 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 $1s$ orbitals of hydrogen.

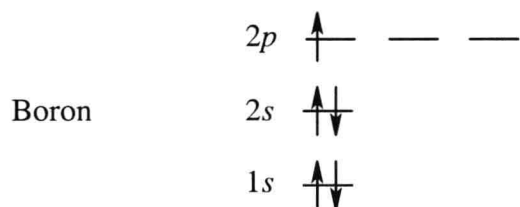
The double bond of ethylene is both shorter and stronger than the C–C bond of ethane.
 5. In the molecular orbital description of ethane, both bonding and antibonding MOs can form from the combination of two p orbitals.
- C. sp Orbitals (Section 1.10).
 1. If one carbon $2s$ orbital combines with one carbon $2p$ 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 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 $1s$ orbitals of hydrogen.

The triple bond of acetylene is the strongest carbon-carbon bond.
- D. Hybridization of nitrogen and oxygen (Section 1.11).
 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.

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.

Solutions to Problems

- 1.1 (a) To find the ground-state electron configuration of an element, first locate its atomic number. For boron, the atomic number is 5; boron thus has 5 protons and 5 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.

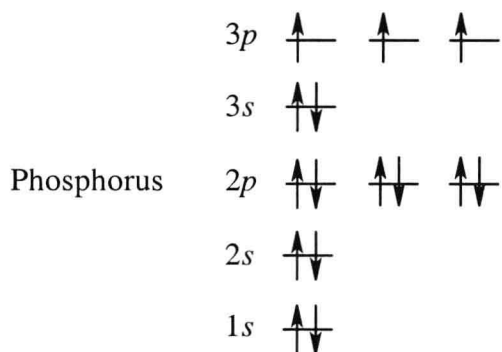


Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

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 boron is $1s^2 2s^2 2p^1$.

Often, we are interested only in the electrons in the outermost shell. We can then represent all filled levels by the symbol for the noble gas having the same levels filled. In the case of boron, the filled $1s$ energy level is represented by $[\text{He}]$, and the valence shell configuration is symbolized by $[\text{He}] 2s^2 2p^1$.

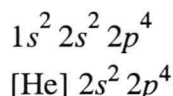
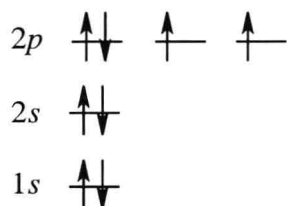
- (b) Let's consider an element with many electrons. Phosphorus, with an atomic number of 15, has 15 electrons. Assigning these to energy levels:



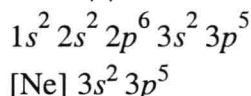
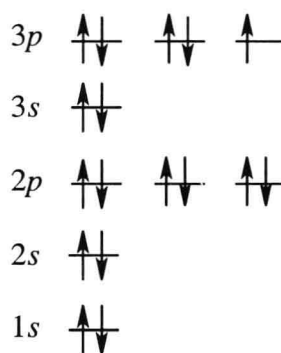
Notice that the $3p$ electrons are all in different orbitals. According to *Hund's rule*, we must place one electron into each orbital of the same energy level until all orbitals are half-filled.

The more concise way to represent ground-state electron configuration for phosphorus: $1s^2 2s^2 2p^6 3s^2 3p^3$ or $[\text{Ne}] 3s^2 3p^3$

(c) Oxygen (atomic number 8)



(d) Chlorine (atomic number 17)

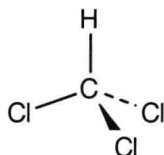
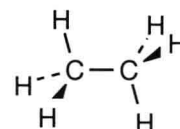
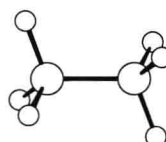
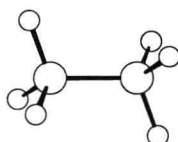


1.2 The elements of the periodic table are organized into groups that are based on the number of outer-shell electrons each element has. For example, an element in group 1A has one outer-shell electron, and an element in group 5A has five outer-shell electrons. To find the number of outer-shell electrons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

