STUDENT SOLUTIONS MANUAL

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Organic Chemistry

A Tenth Edition

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, the discipline of 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 improved competence in other fields.

As you work on 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 *Student 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 *Student Solutions Manual* as clear, attractive, and error-free as possible. Nevertheless, you should *use the Student Solutions Manual in moderation*. The principal use of this book should be to check answers to problems you have already worked out. The *Student 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 Student 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.

I have tried to include many types of study aids in this *Student Solutions Manual*.

Nevertheless, this book can only serve as an adjunct to the larger and more complete textbook. If *Organic Chemistry*: *A Tenth Edition* is the guidebook to your study of organic chemistry, then the *Student Solutions Manual* is the roadmap that shows you how to find what you need.

The Study Guide to accompany *Organic Chemistry: A Tenth Edition*, for the first time, is being published by OpenStax. I am pleased that OpenStax will make this resource freely available to you in honor of my late son, Peter McMurry.

Susan McMurry

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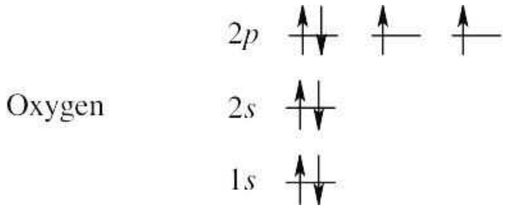
Chapter 1 – Structure and Bonding

Solutions to Problems

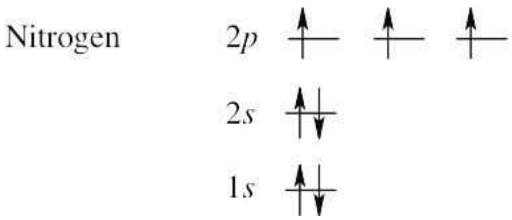
1.1 (a) To find the ground-state electron configuration of an element, first locate its atomic number. For oxygen, the atomic number is 8; oxygen thus has 8 protons and 8 electrons. Next, assign the electrons to the proper energy levels, starting with the lowest level. Fill each level *completely* before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



Notice that the 2*p* 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.

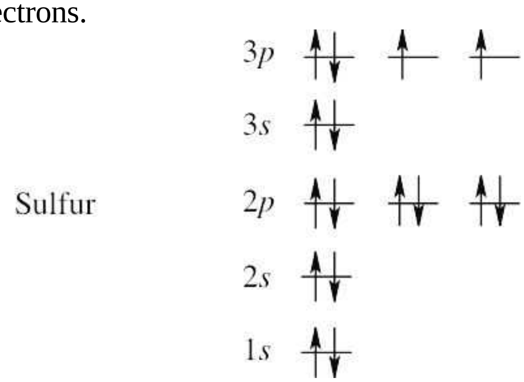
Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

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

(c) Sulfur has 16 electrons.



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

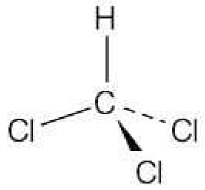
1.2 The elements of the periodic table are organized into groups that are based on the number of outer-shell electrons each element has. For example, an element in group 1A has one outer-shell electron, and an element in group 5A has five outer-shell electrons. To find the number of outer-shell electrons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

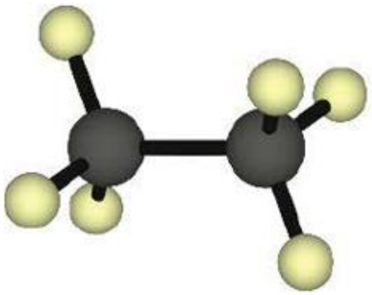
(c) Selenium (group 6A) has six electrons in its outermost shell.

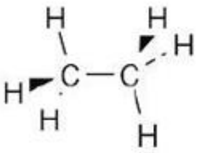
1.3 A solid line represents a bond lying in the plane of the page, a wedged bond represents a bond pointing out of the plane of the page toward the viewer, and a dashed bond represents a bond pointing behind the plane of the page.



Chloroform

1.4





Ethane

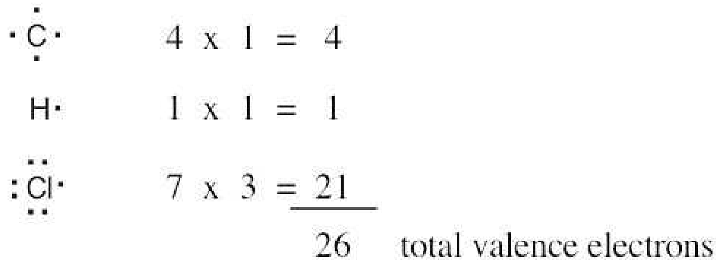
1.5 Identify the group of the central element to predict the number of covalent bonds the element can form.

(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.

