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# PREFACE

This book contains more than just solutions to all of the problems in the textbook. Each chapter of this book also contains a series of exercises that will help you review the concepts, skills and reactions presented in the corresponding chapter of the textbook. These exercises are designed to serve as study tools that can help you identify your weak areas. Each chapter of this solutions manual/study guide has the following parts:

- Review of Concepts. These exercises are designed to help you identify which concepts
  are the least familiar to you. Each section contains sentences with missing words
  (blanks). Your job is to fill in the blanks, demonstrating mastery of the concepts. To
  verify that your answers are correct, you can open your textbook to the end of the
  corresponding chapter, where you will find a section entitled Review of Concepts and
  Vocabulary. In that section, you will find each of the sentences, verbatim.
- Review of Skills. These exercises are designed to help you identify which skills are the
  least familiar to you. Each section contains exercises in which you must demonstrate
  mastery of the skills developed in the SkillBuilders of the corresponding textbook
  chapter. To verify that your answers are correct, you can open your textbook to the end
  of the corresponding chapter, where you will find a section entitled SkillBuilder Review.
  In that section, you will find the answers to each of these exercises.
- Review of Reactions. These exercises are designed to help you identify which reagents
  are not at your fingertips. Each section contains exercises in which you must
  demonstrate familiarity with the reactions covered in the textbook. Your job is to fill in
  the reagents necessary to achieve each reaction. To verify that your answers are correct,
  you can open your textbook to the end of the corresponding chapter, where you will find
  a section entitled Review of Reactions. In that section, you will find the answers to each
  of these exercises.
- Solutions. At the end of each chapter, you'll find solutions to all problems in the
  textbook, including all Skillbuilders, conceptual checkpoints, additional problems,
  integrated problems, and challenge problems.

The sections described above have been designed to serve as useful tools as you study and learn organic chemistry. Good luck!

David Klein Department of Chemistry Johns Hopkins University

# Chapter 1 Electrons, Bonds and Molecular Properties

# Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

isomers share the s	same molecular formula but have different
connectivity of atoms and different	physical properties.
Second-row elements generally obegas electron configuration.	y the rule, bonding to achieve noble
A pair of unshared electrons is calle	ed a
of	tom does not exhibit the appropriate number
An atomic orbital is a region of spa	ace associated with, on of space associated with,
Methane's tetrahedral geometry can hybridized orbitals to achieve its fo	be explained using four degenerate our single bonds.
Ethylene's planar geometry can be e hybridized orbitals.	explained using three degenerate
Acetylene's linear geometry is achie	eved viahybridized carbon atoms.
	can be predicted using valence shell electron
	ich focuses on the number ofbonds
	nds are determined by
forces, the attractive forces between	[15.53] [25.63] [25.63] [25.65] [26.65] [26.65] [26.65] [26.65] [27.65] [26.65] [26.65] [27.65] [27.65] [27.65]
	om the interaction between transient
	ger for larger alkanes due to their larger
surface area and ability to accommo	
\$\frac{1}{2}	
ew of Skills	
the blanks and empty boxes below.	To verify that your answers are correct, look
r textbook at the end of Chapter 1. T	he answers appear in the section entitled
uilder Review.	
nilder 1.1 Determining the Constitution of	f Small Molecules
DETERMINE THE VALENCY (NUMBER OF EXPECTED FOR EACH ATOM IN $C_2H_g{\it C}{\it I}$	STEP 2 - DRAW THE STRUCTURE OF $C_2H_3C$ 1 BY PLACING ATOMS WITH THE HIGHEST VALENCY AT THE CENTER, AND PLACING MONOVALENT ATOMS AT THE PERIPHERY
th carbon atom is expected to form bonds.	THE PERSON NAMED IN A PARTY OF THE PERSON NAMED IN THE PERSON NAME
h hydrogen atom is expected to form bonds.	
chlorine atom is expected to form bonds.	

