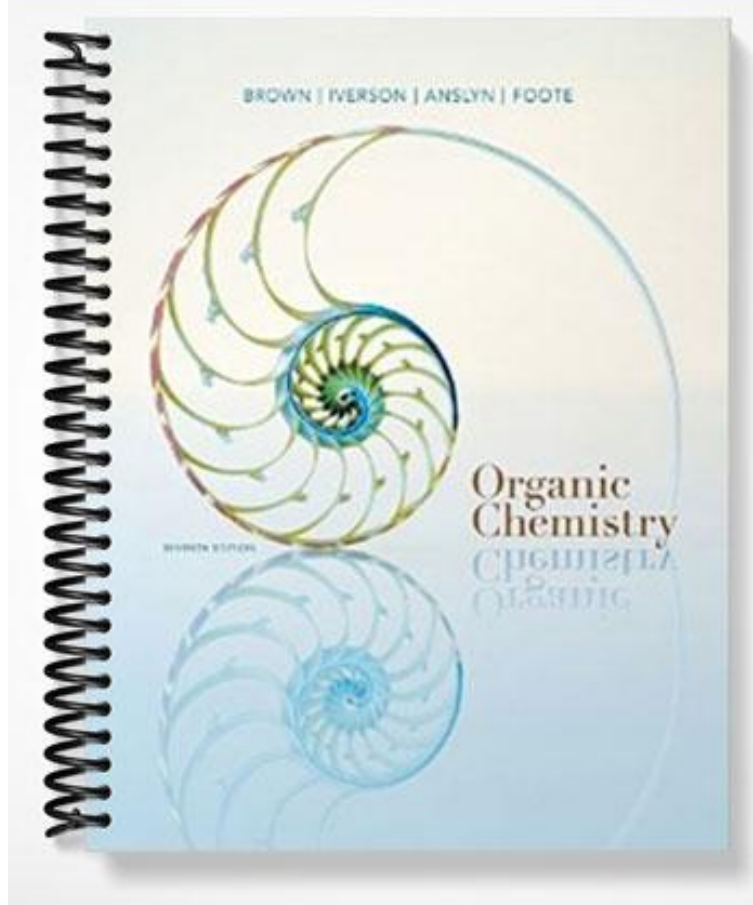


# SOLUTIONS MANUAL



**CHAPTER 1**  
*Solutions to the Problems*

**Problem 1.1** Write and compare the ground-state electron configurations for each pair of elements:

(a) Carbon and silicon

**C (6 electrons)**  $1s^2 2s^2 2p^2$

**Si (14 electrons)**  $1s^2 2s^2 2p^6 3s^2 3p^2$

**Both carbon and silicon have four electrons in their outermost (valence) shells.**

(b) Oxygen and sulfur

**O (8 electrons)**  $1s^2 2s^2 2p^4$

**S (16 electrons)**  $1s^2 2s^2 2p^6 3s^2 3p^4$

**Both oxygen and sulfur have six electrons in their outermost (valence) shells.**

(c) Nitrogen and phosphorus

**N (7 electrons)**  $1s^2 2s^2 2p^3$

**P (15 electrons)**  $1s^2 2s^2 2p^6 3s^2 3p^3$

**Both nitrogen and phosphorus have five electrons in their outermost (valence) shells.**

**Problem 1.2** Show how each chemical change leads to a stable octet.

(a) Sulfur forms  $S^{2-}$ .

(b) Magnesium forms  $Mg^{2+}$ .

**S (16 electrons):**  $1s^2 2s^2 2p^6 3s^2 3p^4$

**Mg (12 electrons):**  $1s^2 2s^2 2p^6 3s^2$

**$S^{2-}$  (18 electrons):**  $1s^2 2s^2 2p^6 3s^2 3p^6$

**$Mg^{2+}$  (10 electrons):**  $1s^2 2s^2 2p^6$

**Problem 1.3** Judging from their relative positions in the Periodic Table, which element in each set is more electronegative?

(a) Lithium or potassium

**In general, electronegativity increases from left to right across a row and from bottom to top of a column in the Periodic Table. This is because electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Lithium is closer to the top of the Periodic Table and thus more electronegative than potassium.**

(b) Nitrogen or phosphorus

**Nitrogen is closer to the top of the Periodic Table and thus more electronegative than phosphorus.**

(c) Carbon or silicon

**Carbon is closer to the top of the Periodic Table and thus more electronegative than silicon.**

**Problem 1.4** Classify each bond as nonpolar covalent, or polar covalent, or state that ions are formed.

(a) S-H (b) P-H (c) C-F (d) C-Cl

**Recall that bonds formed from atoms with an electronegativity difference of less than 0.5 are considered nonpolar covalent and with an electronegativity difference of 0.5 or above are considered a polar covalent bond.**

Bond	Difference in electronegativity	Type of bond
S-H	$2.5 - 2.1 = 0.4$	Nonpolar covalent
P-H	$2.1 - 2.1 = 0$	Nonpolar covalent
C-F	$4.0 - 2.5 = 1.5$	Polar covalent
C-Cl	$3.0 - 2.5 = 0.5$	Polar covalent

**Problem 1.5** Using the symbols  $\delta^-$  and  $\delta^+$ , indicate the direction of polarity in each polar covalent bond.

