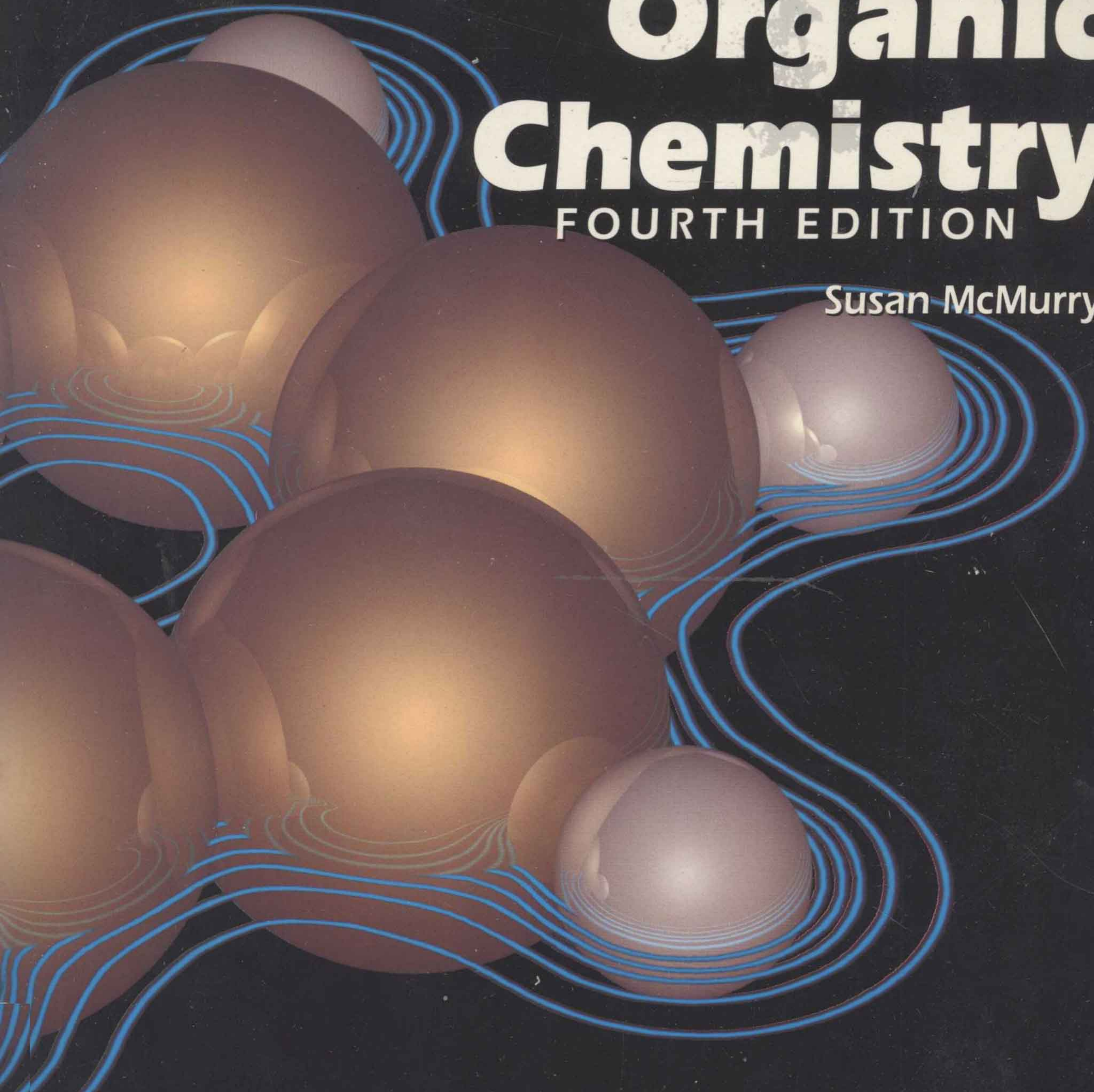
Study Guide and Solutions Manual for McMurry's

Organic Chemistry

FOURTH EDITION

Susan McMurry



Study Guide and Solutions Manual for
Organic Chemistry

Fourth 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.