## SkillBuilder 1.2 Drawing the Lewis Dot Structure of an Atom

STEP 1 - DETERMINE THE NUMBER OF VALENCE ELECTRONS

Nitrogen is in Group \_\_\_ of the periodic table, and is expected to have valence electrons. STEP 2 - PLACE ONE ELECTRON BY ITSELF ON EACH SIDE OF THE ATOM

STEP 3 - IF THE ATOM HAS MORE THAN FOUR VALENCE ELECTRONS, PAIR THE REMAINING ELECTRONS WITH THE ELECTRONS ALREADY DRAWN

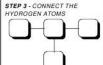
#### SkillBuilder 1.3 Drawing the Lewis Structure of a Small Molecule





STEP 2 - FIRST CONNECT ATOMS THAT FORM MORE THAN ONE BOND

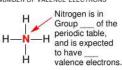




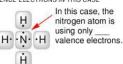
STEP 4 - PAIR ANY UNPAIRED ELECTRONS, SO THAT EACH ATOM ACHIEVES AN OCTET

# SkillBuilder 1.4 Calculating Formal Charge

STEP 1 - DETERMINE THE APPROPRIATE NUMBER OF VALENCE ELECTRONS



STEP 2 - DETERMINE THE NUMBER OF VALENCE ELECTRONS IN THIS CASE



STEP 3 - ASSIGN A FORMAL CHARGE TO THE NITROGEN ATOM IN THIS CASE



## SkillBuilder 1.5 Locating Partial Charges

STEP 1 - CIRCLE THE BONDS BELOW THAT ARE POLAR COVALENT



STEP 2 - FOR EACH POLAR COVALENT BOND. DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT



STEP 3 - INDICATE THE LOCATION OF ALL PARTIAL CHARGES (8+ and 8-)

## SkillBuilder 1.6 Identifying Electron Configurations

STEP 1 - IN THE ENERGY DIAGRAM SHOWN HERE. DRAW THE ELECTRON CONFIGURATION OF NITROGEN (USING ARROWS TO REPRESENT ELECTRONS).



STEP 2 - FILL IN THE BOXES BELOW WITH THE NUMBERS THAT CORRECTLY DESCRIBE THE ELECTRON CONFIGURATION OF NITROGEN



## SkillBuilder 1.7 Identifying Hybridization States



A CARBON ATOM WITH ONE DOUBLE BOND WILL \_\_ HYBRIDIZED



# SkillBuilder 1.8 Predicting Geometry

H

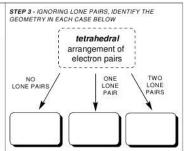
STEP 1 - DETERMINE THE STERIC NUMBER OF THE NITROGEN ATOM BELOW BY ADDING THE NUMBER H-N-HOF SINGLE RONDS AND

LONE PAIRS

# of single bonds =

# of lone pairs = Steric Number = STEP 2 - THE STERIC NUMBER DETERMINES THE HYBRIDIZATION STATE AND ELECTRONIC GEOMETRY. FILL IN

Steric #	Hybridization State	Electronic Geometry
4		
3		
2		



#### SkillBuilder 1.9 Identifying Molecular Dipole Moments

STEP 1 - IDENTIFY THE GEOMETRY OF THE OXYGEN ATOM BELOW



STEP 2 - REDRAW THE COMPOUND. FOR EACH POLAR COVALENT BOND. DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT

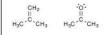


STEP 3 - REDRAW THE COMPOUND, AND DRAW THE NET DIPOLE MOMENT

## SkillBuilder 1.10 Predicting Physical Properties

Dipole-Dipole Interactions CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT

Geometry =



H-Bonding Interactions

CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT

Carbon Skeleton

CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT

# Solutions

1.1.

1.2.

or

## CHAPTER 1

4

1.4.

1.5.

- a) · Ċ · b) : Ċ · c) : Ë · d) H · e) : Br · f) : Ṣ : g) : Cl · h) : I ·
- 1.6. Both nitrogen and phosphorous belong to column 5A of the periodic table, and therefore, each of these atoms has five valence electrons. In order to achieve an octet, we expect each of these elements to form three bonds.
- 1.7. Aluminum is directly beneath boron on the periodic table (Column 3A), and therefore both elements exhibit three valence electrons.
- 1.8. resembles boron because it exhibits three valence electrons.
- 1.9. · c: resembles nitrogen because it exhibits five valence electrons.