(a) C-N

$\delta^+$  C  $\delta^-$  N

**Nitrogen is more electronegative than carbon**

(b) N-O

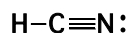
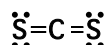
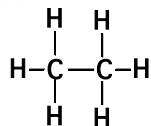
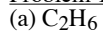
$\delta^+$  N  $\delta^-$  O

**Oxygen is more electronegative than nitrogen**

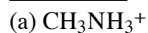


**Chlorine is more electronegative than carbon**

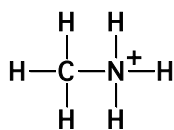
**Problem 1.6** Draw Lewis structures, showing all valence electrons, for these molecules.



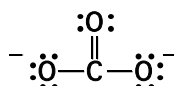
**Problem 1.7** Draw Lewis structures for these ions, and show which atom in each bears the formal charge.



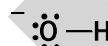
Methylammonium ion



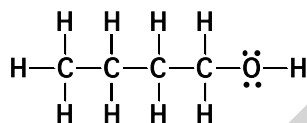
Carbonate ion



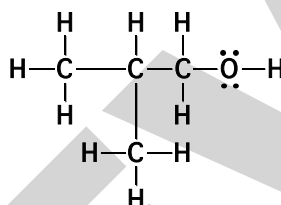
Hydroxide ion



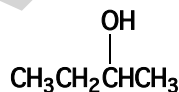
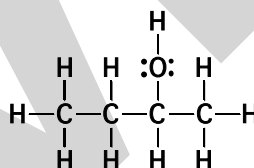
**Problem 1.8** Draw Lewis structures and condensed structural formulas for the four alcohols with molecular formula C<sub>4</sub>H<sub>10</sub>O. Classify each alcohol as primary, secondary, or tertiary.



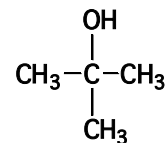
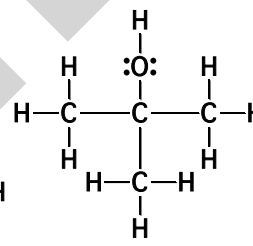
Primary



Primary

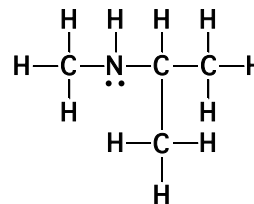
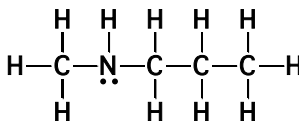
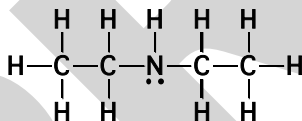


Secondary

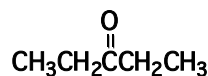
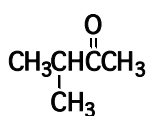
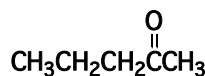


Tertiary

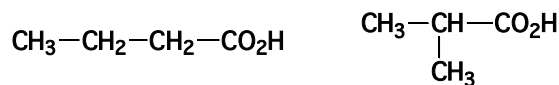
**Problem 1.9** Draw structural formulas for the three secondary amines with molecular formula C<sub>4</sub>H<sub>11</sub>N.



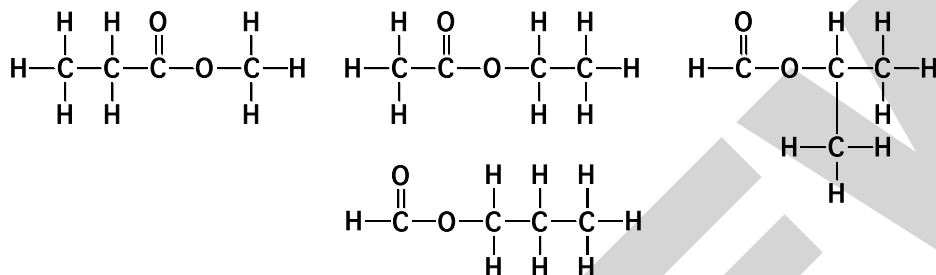
**Problem 1.10** Draw condensed structural formulas for the three ketones with molecular formula C<sub>5</sub>H<sub>10</sub>O.