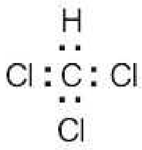
	Element	*Group*	*Likely Formula*
(b)	Al	3A	AlH_3
(c)	C	4A	CH_2Cl_2
(d)	Si	4A	SiF_4
(e)	N	5A	CH_3NH_2

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

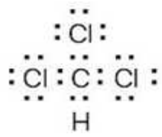
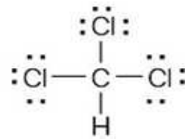
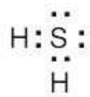
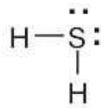
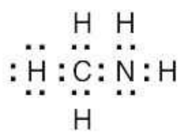
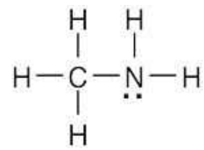
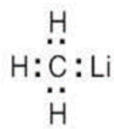
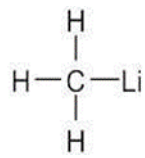
(1) Determine the number of valence, or outer-shell electrons for each atom in the molecule. For chloroform, we know that carbon has four valence electrons, hydrogen has one valence electron, and each chlorine has seven valence electrons.



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

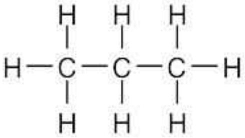


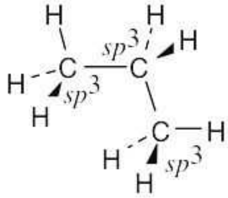
(3) Finally, use the remaining electrons to achieve a noble gas configuration for all atoms. For a line-bond structure, replace the electron dots between two atoms with a line.

	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.

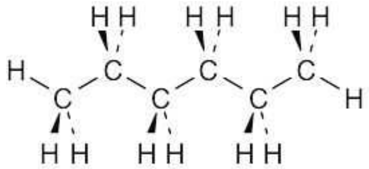


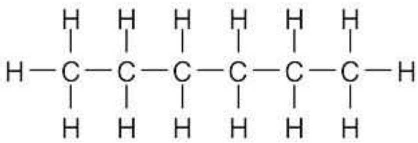


Propane

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

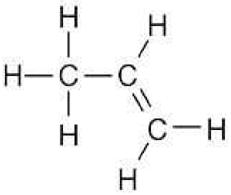
1.9

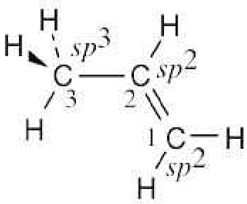




Hexane

1.10





Propene

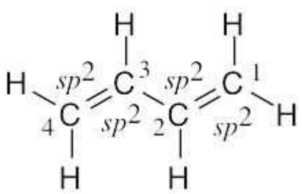
The C3–H bonds are σ bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen.

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^3 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°.

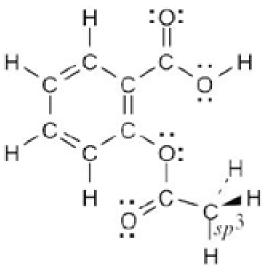
1.11



1,3-Butadiene

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

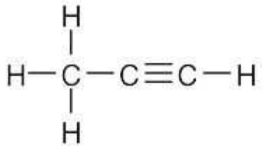
1.12

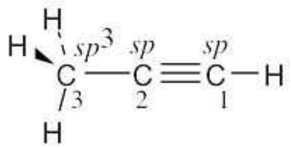


Aspirin.

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^3orbital 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.

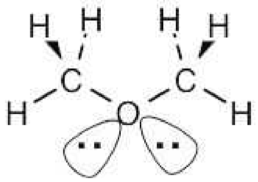
The C2-C3 bond is a σ bond formed by overlap of an *sp* orbital of carbon 2 with an sp^3 orbital of carbon 3.

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 $H–C_1≡C_2$ bond angle is also 180°. The bond angle between hydrogen and the sp^3-hybridized carbon is 109°.

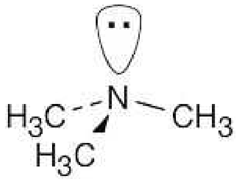
1.14

(a)



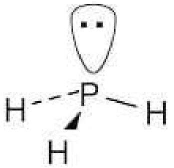
The sp^3-hybridized oxygen atom has tetrahedral geometry.

(b)

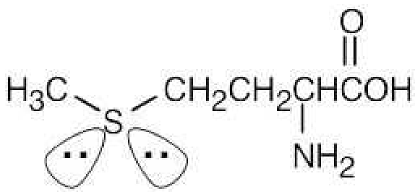


Tetrahedral geometry at nitrogen and carbon.

(c)



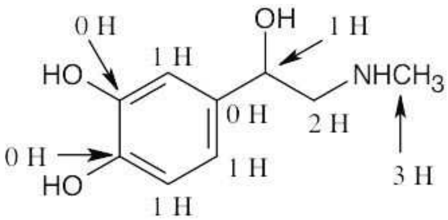
Like nitrogen, phosphorus has five outer-shell electrons. PH_3 has tetrahedral geometry.