1.10.

.11 H The central boron atom lacks an octet of electrons.

1.12

In all of the constitutional isomers above, the nitrogen atom has one lone pair.

1.13.

1.14.

b) Nitrogen has a formal charge

C) Carbon has a formal charge

1.15.

1.16.

1.17.

- a)  $1s^2 2s^2 2p^2$
- b)  $1s^2 2s^2 2p^4$
- c)  $1s^2 2s^2 2p^1$

- d)  $1s^2 2s^2 2p^5$

1.18.

a)  $1s^2 2s^2 2p^3$ 

b)  $1s^2 2s^2 2p^1$ 

c)  $1s^2 2s^2 2p^2$ 

d)  $1s^2 2s^2 2p^5$ 

1.19. The bond angles of an equilateral triangle are 60°, but each bond angle of cyclopropane is supposed to be 109.5°. Therefore, each bond angle is severely strained, causing an increase in energy. This form of strain, called ring strain, will be discussed in Chapter 4. The ring strain associated with a three-membered ring is greater than the ring strain of larger rings, because larger rings do not require bond angles of 60°.

1.20

- a) The C=O bond of formaldehyde is comprised of one sigma bond and one pi bond.
- b) Each C-H bond is formed from the interaction between an  $sp^2$  hybridized orbital from carbon and an s orbital from hydrogen.
- c) The oxygen atom is  $sp^2$  hybridized, so the lone pairs occupy  $sp^2$  hybridized orbitals.
- 1.21. Rotation of a single bond does not cause a reduction in the extent of orbital overlap, because the orbital overlap occurs on the bond axis. In contrast, rotation of a pi bond results in a reduction in the extent of orbital overlap, because the orbital overlap is NOT on the bond axis.

1.22.

All carbon atoms in this molecule are  $s\rho^2$  hybridized, except for the carbon atom highlighted above,

a) which is  $sp^3$  hybridized

The carbon atoms highlighted above are  $sp^3$  hybridized. b) All other carbon atoms in this compound are  $sp^2$  hybridized 1.23.

$$\begin{array}{c}
\mathsf{H} \\
\mathsf{C} = \mathsf{C} = \mathsf{C} \\
\mathsf{H}
\end{array}$$

$$\begin{array}{c}
\mathsf{Sp}^2 \\
\mathsf{H}
\end{array}$$

$$b) H \xrightarrow{\vdots} b f$$

1.24.

c < b < a

a is the longest bond and c is the shortest bond

- 1.25.
- a) The nitrogen atom has three bonds and one lone pair, and is therefore trigonal pyramidal.
- b) The oxygen atom has three bonds and one lone pair, and is therefore trigonal pyramidal.
- c) The boron atom has four bonds and no lone pairs, and is therefore tetrahedral.
- d) The boron atom has three bonds and no lone pairs, and is therefore trigonal planar.
- e) The boron atom has four bonds and no lone pairs, and is therefore tetrahedral.
- f) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.
- g) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.
- h) The carbon atom has four bonds and no lone pairs, and is therefore tetrahedral.

1.26.

All carbon atoms in this molecule are tetrahedral except for the highlighted carbon atom, which is trigonal planar.

The oxygen atom (of the OH group)
has bent geometry,
and the nitrogen atom is trigonal pyramidal.

(a)

(b)

All carbon atoms are tetrahedral except for the carbon atoms highlighted, which are trigonal planar.

The oxygen atom and the highlighted nitrogen atom have bent geometry, and the other nitrogen atom is trigonal pyramidal.

All carbon atoms are trigonal planar.