**Problem 1.11** Draw condensed structural formulas for the two carboxylic acids with molecular formula  $C_4H_8O_2$ .

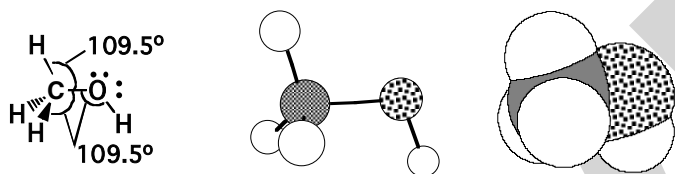


**Problem 1.12** Draw structural formulas for the four esters with molecular formula  $C_4H_8O_2$ .

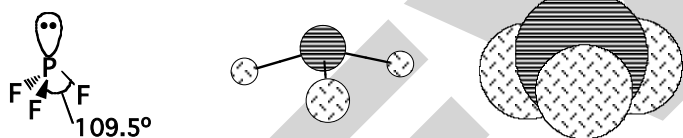


**Problem 1.13** Predict all bond angles for these molecules.

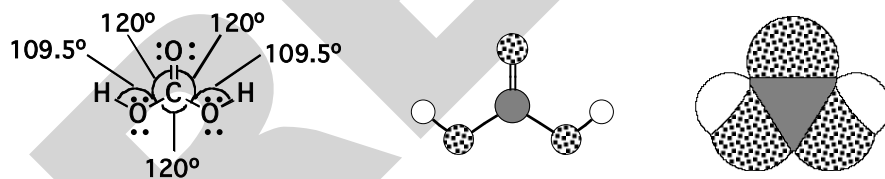
(a)  $CH_3OH$



(b)  $PF_3$



(c)  $H_2CO_3$  (Carbonic Acid)



### MCAT Practice: Questions Fullerenes

A. The geometry of carbon in diamond is tetrahedral, while carbon's geometry in graphite is trigonal planar. What is the geometry of the carbons in  $C_{60}$ ?

1. They are all tetrahedral.
2. They are all trigonal planar.
3. They are all pyramidal with bond angles near  $109.5^\circ$ .
4. **They are not perfectly trigonal planar but have an extent of pyramidalization. The curve of the buckyball surface is curved requiring some extent of pyramidalization.**

B. Because of their spherical shape,  $C_{60}$  molecules are used as nanoscale ball bearings in grease and lubricants. We can estimate the size of these ball bearings by examining C-C bond distances. Carbon-carbon bond distances vary between approximately 120 pm (pm = picometers) and 155 pm. Roughly, what is the diameter of  $C_{60}$ ?

1. 10 pm
2. 100 pm
3. **1,000 pm  $C_{60}$  is approximately 8 bonds across so approximately 1,000 pm in diameter.**
4. 10,000 pm

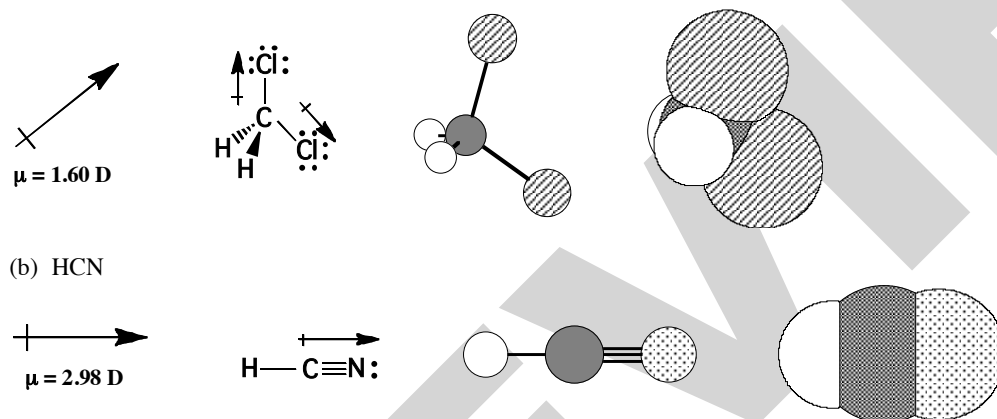
C. What best describes the C-C-C bond angles in  $C_{60}$ ?

1. They are exactly  $120^\circ$ .
2. They are a bit larger than  $120^\circ$ .
3. **They are a bit smaller than  $120^\circ$ . The five-membered rings in the  $C_{60}$  structure reduce bond angles.**
4. They are near  $109.5^\circ$ .