(d) 

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

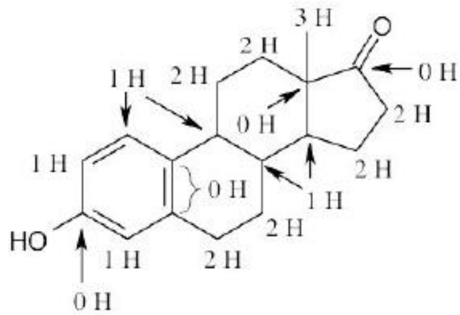
1.15 Remember that the end of a line represents a carbon atom with 3 hydrogens, a two-way intersection represents a carbon atom with 2 hydrogens, a three-way intersection represents a carbon with 1 hydrogen and a four-way intersection represents a carbon with no hydrogens.

(a)



Adrenaline – $C_9H_{13}NO_3$

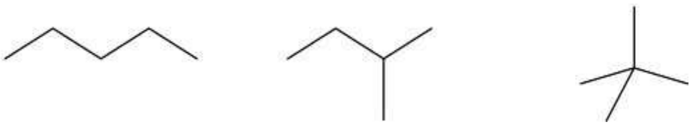
(b)



Estrone – $C_{18}H_{22}O_2$

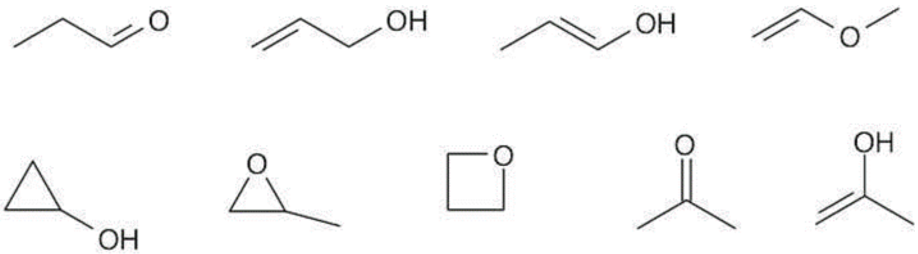
1.16 Several possible skeletal structures can satisfy each molecular formula.

(a) C_5H_{12}

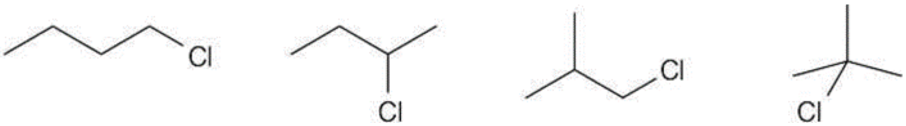


(b) C_2H_7N

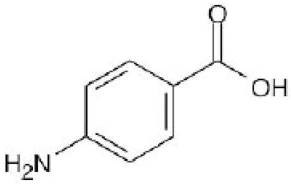
(c) C_3H_6O



(d) C_4H_9Cl



1.17

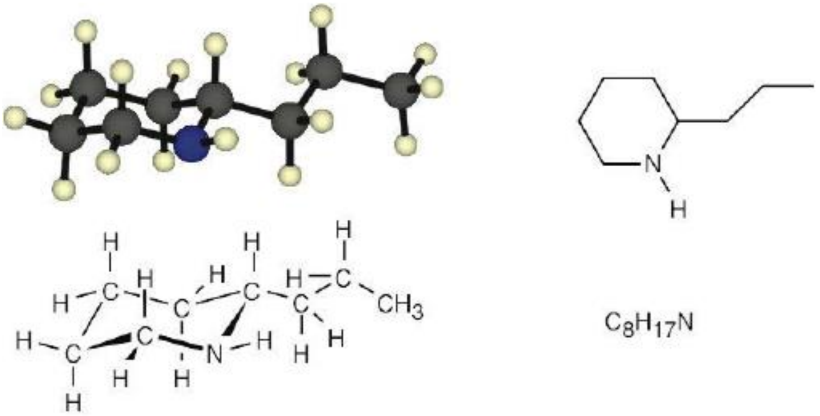


PABA

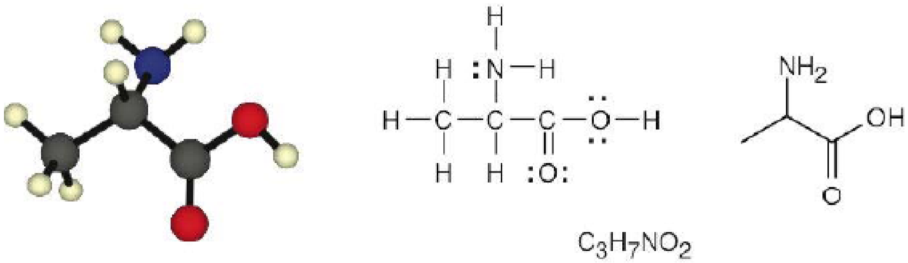
Additional Problems

Visualizing Chemistry

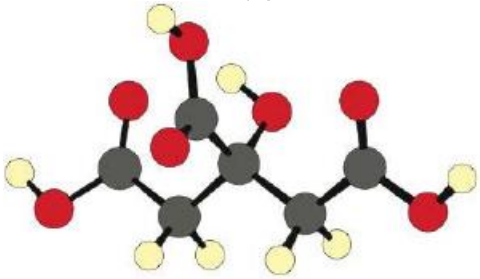
1.18 (a)