- 1.27. The carbon atom of the carbocation has three bonds and no lone pairs, and is therefore trigonal planar. The carbon atom of the carbanion has three bonds and one lone pair, and is therefore trigonal pyramidal.
- 1.28. Every carbon atom in benzene is  $sp^2$  hybridized and trigonal planar. Therefore, the entire molecule is planar (all of the atoms in this molecule occupy the same plane).

1.29.

- 1.30. CHCl<sub>3</sub> is expected to have a larger dipole moment than CBrCl<sub>3</sub>, because the bromine atom in the latter compound serves to nearly cancel out the effects of the other three chlorine atoms (as is the case in CCl<sub>4</sub>).
- 1.31. The carbon atom of CO<sub>2</sub> has a steric number of two, and therefore has linear geometry. As a result, the individual dipole moments of each C=O bond cancel each other completely to give no overall molecular dipole moment. In contrast, the sulfur atom in SO<sub>2</sub> has a steric number of three (because it also has a lone pair, in addition to the two S=O bonds), which means that it has bent geometry. As a result, the individual dipole moments of each S=O bond do NOT cancel each other completely, and the molecule does have a molecular dipole moment.

- 1.32.
- a) The latter, because it is less branched.
- b) The latter, because it has more carbon atoms.
- c) The latter, because it has an OH bond.
- d) The former, because it is less branched.

## 1.33.

1.34.

# 1.35.

a)

1.36.

1.37.

- a) NaBr, because the difference in electronegativity between Na and Br is greater than the difference in electronegativity between H and Br.
- b) FCl, because the disparity in electronegativity between F and Cl is greater than the disparity in electronegativity Br and Cl.

1.38.

1.39.

All carbon atoms in this molecule are tetrahedral except for the carbon atom bearing the negative charge, which is trigonal pyramidal.

The highlighted carbon atom is tetrahedral, and the other two carbon atoms are trigonal planar.

The oxygen atom is trigonal pyramidal.

Both carbon atoms and the nitrogen atom are tetrahedral. The oxygen atom is bent.

All three carbon atoms in this molecule are tetrahedral. The geometry of the oxygen atom is not relevant because it is only attached to one other group.

1.40.

The nitrogen atom has trigonal pyramidal geometry. The compound is expected to have the following molecular dipole moment:

1.41.

The central aluminum has tetrahedral geometry.

1.42.

1.43.

- a) No
- b) Yes
- c) Yes
- d) No
- 5) No
- 6)Yes

1.44.

- a) Oxygen b) Fluorine
- c) Carbon
- d) Nitrogen
- e) Chlorine

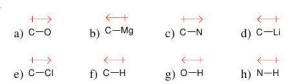
1.45.

- a) ionic
- b) Na-O is ionic, and O-H is polar covalent
- Na-O is ionic, O-C is polar covalent, and each C-H bond is covalent
- d) The O-H and C-O bonds are polar covalent, and each C-H bond is covalent
- e) The C=O bond is polar covalent, and each C-H bond is covalent

1.46.

## 1.47.

## 1.48.



## 1.49.

- a) All bond angles are approximately 109.5°, except for the C-O-H bond angle which is expected to be less than 109.5° as a result of the repulsion of the lone pairs on the oxygen.
- b) All bond angles are approximately 120°.
- c) All bond angles are approximately 120°.
- d) All bond angles are 180°.
- e) All bond angles are approximately 109.5°, except for the C-O-C bond angle which is expected to be less than 109.5° as a result of the repulsion of the lone pairs on the oxygen.
- f) All bond angles are approximately 109.5°.
- g) All bond angles are approximately 109.5°.
- h) All bond angles are approximately  $109.5^{\circ}$  except for the C-C $\equiv$ N bond angle which is  $180^{\circ}$ .

# 1.50.

- a) sp<sup>3</sup>, trigonal pyramidal
- b)  $sp^2$ , trigonal planar
- c) sp<sup>2</sup>, trigonal planar
- d)  $sp^3$ , trigonal pyramidal
- e)  $sp^3$ , trigonal pyramidal

# 1.51. Sixteen sigma bonds and three pi bonds.

#### 1.52.

- a) the second, because it possesses an O-H bond.
- b) the second, because it has more carbon atoms.
- c) the first, because it has a polar bond.