**Problem 1.14** Which molecules are polar? For each molecule that is polar, specify the direction of its dipole moment.

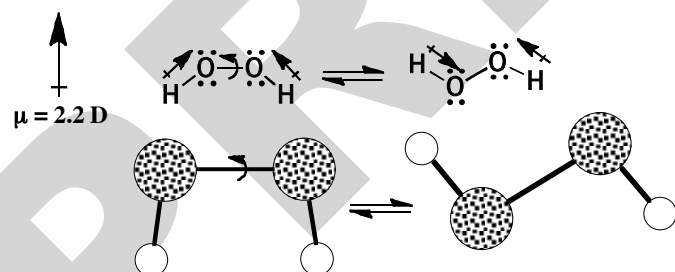
(a)  $CH_2Cl_2$

A molecular dipole moment is determined as the vector sum of the bond dipoles in three-dimensional space. Thus, by superimposing the bond dipoles on a three-dimensional drawing, the molecular dipole moment can be determined. Note that on the following diagrams, the dipole moments from the C-H bonds are ignored because they are small.

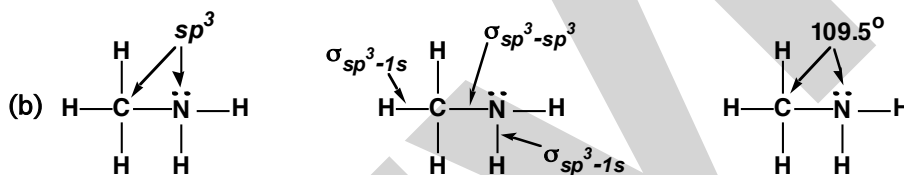
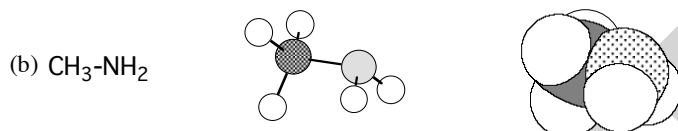
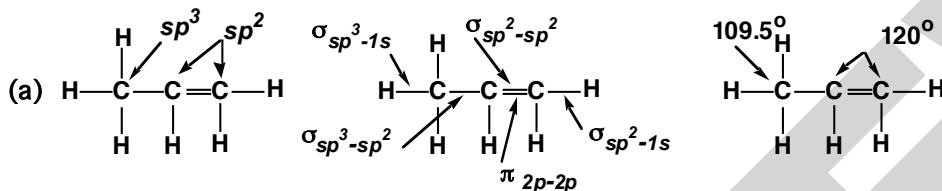
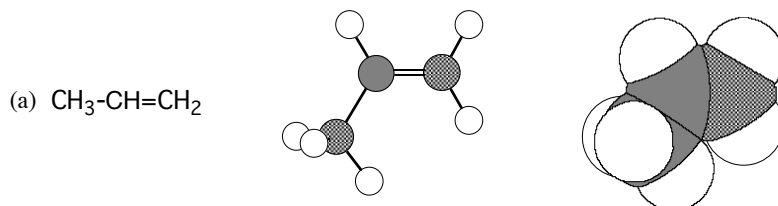


(c)  $H_2O_2$

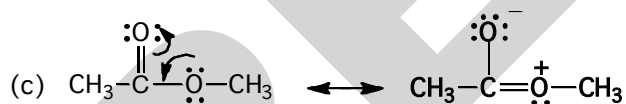
The  $H_2O_2$  molecule can rotate around the O-O single bond, so we must consider the molecular dipole moments in the various possible conformations. Conformations such as the one on the left have a net molecular dipole moment, while conformations such as the one the right below do not. The presence of at least some conformations (such as that on the left) that have a molecular dipole moment means that the entire molecule must have an overall dipole moment, in this case  $\mu = 2.2$  D.



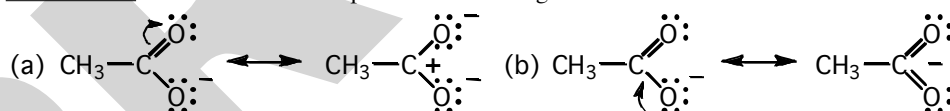
**Problem 1.15** Describe the bonding in these molecules in terms of hybridization of C and N, and the types of bonds between carbon and nitrogen, and if there are any lone pairs, describe what type of orbital contains these electrons.



**Problem 1.16** Draw the contributing structure indicated by the curved arrows. Show all valence electrons and all formal charges.