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. My appreciation goes to Virginia Severn Goodman, Sonja Erion, Melba Wallace and Sherrie Yourstone, all of whom were involved in producing previous editions of this book. Many people at Brooks/Cole Publishing company have given me encouragement during this project; special thanks are due to Harvey Pantzis, Connie Jirovsky, Elizabeth Rammel and Joan Marsh. I am grateful to Elmer Ewing, my supervisor at Cornell University, for allowing me the flexible work schedule that I needed in order to finish this book. For this edition, all manuscript preparation was done by the author, using a Macintosh computer and the programs WordPerfect and ChemIntosh,which was easy to learn and fun to use. Finally, I would like to thank our seven-year-old son Paul McMurry, who patiently watched me work on this book, while wishing that he could be playing games on the computer instead.

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Solutions to Problems

Appendices

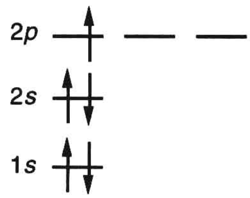
Chapter 1 – Structure and Bonding

1.1 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.

1.2 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:

Boron



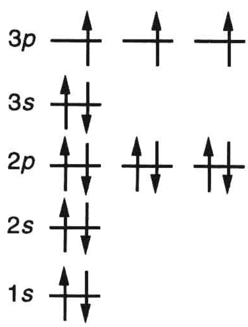
Remember that only two electrons can occupy the same orbital, and that they must be of opposite spin.

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 $1s^2\ 2s^2\ 2p$.

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 [He], and the valence shell configuration is symbolized by [He] $2s^2\ 2p$.

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

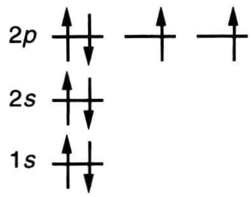
Phosphorus



Notice that the 3*p* 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 [Ne] $3s^2\ 3p^3$

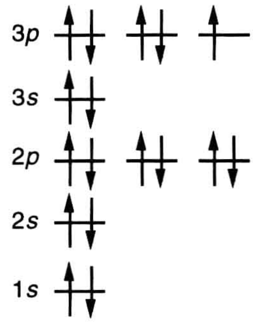
c) Oxygen (atomic number 8)



$1s^2\,2s^2\,2p^4$

[He] $2s^2\,2p^4$

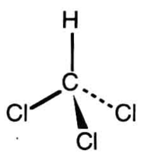
d) Chlorine (atomic number 17)



$1s^2\,2s^2\,2p^6\,3s^2\,3p^5$

[Ne] $3s^2\,3p^5$

1.3



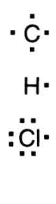
Chloroform

1.4 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

1.5 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, and each chlorine has seven.



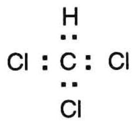
4 x 1 = 4

1 x 1 = 1

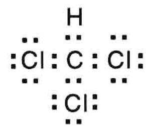
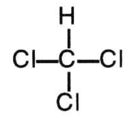
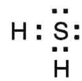
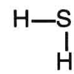
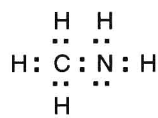
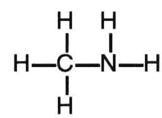
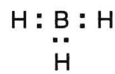
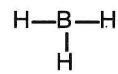
7 x 3 = 21

26 total valence electrons

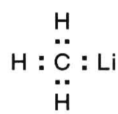
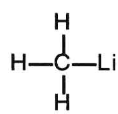
(2) Next, use two electrons for each single bond.