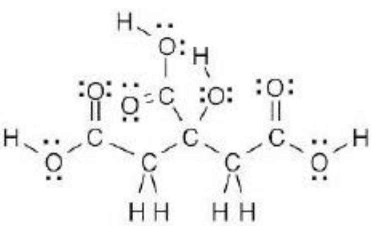
(b)



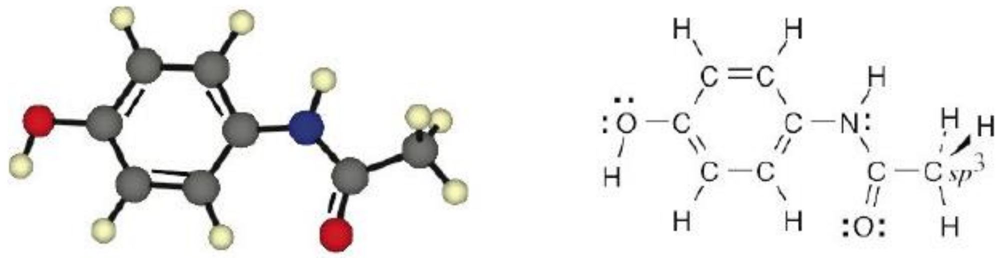
1.19 Citric acid ($C_6H_8O_7$) contains seven oxygen atoms, each of which has two electron lone pairs. Three of the oxygens form double bonds with carbon.



Citric acid



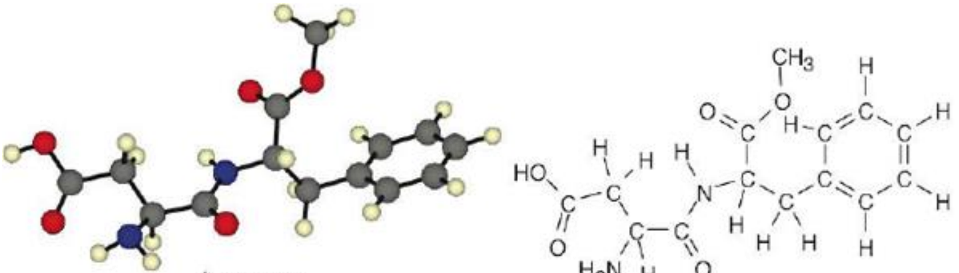
1.20



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

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

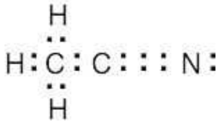
1.24 (a) NH_2OH (b) $AlCl_3$ (c) CF_2Cl_2 (d) CH_2O

1.25 (a) The 4 valence electrons of carbon can form bonds with a maximum of 4 hydrogens. Thus, it is not possible for the compound CH_5 to exist.

(b) If you try to draw a molecule with the formula C_2H_6N, you will see that it is impossible for both carbons and nitrogen to have a complete octet of electrons. Therefore, C_2H_6N is unlikely to exist.

(c) A compound with the formula $C_3H_5Br_2$ doesn't have filled outer shells for all atoms and is thus unlikely to exist.

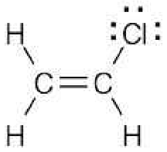
1.26



Acetonitrile

In the compound acetonitrile, nitrogen has eight electrons in its outer electron shell. Six are used in the carbon-nitrogen triple bond, and two are a nonbonding electron pair.

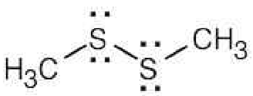
1.27

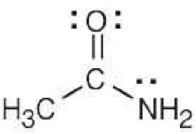


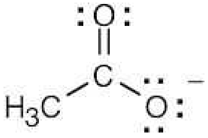
Vinyl chloride

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.

1.28 (a) (b) (c)





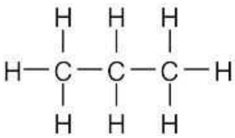


1.29 In molecular formulas of organic molecules, carbon is listed first, followed by hydrogen. All other elements are listed in alphabetical order.