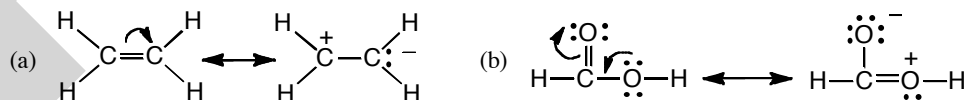


**Problem 1.17** Which sets are valid pairs of contributing structures?



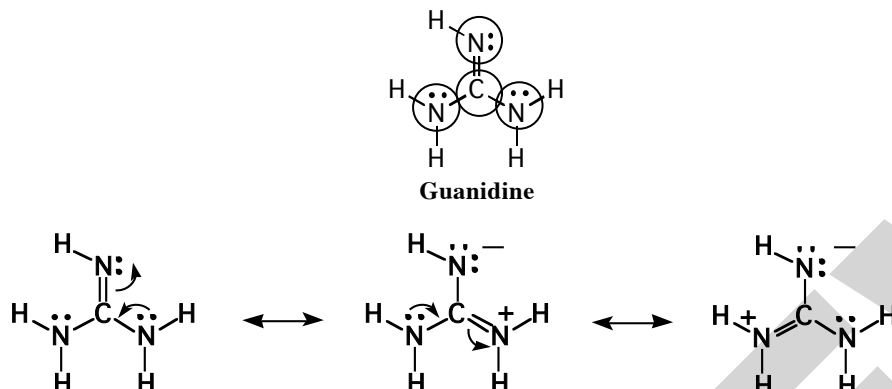
The set in (a) is a pair of contributing structures, while the set in (b) is not. The structure on the right in set (b) is not a viable contributing structure because there are five bonds to the carbon atom, implying 10 electrons in the valence shell, which can only hold a maximum of 8 electrons.

**Problem 1.18** Estimate the relative contribution of the members in each set of contributing structures.

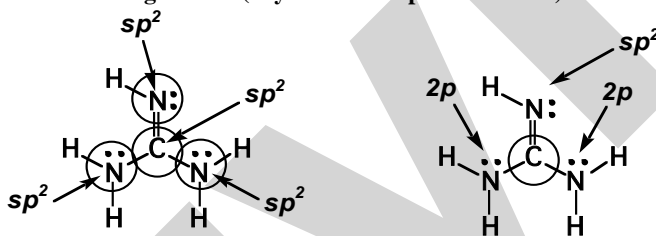


The first structure makes the greater contribution in (a) and (b). In both cases, the second contributing structure involves the disfavored creation and separation of unlike charges.

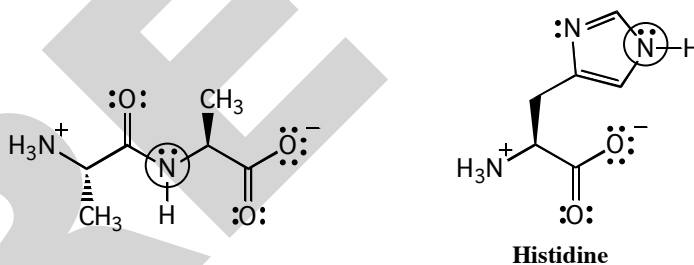
**Problem 1.19** Draw three contributing structures of the following compound (called guanidine) and state the hybridization of the four highlighted atoms. In which orbitals do the three lone pairs drawn reside



Remember that if any significant contributing structure contains a  $\pi$  bond, then the hybridization of that atom must be able to accommodate the  $\pi$  bond. Consideration of the three significant contributing structures indicates that all of the nitrogen atoms are  $sp^2$  hybridized because of the  $\pi$  bonding. To be consistent with the contributing structures, two of the lone pairs on the original structure are in  $2p$  orbitals, while the third resides in an  $sp^2$  orbital. Guanidine is one of many examples you will encounter in which the lone pair on nitrogen is delocalized into an adjacent  $\pi$  bond. Such delocalization of electron density in  $\pi$  orbitals is stabilizing and therefore favorable, a phenomenon that is best explained using quantum mechanical arguments (beyond the scope of this text).



MCAT Practice: Questions  
VSEPR and Resonance



A. What is the hybridization state of the circled nitrogens. What kind of orbital contains the lone pairs identified in these circles?

1.  $sp^3$ ,  $2p$
2.  $sp^3$ ,  $sp^2$
3.  $sp^3$ ,  $2p$

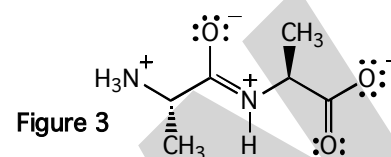
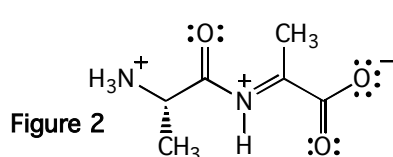
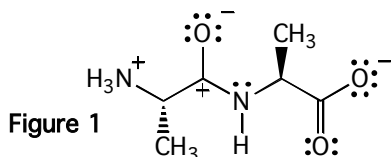
4.  $sp^2$ ,  $2p$  The circled N atoms are each part of delocalized pi systems explaining their  $sp^2$  hybridization. Write contributing structures to help understand this point. An  $sp^2$  hybridized N atom with bonds to three other atoms must have the lone pair in  $2p$  orbital.

B. The molecule shown on the right in the example is the amino acid histidine, and the five-membered ring is known as aromatic. An aromatic ring has 2, 6, 10, or 14, etc. electrons placed in  $p$ -orbitals around a ring. Indicate which statements must therefore also be true.