#### 1.53.

- a) yes
- b) no (this compound can serve as a hydrogen bond acceptor, but not a hydrogen bond donor)
- c) no

- d) no
- e) no (this compound can serve as a hydrogen bond acceptor, but not a hydrogen bond donor)
- f) yes
- g) no
- h) yes
- 1.54.
- a) 3
- b) 4
- c) 3
- d) 2

1.55.

The highlighted carbon atoms are  $sp^2$  hybridized and trigonal planar. The remaining four carbon atoms are sp hybridized and linear.

The highlighted carbon atom is  $sp^2$  hybridized and trigonal planar. The remaining three carbon atoms are  $sp^3$  hybridized and tetrahedral.

All carbon atoms are  $\mathit{sp}^3$  hybridized and tetrahedral.

1.56.

The highlighted carbon atoms are  $sp^3$  hybridized and tetrahedral. The remaining carbon atoms are  $sp^2$  hybridized and trigonal planar.

1.57.

- a) oxygen
- b) fluorine
- c) carbon

1.58.

$$sp^2$$
, bent

H

C

H

H

Sp<sup>3</sup>, trigonal pyramidal

H

C

H

H

H

H

H

H

H

H

H

nicotine

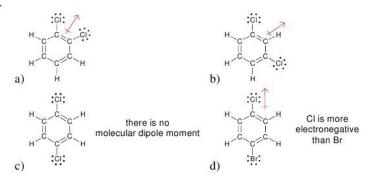
1.59.

caffeine

1.60. The two isomers are:

The first will have a higher boiling point because it possesses an OH group which can form hydrogen bonds.

1.61.



- 1.62. The third chlorine atom in chloroform partially cancels the effects of the other two chlorine atoms, thereby reducing the molecular dipole moment relative to methylene chloride.
- 1.63.
- a) Compound A and Compound B
- b) Compound B
- c) Compound B
- d) Compound C
- e) Compound C
- f) Compound A
- g) Compound B
- h) Compound A is capable of hydrogen bonding

# 1.64.

a)

b)

c)

d)

NEC-CEC-CEC-CEN

1.65.

1.66.

1.67.

# Chapter 2 Molecular Representations

# **Review of Concepts**

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

In bond-l	ine structures,	atoms and most	atoms are not drawn.
		haracteristic group of atom	s/bonds that show a
	le behavior.		
		ither a positive charge or a	negative charge, it will
	, rather th		
		dge represents a group con	ning the page,
while a d	ash represents a gro	oup the page.	
	arrows are too	ols for drawing resonance s	tructures.
When dra	wing curved arrow	s for resonance structures,	avoid breaking a
	name i anno a la farita de la companie de la filipa de la companie de la filipa de la companie de la filipa de	for second-row	200 Mg (190 MB)
There are	three rules for ider	ntifying significant resonan	ce structures:
1. M	inimize		
	lectronegative atom	s can bear a positive chargerons.	e, but only if they possess
3. A	void drawing a reso char	onance structure in which to ges.	wo carbon atoms bear
A	lone pai	r participates in resonance	and is said to occupy a
orbi	tal.	T 200	7-7
A	lone pair	does not participate in reso	nance.

# **Review of Skills**

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. The answers appear in the section entitled *SkillBuilder Review*.

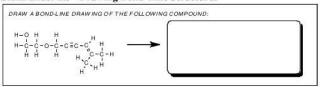
## SkillBuilder 2.1 Converting Between Different Drawing Styles

DRAW THE LEWIS STRUCTURE OF THE FOL	LOW ING COMPOUND
(CH <sub>3</sub> ) <sub>3</sub> COCH <sub>3</sub>	

#### SkillBuilder 2.2 Reading Bond-Line Structures



## SkillBuilder 2.3 Drawing Bond-Line Structures



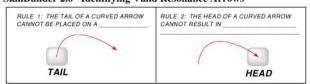
## SkillBuilder 2.4 Identifying Lone Pairs on Oxygen Atoms