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

Molecule	Lewis structure	Line-bond structure
a) $CHCl_3$		
b) H_2S 8 valence electrons		
c) CH_3NH_2 14 valence electrons		
d) BH_3 6 valence electrons		

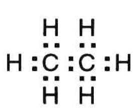
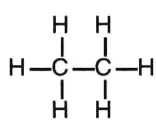
Borane can't achieve a noble-gas configuration because it has only six valence electrons.

e) NaH 2 valence electrons	Na: H	Na—H
f) CH_3Li 8 valence electrons		

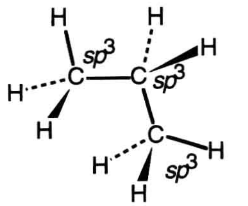
1.6 Bonds formed between an element on the right side of the periodic table and an element on the left side are ionic. Bonds formed between an element in the middle of the periodic table and another element are most often covalent.

Ionic bonds: LiI, KBr, $MgCl_2$
Covalent bonds: CH_4, CH_2Cl_2, Cl_2

1.7

 Ethane 

1.8

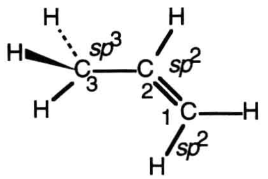


Propane

All carbon atoms are tetrahedral, and all bond angles are approximately 109.5°.

1.9 The two carbons bond to each other by overlap of two sp^3 hybrid orbitals. Six sp^3 hybrid orbitals (three from each carbon) are left over, and they can bond with a maximum of six hydrogens. Thus, a formula such as C_2H_7 is not possible.

1.10



Propene

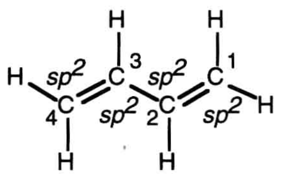
The C3–H bonds are σ bonds formed by overlap of an sp^3 orbital of carbon 3 with an *s* orbital of hydrogen.

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.

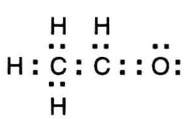
There are two C1–C2 bonds. One is a σ bond formed by overlap of an sp^2 orbital of carbon 1 with an sp^2 orbital of carbon 2. The other is a π bond formed by overlap of a *p* orbital of carbon 1 with a *p* orbital of carbon 2. All four atoms connected to the carbon-carbon double bond lie in the same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

1.11

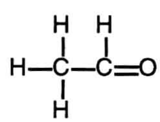


All atoms lie in the same plane, and all bond angles are approximately 120°

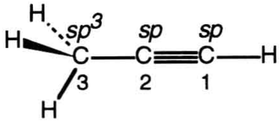
1.12



Acetaldehyde



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 or carbon 1 with an *s* orbital of hydrogen.

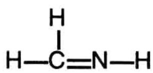
The C2-C3 bond is a σ bond formed by overlap of an *sp* orbital of carbon 2 with an sp^3 orbital of carbon 3.

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°.

1.14

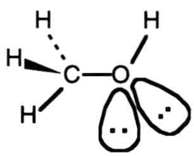
Formaldimine



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

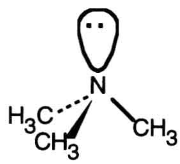
1.15

a)



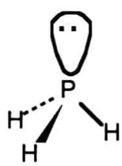
The sp^3 -hybridized oxygen atom has tetrahedral geometry.

b)



Tetrahedral geometry

c)



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

1.16

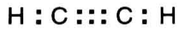
Element	*Atomic Number*	*Number of valence electrons*
a) Magnesium	12	2
b) Sulfur	16	6
c) Bromine	35	7

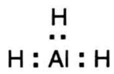
1.17

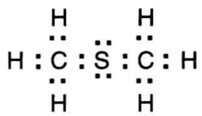
Element	Atomic Number	Ground-state Electron configuration
a) Sodium	11	$1s^2\,2s^2\,2p^6\,3s$
b) Aluminum	13	$1s^2\,2s^2\,2p^6\,3s^2\,3p$
c) Silicon	14	$1s^2\,2s^2\,2p^6\,3s^2\,3p^2$
d) Calcium	20	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$