- (a) Potassium (group 1A) has one electron in its outermost shell.
- (b) Aluminum (group 3A) has three outer-shell electrons.
- (c) Krypton is a noble gas and has eight 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**

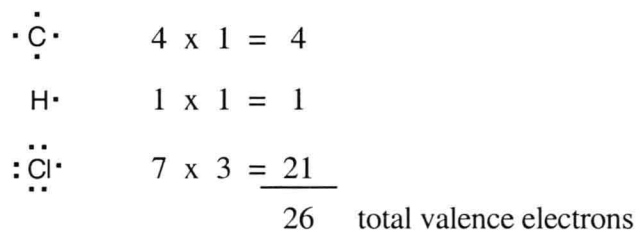
1.5 (a) Germanium (Group 4A) has four electrons in its valence shell and forms four bonds to achieve the noble-gas configuration of neon. A likely formula is GeCl_4 .

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

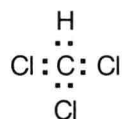
6 Chapter 1

1.6 Follow these three steps for drawing the Lewis structure of a 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.



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

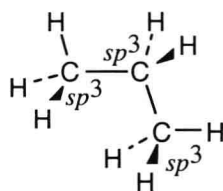


- (3) Finally, use the remaining electrons to achieve an noble gas configuration for all atoms.

<i>Molecule</i>	<i>Lewis structure</i>	<i>Line-bond structure</i>
(a) CHCl_3	$ \begin{array}{c} \text{H} \\ \vdots \\ :\ddot{\text{Cl}}: \text{C} : \ddot{\text{Cl}}: \\ \vdots \\ :\ddot{\text{Cl}}: \end{array} $	$ \begin{array}{c} \text{H} \\ \\ \text{Cl} - \text{C} - \text{Cl} \\ \\ \text{Cl} \end{array} $
(b) H_2S 8 valence electrons	$ \begin{array}{c} \cdot\cdot \\ \text{H} : \text{S} : \\ \cdot\cdot \\ \text{H} \end{array} $	$ \begin{array}{c} \text{H} - \text{S} \\ \\ \text{H} \end{array} $
(c) CH_3NH_2 14 valence electrons	$ \begin{array}{c} \text{H} \quad \text{H} \\ \vdots \quad \vdots \\ :\text{H}: \text{C} : \text{N}: \text{H} \\ \vdots \quad \vdots \\ :\text{H}: \end{array} $	$ \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{N} - \text{H} \\ \\ \text{H} \end{array} $
(d) NaH 2 valence electrons	$ \text{Na} : \text{H} $	$ \text{Na} - \text{H} $
(e) CH_3Li 8 valence electrons	$ \begin{array}{c} \text{H} \\ \vdots \\ \text{H} : \text{C} : \text{Li} \\ \vdots \\ \text{H} \end{array} $	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{Li} \\ \\ \text{H} \end{array} $

- 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.

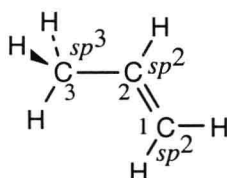
1.8



Propane

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

1.9



Propene

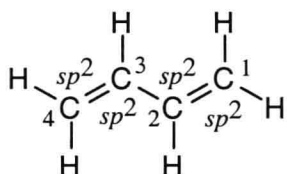
The C3–H bonds are σ bonds formed by overlap of an sp^3 orbital of carbon 3 with an s orbital of hydrogen.

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° .

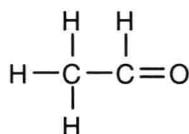
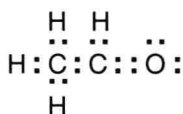
1.10



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

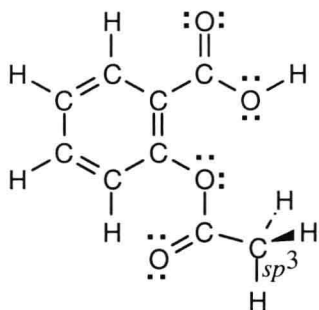
1,3-Butadiene

- 1.11 The atoms of acetaldehyde contribute 18 valence electrons. Ten electrons take part in the 5 single bonds, 4 electrons are involved in the carbon-oxygen double bond, and 4 electrons form the 2 lone pairs of electrons on oxygen.