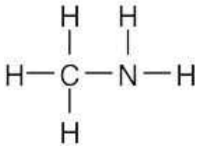
	Compound	*Molecular Formula*
(a)	Aspirin	$C_9H_8O_4$
(b)	Vitamin C	$C_6H_8O_6$
(c)	Nicotine	$C_{10}H_{14}N_2$
(d)	Glucose	$C_6H_{12}O_6$

1.30 To work a problem of this sort, you must draw 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.

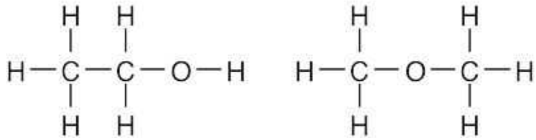
(a)



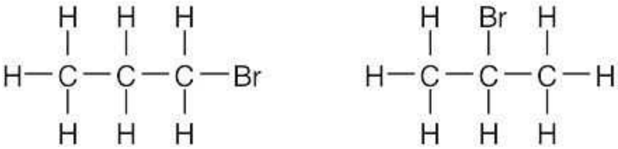
(b)



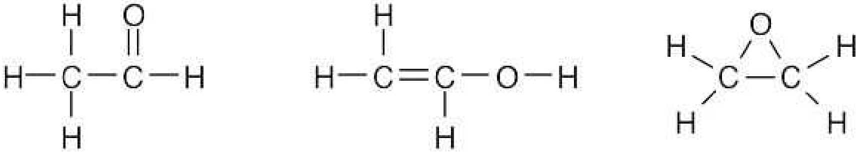
(c)



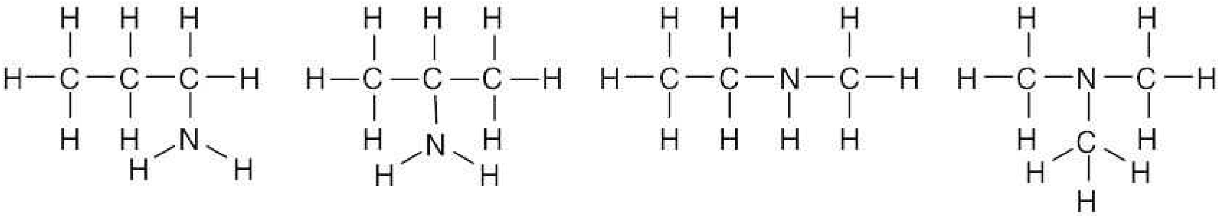
(d)



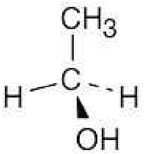
(e)



(f)

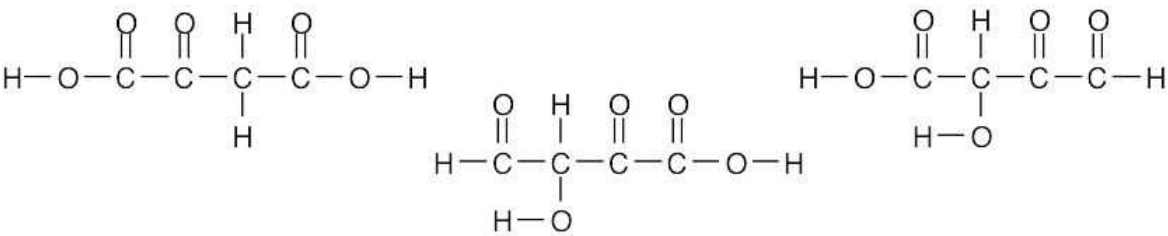


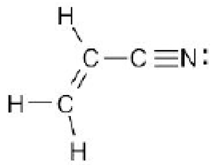
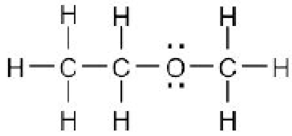
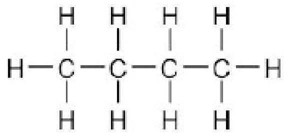
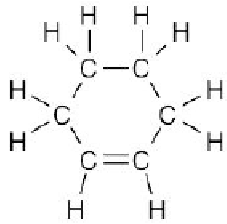
1.31



Ethanol

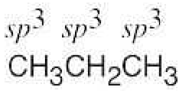
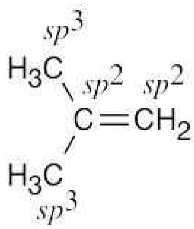
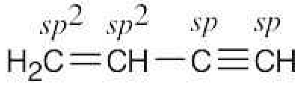
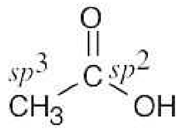
1.32



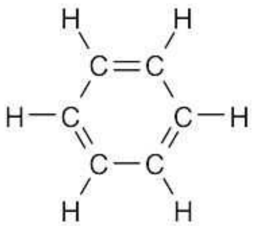
1.33 (a)

(b)

(c)

(d)


Hybridization

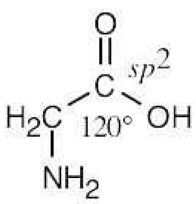
1.34 The H_3C– carbon is *sp*^{3} hybridized, and the –CN carbon is *sp* hybridized.