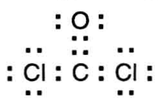
1.18 (a) $AlCl_3$ (b) CF_2Cl_2 (c) NI_3

1.19

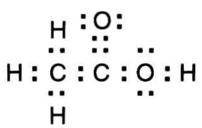
a)  10 valence electrons

b)  6 valence electrons

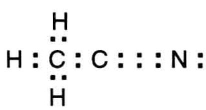
c)  20 valence electrons

d)  24 valence electrons

e)  22 valence electrons

f)  24 valence electrons

1.20

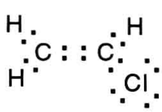


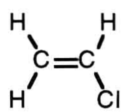
Acetonitrile

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.

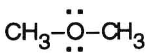
1.21 The H_3C– carbon is sp^3 hybridized, and the –CN carbon is sp hybridized.

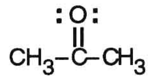
1.22

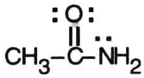


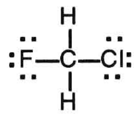


1.23

a) 

b) 

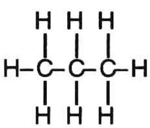
c) 

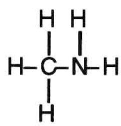
d) 

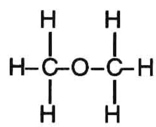
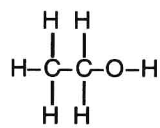
1.24 In molecular formulas of organic molecules, carbon is listed first, followed by hydrogen. All other elements are listed in alphabetical order.

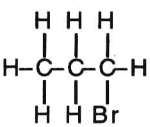
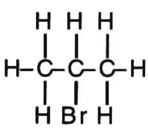
Compound	*Molecular Formula*
a) Phenol	C_6H_6O
b) Aspirin	$C_9H_8O_4$
c) Vitamin C	$C_6H_8O_6$
d) Nicotine	$C_{10}H_{14}N_2$
e) Novocain	$C_{13}H_{21}ClN_2O_2$
f) Glucose	$C_6H_{12}O_6$

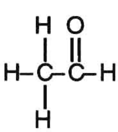
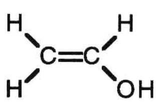
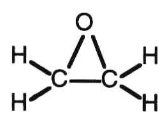
1.25 To work a problem of this sort, you must examine all possible structures consistent with the rules of valence. You must systematically consider all possible attachments, including those that have branches, rings and multiple bonds.

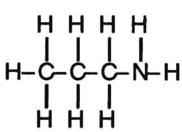
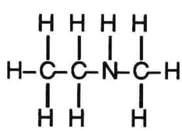
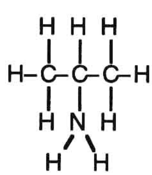
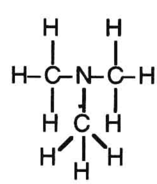
a) 

b) 

c)  and 

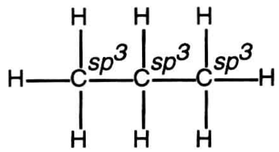
d)  and 

e)   

f)    

1.26

a)



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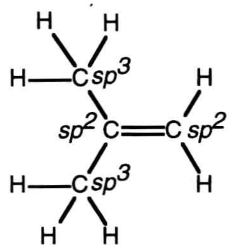

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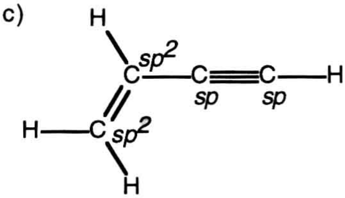
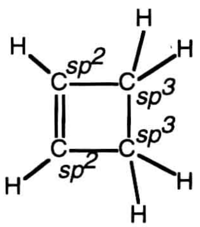
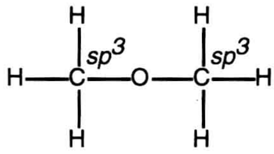