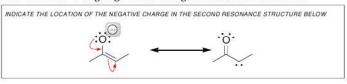
## SkillBuilder 2.5 Identifying Lone Pairs on Nitrogen Atoms



## SkillBuilder 2.6 Identifying Valid Resonance Arrows

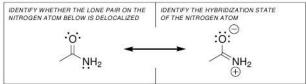


## SkillBuilder 2.7 Assigning Formal Charges in Resonance Structures



## SkillBuilder 2.8 Drawing Significant Resonance Structures

# SkillBuilder 2.9 Identifying Localized and Delocalized Lone Pairs



- 2.2 (CH<sub>3</sub>)<sub>3</sub>CÖCH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>CHÖCH<sub>2</sub>CH<sub>3</sub>
- 2.3 Six
- 2.4 H<sub>2</sub>C=CHCH<sub>3</sub>

2.5.

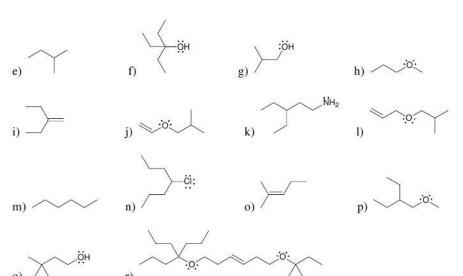
2.6

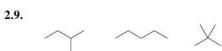
- a) decrease  $(7 \rightarrow 6)$
- c) no change  $(8 \rightarrow 8)$
- b) no change  $(8 \rightarrow 8)$
- d) increase  $(5 \rightarrow 7)$

2.7

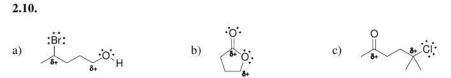
- a) increase  $(12 \rightarrow 14)$
- b) decrease  $(8 \rightarrow 6)$

2.8.

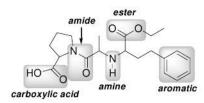




 $\sim$   $\times$ 



2.11.

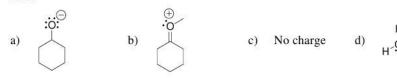


# 2.12.

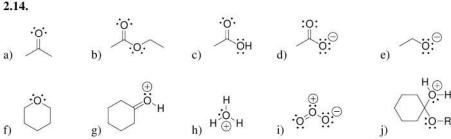
alcohol



# 2.13.



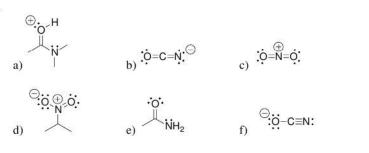
## 2.14.



2.15. There are no hydrogen atoms attached to the central carbon atom. The carbon atom has four valence electron. Two valence electrons are being used to form bonds, and the remaining two electrons are a lone pair. This carbon atom is using the appropriate number of valence electrons.

## 2.16.

2.17.



2.18.

a) one b) zero c) one d) five

# 2.19 Five lone pairs:

$$\begin{array}{c} \overset{\bullet}{\circ}\overset{\bullet}{\circ} \\ \text{$\oplus$NH$}_3 \end{array} \overset{\circ}{\circ} \overset{\circ}{\circ}$$

## 2.20

a)
HO
Troglitazone

Rosiglitazone

Pioglitazone

b) Yes, it contains the likely pharmacophore highlighted above.

## 2.21

- a) Violates second rule by giving a fifth bond to a nitrogen atom.
- b) Does not violate either rule.
- c) Violates second rule by giving five bonds to a carbon atom.
- d) Violates second rule by giving three bonds and two lone pairs to an oxygen atom.
- e) Violates second rule by giving five bonds to a carbon atom.
- f) Violates second rule by giving five bonds to a carbon atom.
- g) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.
- h) Violates second rule by giving five bonds to a carbon atom, and violates second rule by breaking a single bond.
- i) Does not violate either rule.
- j) Does not violate either rule.
- k) Violates second rule by giving five bonds to a carbon atom.
- l) Violates second rule by giving five bonds to a carbon atom.