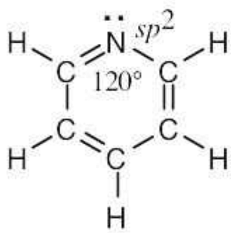
1.35 (a)

(b)

(c)

(d)


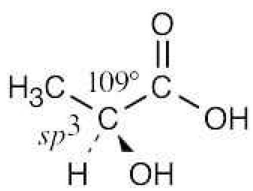
1.36


Benzene

All carbon atoms of benzene are *sp*^{2} hybridized, and all bond angles of benzene are 120°. Benzene is a planar molecule.

1.37 (a)

Glycine

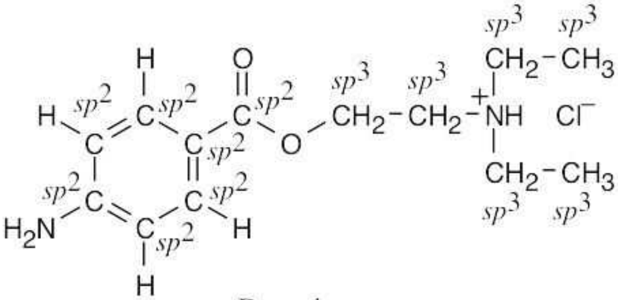
(b)

Pyridine

(c)

Lactic acid

1.38 Examples:

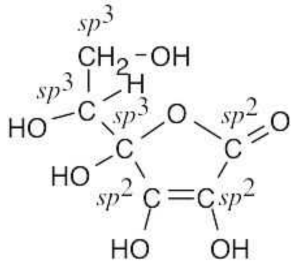
(a) $CH_3CH_2CH{=}CH_2$ (b) $H_2C{=}CH–CH{=}CH_2$ (c) $H_2C{=}CH–C{\equiv}CH$

1.39 (a)



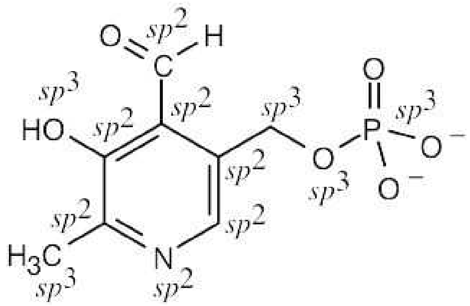
Procaine

(b)



Vitamin C

1.40

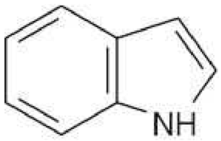


Pyridoxal phosphate

The bond angles formed by atoms having sp^3 hybridization are approximately 109°.
The bond angles formed by atoms having sp^2 hybridization are approximately 120°.

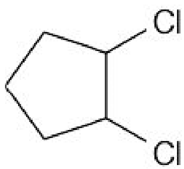
Skeletal Structures

1.41 (a)

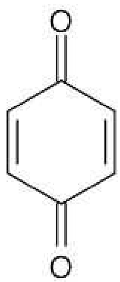


(b)

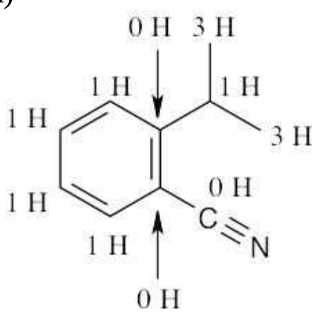
(c)



(d)

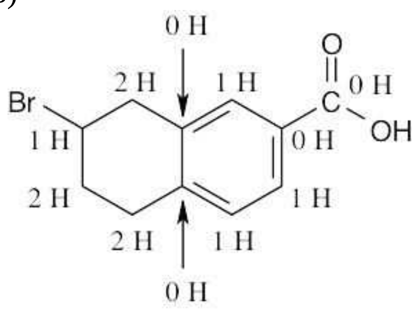


1.42 (a)



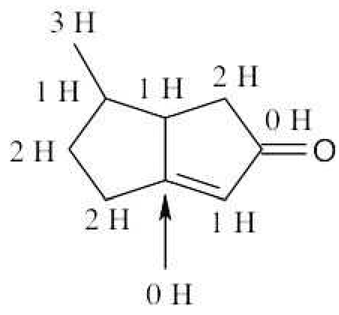
$C_{10}H_{11}N$

(b)



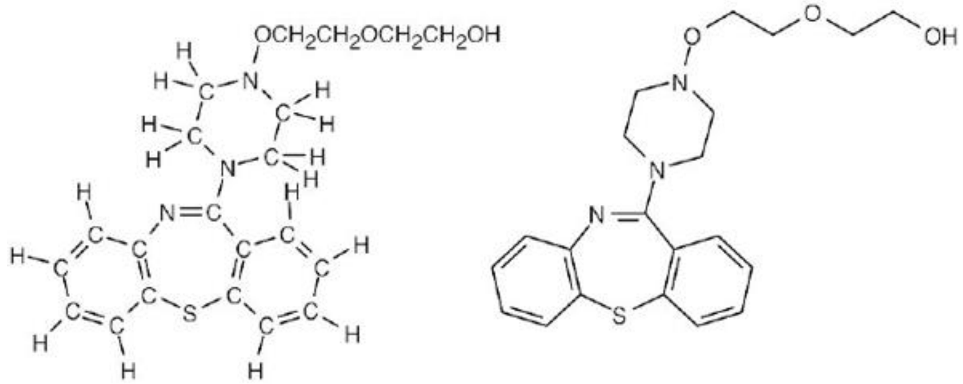
$C_{11}H_{11}BrO_2$

(c)