Acetaldehyde

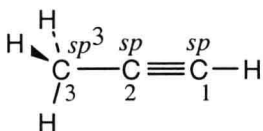
1.12



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 on a straight line; the bond angle is 180° . The H-C₁=C₂ bond angle is also 180° .

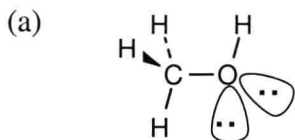
1.14



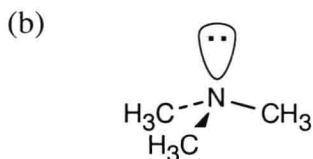
Formaldimine

Four electrons are shared in the carbon-nitrogen double bond. The nitrogen atom is sp^2 hybridized.

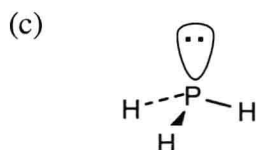
1.15



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



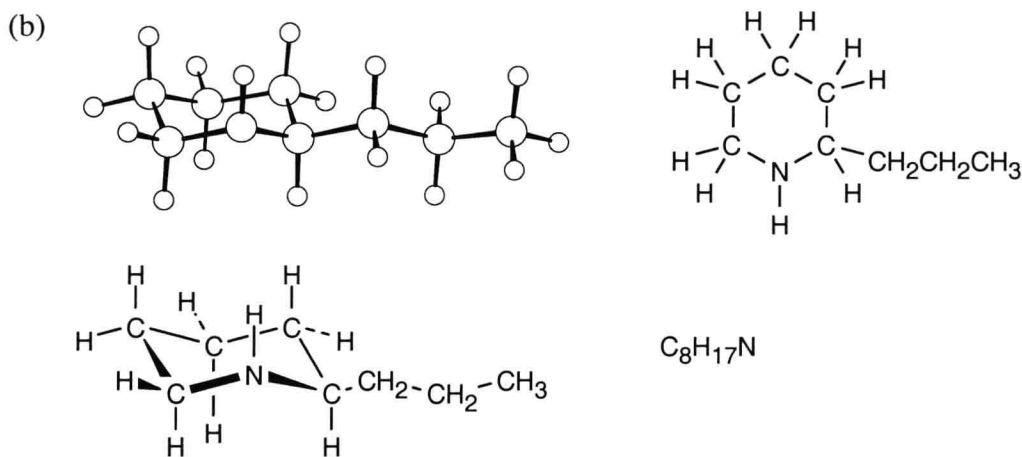
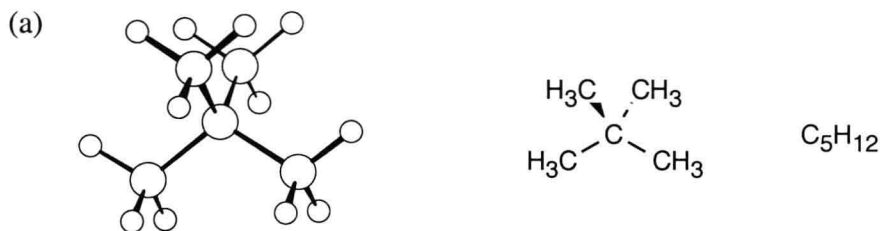
Tetrahedral geometry at nitrogen and carbon.