## 2.22.

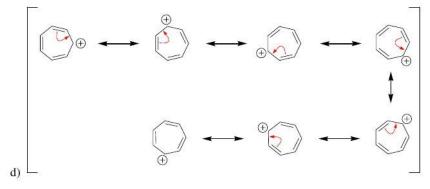
#### 2.23.

$$_{a)}\Big[ \underset{\oplus}{ \longleftrightarrow} \underset{\oplus}{ \longleftrightarrow} \Big] \qquad \qquad \underset{b)}{ \left[ \underset{\ominus}{ \longleftrightarrow} \underset{\ominus}{ \longleftrightarrow} \underset{\ominus}{ \longleftrightarrow} \Big] } \Big]$$

$$\operatorname{d}_{\mathrm{d}} \left[ \begin{array}{c} \ddot{\mathsf{n}} \\ \vdots \\ \ddot{\mathsf{n}} \end{array} \right]$$

2.26.

$$\begin{bmatrix} \bigoplus_{a} & \bigoplus_{b} & \bigoplus_{b} \end{bmatrix} \qquad \begin{bmatrix} \bigoplus_{b} & \bigoplus_{c} & \bigoplus_{c}$$



2.27.

2.28.

2.29.

2.30.

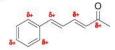
$$\begin{bmatrix} HO & OH & HO & OH \\ H_2N & & & H_2N & & \end{bmatrix}$$

# 2.32.

a) 
$$\begin{bmatrix} \dot{N} & \dot{M} & \dot{O} & \dot{M} & \dot{O} & \dot{M} & \dot{O} & \dot{M} & \dot{$$

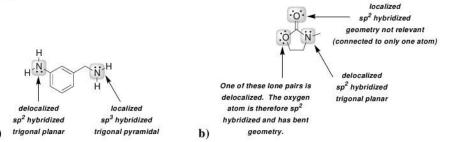
2.33.

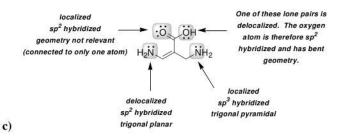
# 2.34.

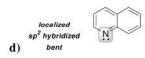


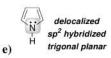
## 2.35.

## 2.36.

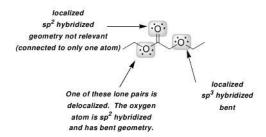








f)



**2.37.** Both lone pairs are localized and, therefore, both are expected to be reactive.

2.38.

2.39.

2.40.

$$\sim$$
  $\downarrow$ 

2.41.

$$\sim$$
  $\downarrow$   $\times$ 

2.42.

# 2.43. Twelve (each oxygen atom has two lone pairs)

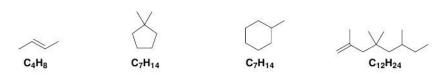
## 2.44.

# 2.45.

## 2.46.

$$C_4H_{10}$$
  $C_6H_{14}$   $C_8H_{18}$   $C_{12}H_{26}$ 

In each of the compounds above, the number of hydrogen atoms is equal to two times the number of carbon atoms, plus two.



In each of the compounds above, the number of hydrogen atoms is two times the number of carbon atoms.

c) 
$$- = -\langle \qquad \qquad \downarrow \qquad \qquad \downarrow \\ C_6H_{10} \qquad C_9H_{16} \qquad C_9H_{16} \qquad C_7H_{12}$$

In each of the compounds above, the number of hydrogen atoms is two times the number carbon atoms, minus two.

d) A compound with molecular formula  $C_{24}H_{48}$  must have either one double bond or one ring. It cannot have a triple bond, but it may have a double bond.

- 2.47.
- a) an sp2 hybridized atomic orbital
- b) a p orbital
- c) a p orbital
- 2.48.