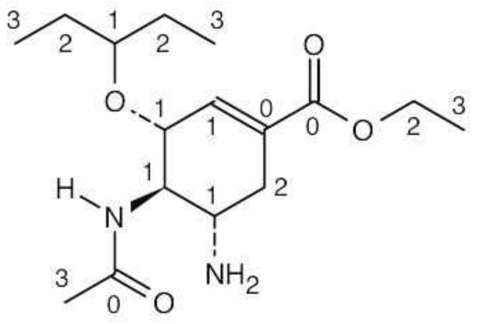
$C_9H_{12}O$

1.43

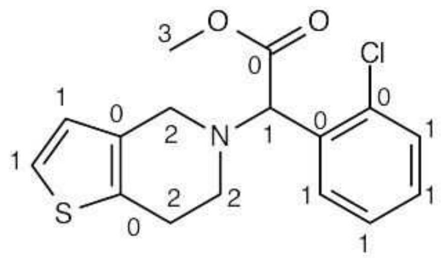


Quetiapine (Seroquel) $C_{21}H_{25}N_3O_2S$

1.44



Oseltamivir
(Tamiflu)
$C_{16}H_{28}N_2O_4$

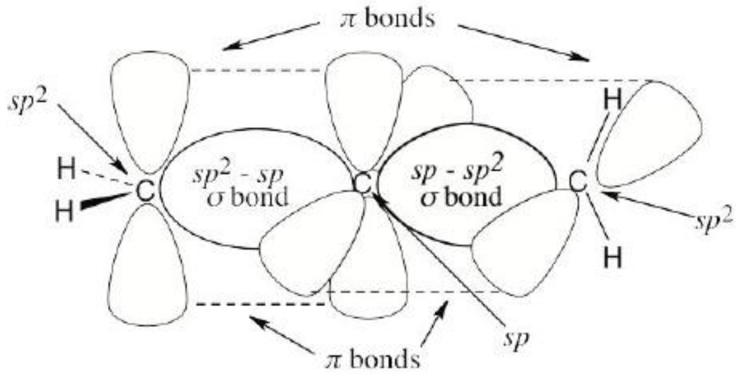


Clopidogrel
(Plavix)
$C_{16}H_{16}ClNO_2S$

General Problems

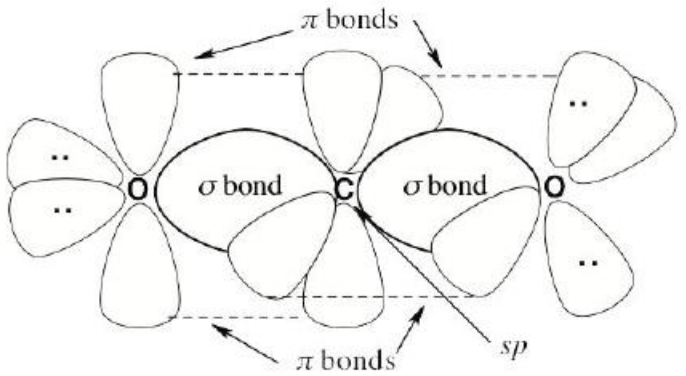
1.45 In a compound containing a carbon–carbon triple bond, atoms bonded to the *sp*-hybridized carbons must lie in a straight line. It is not possible to form a five-membered ring if four carbons must have a linear relationship.

1.46



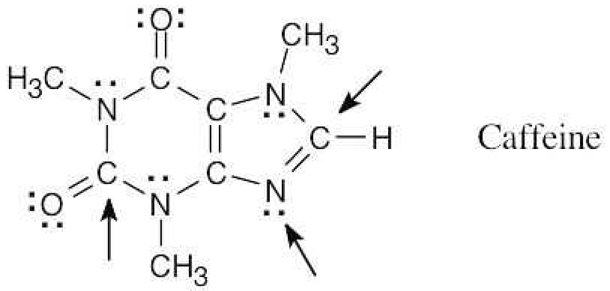
The central carbon of allene forms two σ bonds and two π bonds. The central carbon is *sp*-hybridized, and the two terminal carbons are sp^2-hybridized. The bond angle formed by the three carbons is 180°, indicating linear geometry for the carbons of allene.

1.47



Carbon dioxide is a linear molecule.

1.48



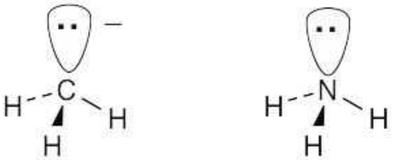
All of the indicated atoms are sp^2-hybridized.