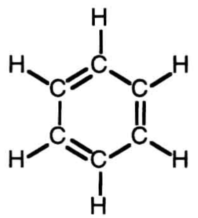
d)



e)



1.27



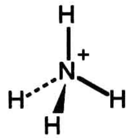
Benzene

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

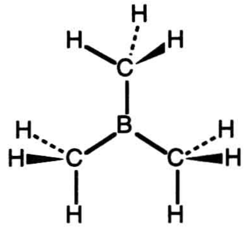
1.28 All angles are approximate.
a) 109° b) 109° c) 109° d) 120°

1.29 a) sp^3 b) sp^3 c) sp^2

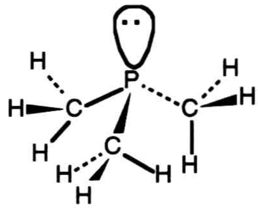
1.30

a) 

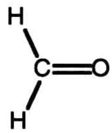
The ammonium ion is tetrahedral because nitrogen is sp^3 hybridized

b) 

The boron-carbon portion of the molecule is planar because of sp^2 hybridization at boron. The $-CH_3$ portions are tetrahedral.

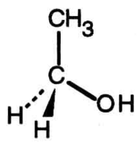
c) 

Trimethylphosphine is pyramidal. The $-CH_3$ portions are tetrahedral.

d) 

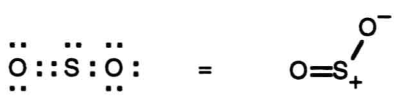
Formaldehyde is planar because carbon is sp^2 hybridized.

1.31

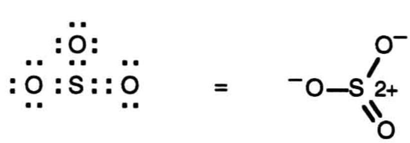


Ethanol

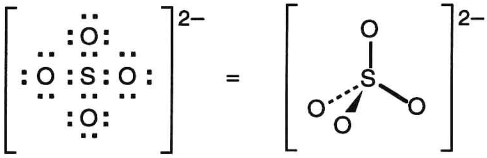
1.32 a) SO_2 has eighteen valence electrons (six from sulfur and six from each oxygen). The oxygen-sulfur-oxygen bond angle is approximately 120°.



b) SO_3 has 24 valence electrons and is a planar molecule.

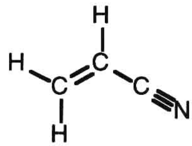


c) Four oxygens and one sulfur contribute 30 valence electrons. In addition, there are two electrons that give SO_4^{2-} its negative charge. The total number of electrons used to draw the Lewis structure is 32. SO_4^{2-} is a tetrahedral anion.



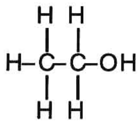
1.33

a)



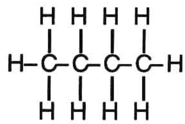
Acrylonitrile

b)



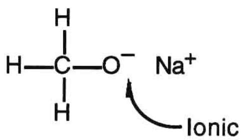
Ethanol

c)



Butane

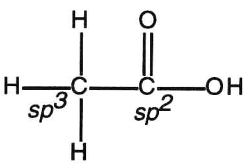
1.34



All other bonds are covalent.

1.35

a)



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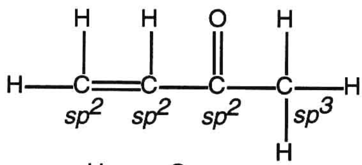
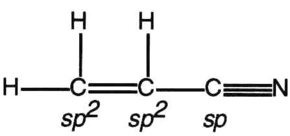
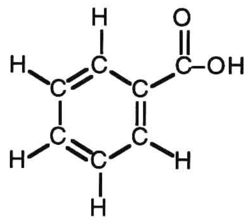


c)



d)