1. There are a total of 6 electrons in the pi system (defined as electrons in  $p$ -orbitals), including the lone pair that is on the ring N that is not circled.
2. There are a total of 6 electrons in the pi system, including the lone pair that is on the ring N atom that is circled.
3. The lone pair on the ring N atom that is not circled resides in an  $sp^2$  orbital on an  $sp^2$  hybridized nitrogen atom.

4. Both B and C. A lone pair will be part of an aromatic pi system if it contributes to the aromatic number (in this case 6 pi electrons) like the circled N atom, while a lone pair will be in an  $sp^2$  orbital of the N atom already has a pi bond without counting the lone pair like the non-circled N atom.

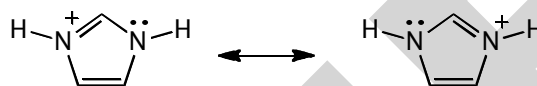
C. Which of the following are reasonable contributing structures for the amide bond of the molecule shown on the left in the example above?



1. Figure 1
2. Figure 2
3. Figure 3

**4. Both Figures 1 and 3. Figure 2 makes no sense because it involves removal of an H atom so is therefore not a contributing structure. Both 1 and 3 are reasonable contributing structures for an amide bond.**

D) The following structure is called imidazolium. Which of the following statements about imidazolium are true?



**Imidazolium**

- Both nitrogens are  $sp^2$  hybridized, and the lone pair of electrons is in  $2p$  orbitals.
- The nitrogen on the right is  $sp^3$  hybridized while the nitrogen on the left is  $sp^2$  hybridized, and the lone pair of electrons shown is in an  $sp^3$  hybrid orbital.
- The molecule has an identical contributing structure not shown.
- The molecule has no reasonable contributing structures.

**1. Statements a. and c. are true. Both N atoms in imidazolium are  $sp^2$  hybridized and there is a symmetric contributing structure that moves the upper double bond and interconverts the locations of the plus charge and lone pair as shown above.**

2. Statements a. and d. are true.

3. Statements b. and c. are true.

4. Statements b. and d. are true.

### Electronic Structures of Atoms

**Problem 1.20** Write ground-state electron configuration for each atom. After each atom is its atomic number in parentheses.

(a) Sodium (11) **Na (11 electrons)  $1s^2 2s^2 2p^6 3s^1$**

(b) Magnesium (12) **Mg (12 electrons)  $1s^2 2s^2 2p^6 3s^2$**

(c) Oxygen (8) **O (8 electrons)  $1s^2 2s^2 2p^4$**

(d) Nitrogen (7) **N (7 electrons)  $1s^2 2s^2 2p^3$**

**Problem 1.21** Identify the atom that has each ground-state electron configuration.

(a)  $1s^2 2s^2 2p^6 3s^2 3p^4$

**Sulfur (16) has this ground-state electron configuration**

(b)  $1s^2 2s^2 2p^4$

**Oxygen (8) has this ground-state electron configuration**

**Problem 1.22** Define valence shell and valence electron.

**The valence shell is the outermost occupied shell of an atom. A valence electron is an electron in the valence shell.**

**Problem 1.23** How many electrons are in the valence shell of each atom?

(a) Carbon

**With a ground-state electron configuration of  $1s^2 2s^2 2p^2$ , there are four electrons in the valence shell of carbon.**

(b) Nitrogen

**With a ground-state electron configuration of  $1s^2 2s^2 2p^3$ , there are five electrons in the valence shell of nitrogen.**



(c) Chlorine

With a ground-state electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^5$ , there are seven electrons in the valence shell of chlorine.

(d) Aluminum

With a ground-state electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^1$ , there are three electrons in the valence shell of aluminum.

### Lewis Structures and Formal Charge

**Problem 1.24** Judging from their relative positions in the Periodic Table, which atom in each set is more electronegative?

(a) Carbon or nitrogen

In general, electronegativity increases from left to right across a row (period) and from bottom to top of a column in the Periodic Table. This is because electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Nitrogen is farther to the right than carbon in Period 2 of the Periodic Table. Thus, nitrogen is more electronegative than carbon.

(b) Chlorine or bromine

Chlorine is higher up than bromine in column 7A of the Periodic Table. Thus, chlorine is more electronegative than bromine.

(c) Oxygen or sulfur

Oxygen is higher up than sulfur in column 6A of the Periodic Table. Thus, oxygen is more electronegative than sulfur.