1.49 (a) The positively charged carbon atom is surrounded by six valence electrons; carbon has three valence electrons, and each hydrogen brings three valence electrons.

(b) The positively charged carbon is *sp*^{2}-hybridized.

(c) A carbocation is planar about the positively charged carbon.

1.50



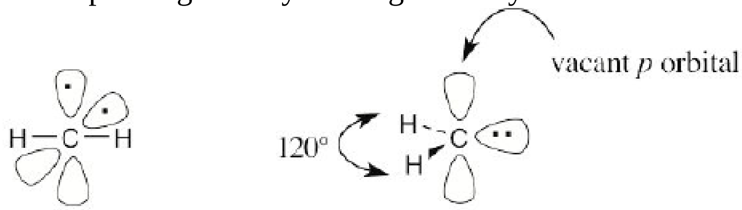
(a) A carbanion is isoelectronic with (has the same number of electrons as) a trivalent nitrogen compound.

(b) The negatively charged carbanion carbon has eight valence electrons.

(c) The carbon atom is *sp*^{3}-hybridized.

(d) A carbanion is tetrahedral.

1.51 According to the Pauli Exclusion Principle, two electrons in the same orbital must have opposite spins. Thus, the two electrons of triplet (spin-unpaired) methylene must occupy different orbitals. In triplet methylene, *sp*-hybridized carbon forms one bond to each of two hydrogens. Each of the two unpaired electrons occupies a *p* orbital. In singlet (spin-paired) methylene the two electrons can occupy the same orbital because they have opposite spins. Including the two C–H bonds, there are a total of three occupied orbitals. We predict *sp*^{2} hybridization and planar geometry for singlet methylene.

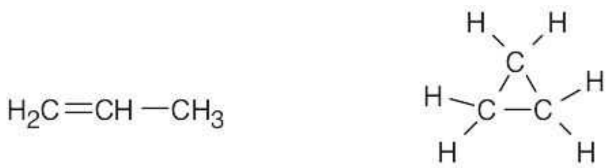


Triplet methylene (linear)   Singlet methylene (planar)

1.52

The two compounds differ in the way that the carbon atoms are connected.

1.53

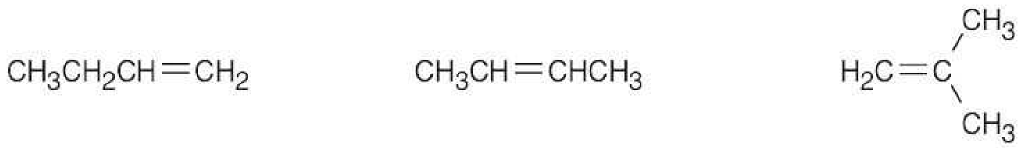


One compound has a double bond, and one has a ring.

1.54 CH_3CH_2OH CH_3OCH_3

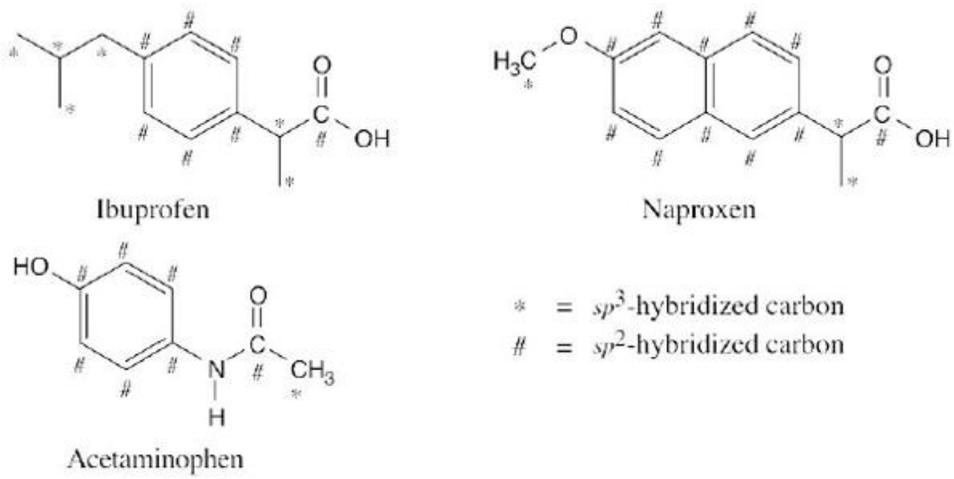
The two compounds differ in the location of the oxygen atom.

1.55



The compounds differ in the way that the carbon atoms are connected and in the location of the double bond.

1.56



(a), (b)

Compound	*sp^3-Hybridized carbons*	*sp^2-Hybridized carbons*
Ibuprofen	6	7
Naproxen	3	11
Acetaminophen	1	7

(c) Each of the structures has a six-membered ring containing three double bonds, each has a methyl group, and each has a C=O group.