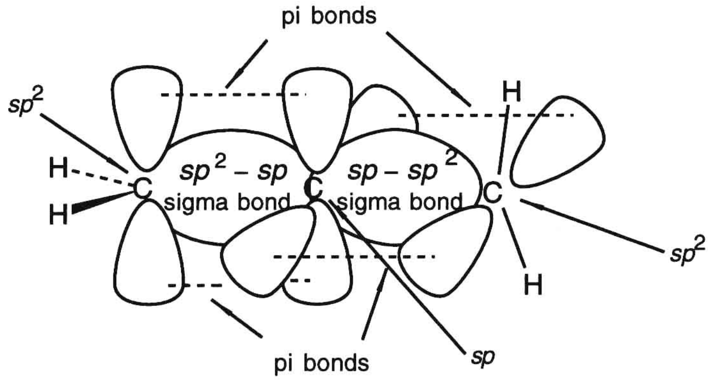
All carbon atoms of benzoic acid are sp^2 hybridized.

1.36 All angles are approximate.
a) 109° b) 120° c) 180° d) 109°

1.37 a) sp^3 b) sp^2 c) sp d) sp^3

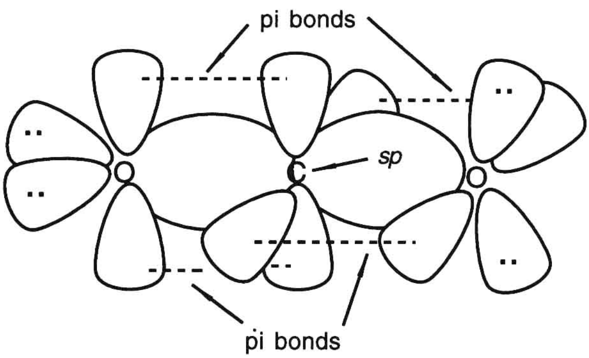
1.38 Ionic: NaCl
Covalent: CH_3Cl, Cl_2, HOCl

1.39



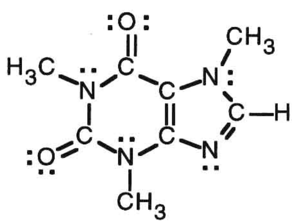
The central carbon of allene forms two σ bonds and two π bonds. The central carbon is *sp*–hybridized, and the two terminal carbons are sp^2–hybridized. The carbon-carbon bond angle is 180°, indicating linear geometry for the carbons.

1.40



Carbon dioxide is a linear molecule.

1.41



All the indicated atoms are sp^2 hybridized.

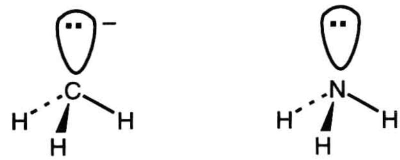
1.42 a) A carbocation is isoelectronic with (has the same number of electrons as) a trivalent boron compound.

b) The positively charged carbon atom has six valence shell electrons.

c) A carbocation is sp^2–hybridized.

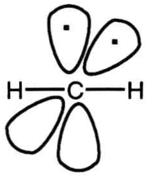
d) A carbocation is planar.

1.43

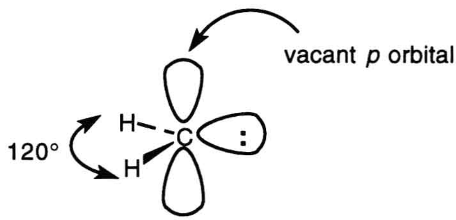


The negatively charged carbanion carbon has eight valence electrons and is sp^3–hybridized. A carbanion is tetrahedral and is isoelectronic with a trivalent nitrogen compound.

1.44 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)

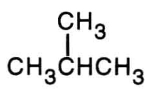


Singlet methylene
(planar)

1.45 a) $CH_3CH_2CH{=}CH_2$ b) $CH_2{=}CHCH{=}CH_2$ c) $CH_2{=}CHC{\equiv}CH$

1.46

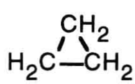
$CH_3CH_2CH_2CH_3$



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

1.47

$CH_3CH{=}CH_2$



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

1.48

CH_3CH_2OH CH_3OCH_3

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