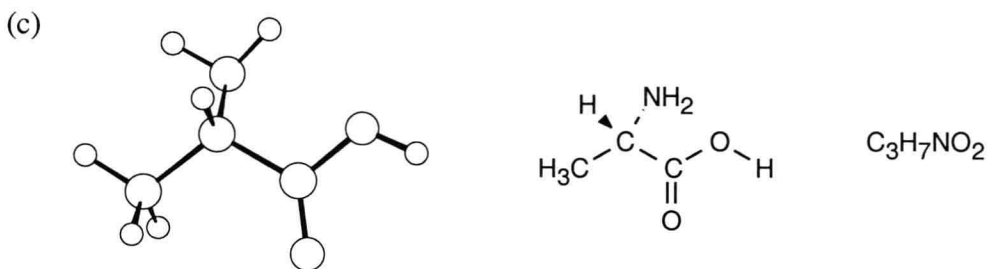
Like nitrogen, phosphorus has five outer-shell electrons. PH_3 has tetrahedral geometry.

Visualizing Chemistry

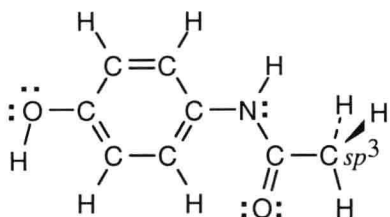
1.16



This drawing is more difficult to interpret because of the six-membered ring. Two structures are illustrated; the first one shows a flat ring, and the other shows the ring in three dimensions.

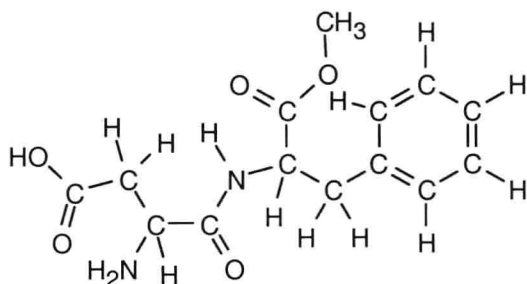


1.17



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.

1.18



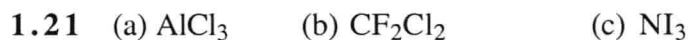
Additional Problems

1.19

<i>Element</i>	<i>Atomic Number</i>	<i>Number of valence electrons</i>
(a) Magnesium	12	2
(b) Sulfur	16	6
(c) Bromine	35	7

1.20

<i>Element</i>	<i>Atomic Number</i>	<i>Ground-state Electron configuration</i>
(a) Sodium	11	$1s^2 2s^2 2p^6 3s^1$
(b) Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
(c) Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
(d) Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$



1.22



Nitrogen has five electrons in its outer electron shell. Three are used in the carbon-nitrogen triple bond, and two are a nonbonding electron pair.

1.23 The $\text{H}_3\text{C}-$ carbon is sp^3 hybridized, and the $-\text{CN}$ carbon is sp hybridized.

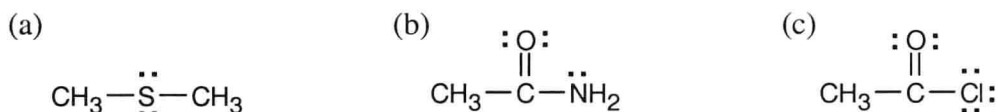
1.24



Vinyl chloride has 18 valence electrons. Eight electrons are used for 4 single bonds, 4 electrons are used in the carbon-carbon double bond, and 6 electrons are in the 3 lone pairs that surround chlorine.

Note that electron pairs in Lewis structures are generally shown as either vertical or horizontal.

1.25



1.26 In molecular formulas of organic molecules, carbon is listed first, followed by hydrogen. All other elements are listed in alphabetical order.

Compound *Molecular Formula*

(a) Aspirin	$\text{C}_9\text{H}_8\text{O}_4$
(b) Vitamin C	$\text{C}_6\text{H}_8\text{O}_6$
(c) Nicotine	$\text{C}_{10}\text{H}_{14}\text{N}_2$
(d) Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$

1.27 To work a problem of this sort, you must examine all possible structures consistent with the rules of valence. You must systematically consider all possible attachments, including those that have branches, rings and multiple bonds.