**Problem 1.25** Which compounds have nonpolar covalent bonds, which have polar covalent bonds, and which have ions?

(a) LiF      (b)  $\text{CH}_3\text{F}$       (c)  $\text{MgCl}_2$       (d) HCl

Using the rule that ions are formed between atoms with an electronegativity difference of 1.9 or greater, the following table can be constructed:

Bond	Difference in electronegativity	Type of bond
Li-F	$4.0 - 1.0 = 3.0$	Ions
C-H	$2.5 - 2.1 = 0.4$	Nonpolar covalent
C-F	$4.0 - 2.5 = 1.5$	Polar covalent
Mg-Cl	$3.0 - 1.2 = 1.8$	Polar covalent
H-Cl	$3.0 - 2.1 = 0.9$	Polar covalent

Based on these values, only LiF has ions. The other compounds have nonpolar covalent (C-H) or polar covalent (C-F, Mg-Cl, H-Cl) bonds.

**Problem 1.26** Using the symbols  $\delta^-$  and  $\delta^+$ , indicate the direction of polarity, if any, in each covalent bond.

(a) C-Cl       $\delta^+ \quad \delta^-$   
C-Cl      Chlorine is more electronegative than carbon.

(b) S-H       $\delta^- \quad \delta^+$   
S-H      Sulfur is more electronegative than hydrogen.

(c) C-S      Carbon and sulfur have the same electronegativity so there is no polarity in a C-S bond.

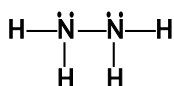
(d) P-H      Phosphorus and hydrogen have the same electronegativity, so there is no polarity in a P-H bond.

**Problem 1.27** Write Lewis structures for these compounds. Show all valence electrons. None of them contains a ring of atoms.

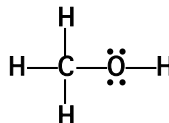
(a)  $\text{H}_2\text{O}_2$   
Hydrogen peroxide



(b)  $\text{N}_2\text{H}_4$   
Hydrazine

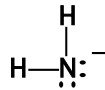


(c)  $\text{CH}_3\text{OH}$   
Methanol

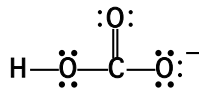


**Problem 1.28** Write Lewis structures for these ions. Show all valence electrons and all formal charges.

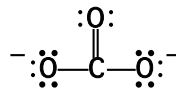
(a)  $\text{NH}_2^-$   
Amide ion



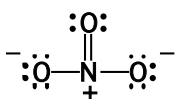
(b)  $\text{HCO}_3^-$   
Bicarbonate ion



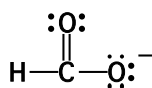
(c)  $\text{CO}_3^{2-}$   
Carbonate ion



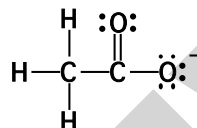
(d)  $\text{NO}_3^-$   
Nitrate ion



(e)  $\text{HCOO}^-$   
Formate ion

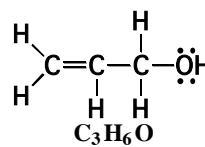
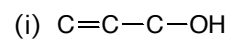
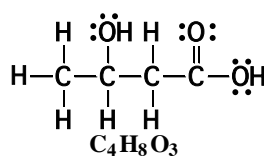
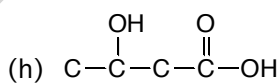
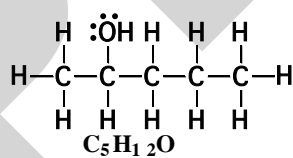
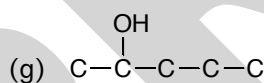
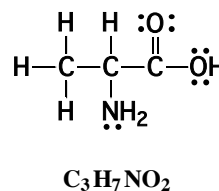
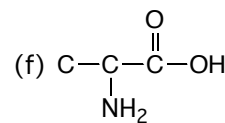
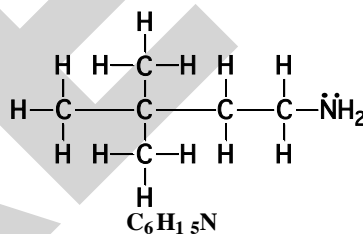
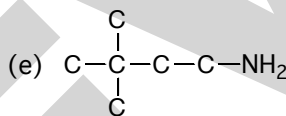
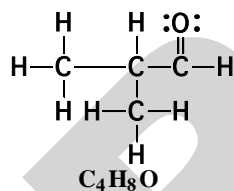
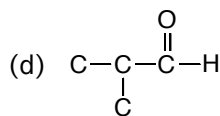
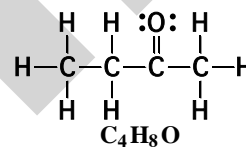
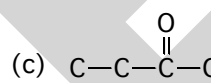
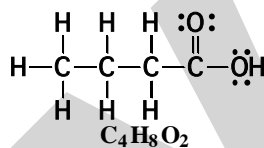
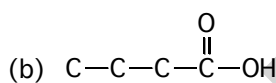
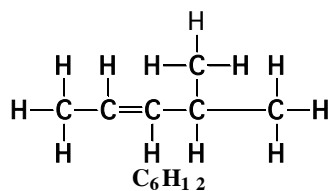
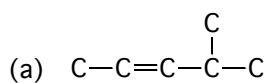