- 2.49.
- a) (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>
- b) (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH
- c) CH<sub>3</sub>CH<sub>2</sub>CH=C(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>

## 2.50.

- a) C<sub>9</sub>H<sub>20</sub>
- b) C<sub>6</sub>H<sub>14</sub>O
- c) C<sub>8</sub>H<sub>16</sub>

## 2.51.

(d) is not a valid resonance structure, because it violates the octet rule. The nitrogen atom has five bonds in this drawing, which is not possible, because the nitrogen atom only has four orbitals with which it can form bonds.

## 2.52. 15 carbon atoms and 18 hydrogen atoms:

## 2.53.

# 2.54.

$$\downarrow$$

## 2.55.

$$\begin{bmatrix} H_{\stackrel{\bullet}{N}} H & H_{\stackrel{\bullet}{N}} H & H_{\stackrel{\bullet}{N}} H & H_{\stackrel{\bullet}{N}} H & H_{\stackrel{\bullet}{N}} H \\ & & & & & & & & & & & & & \end{bmatrix}$$

**2.56.** These structures do not differ in their connectivity of atoms. They differ only in the placement of electrons, and are therefore resonance structures.

# 2.57.

- a) constitutional isomers
- b) same compound
- c) different compounds that are not isomeric
- d) constitutional isomers

# 2.58.

a) 
$$b$$
  $c$   $b$ 

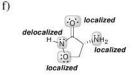
**2.59.** The nitronium ion does *not* have any significant resonance structures because any attempts to draw a resonance structure will either 1) exceed an octet for the nitrogen atom or 2) generate a nitrogen atom with less than an octet of electrons, or 3) generate a structure with three charges. The first of these would not be a valid resonance structure, and the latter two would not give significant resonance structures.

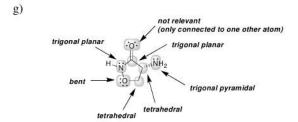
2.60.

**2.61.** Both nitrogen atoms are sp<sup>2</sup> hybridized and trigonal planar, because in each case, the lone pair participates in resonance.

## 2.63.

- a) The molecular formula is C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>
- b) There are two  $sp^3$  hybridized carbon atoms
- c) There is one  $sp^2$  hybridized carbon atom
- d) There are no sp hybridized carbon atoms
- e) There are six lone pairs (each nitrogen atom has one lone pair and each oxygen atom has two lone pairs)





## 2.64.

- a) The molecular formula is C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>
- b) There are nine  $sp^3$  hybridized carbon atoms
- c) There is seven  $sp^2$  hybridized carbon atoms
- d) There are no sp hybridized carbon atoms
- There are five lone pairs (the nitrogen atom has one lone pair and each oxygen atom has two lone pairs)
- f) The lone pairs on the oxygen of the C=O bond are localized. One of the lone pairs on the other oxygen atom is delocalized. The lone pair on the nitrogen atom is delocalized.
- g) All  $sp^2$  hybridized carbon atoms are trigonal planar. All  $sp^3$  hybridized carbon atoms are tetrahedral. The nitrogen atom is trigonal planar. The oxygen atom of the C=O bond does not have a geometry because it is connected to only one other atom, and the other oxygen atom has bent geometry.

2.65.

## 2.66.

a) Compound B has one additional resonance structure that Compound A lacks, because of the relative positions of the two groups on the aromatic ring. Specifically, Compound B has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:

Compound A does *not* have a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge. That is, Compound A has fewer resonance structures than Compound B. Accordingly, Compound B has greater resonance stabilization.

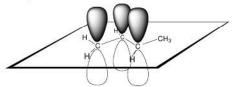
b) Compound C is expected to have resonance stabilization similar to that of Compound B, because Compound C also has a resonance structure in which one oxygen atom has a negative charge and the other oxygen atom has a positive charge:

## 2.67.

The single bond mentioned in this problem has some double bond character, as a result of resonance:



Each of the carbon atoms of this single bond uses an atomic p orbital to form a conduit (as described in Section 2.7):



Rotation about this single bond will destroy the overlap of the p orbitals, thereby destroying the resonance stabilization. This single bond therefore exhibits a large barrier to rotation.