(f)  $\text{CH}_3\text{COO}^-$   
Acetate ion

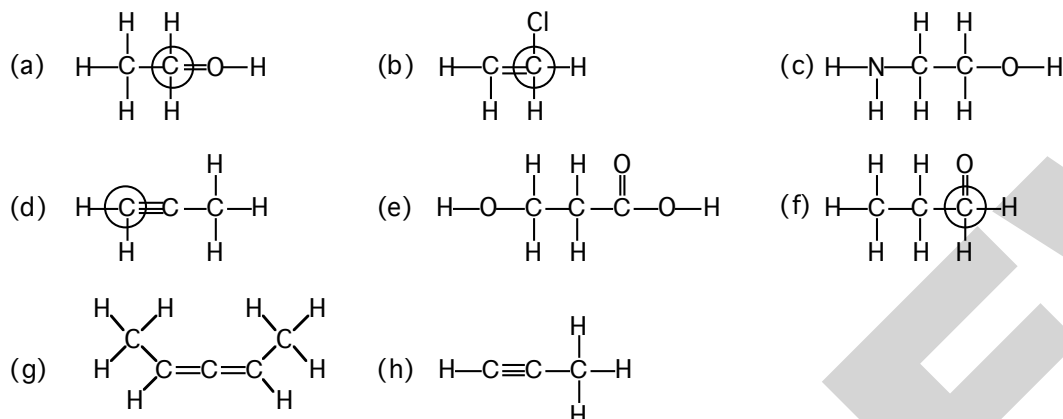


**Problem 1.29** Complete these structural formulas by adding enough hydrogens to complete the tetravalence of each carbon. Then write the molecular formula of each compound.

Lone pairs were added to the following structural formulas for clarity.



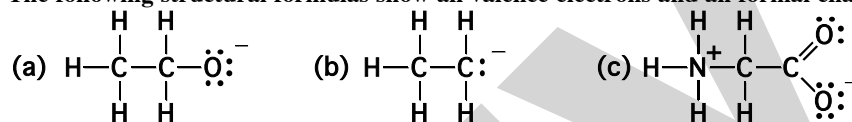
**Problem 1.30** Some of these structural formulas are incorrect (i.e. they do not represent a real compound) because they have atoms with an incorrect number of bonds. Which structural formulas are incorrect, and which atoms in them have an incorrect number of bonds?



The molecules in (a), (b), (d), and (f) are incorrect, because there are five bonds to the circled carbon atom, not four.

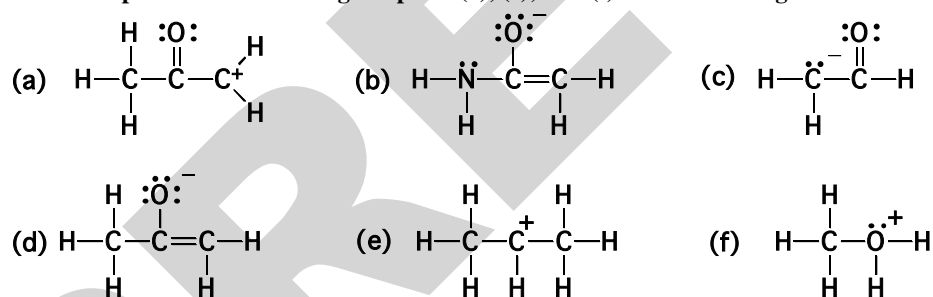
**Problem 1.31** Following the rule that each atom of carbon, oxygen, and nitrogen reacts to achieve a complete outer shell of eight valence electrons, add unshared pairs of electrons as necessary to complete the valence shell of each atom in these ions. Then assign formal charges as appropriate.

The following structural formulas show all valence electrons and all formal charges for clarity.



**Problem 1.32** Following are several Lewis structures showing all valence electrons. Assign formal charges in each structure as appropriate.

There is a positive formal charge in parts (a), (e), and (f). There is a negative formal charge in parts (b), (c), and (d).



### Polarity of Covalent Bonds

**Problem 1.33** Which statements are true about electronegativity?

- Electronegativity increases from left to right in a period of the Periodic Table.
- Electronegativity increases from top to bottom in a column of the Periodic Table.
- Hydrogen, the element with the lowest atomic number, has the smallest electronegativity.
- The higher the atomic number of an element, the greater its electronegativity.

Electronegativity *increases* from left to right across a period and from bottom to top of a column in the Periodic Table. Thus, statement (a) is true, but (b), (c), and (d) are false.

**Problem 1.34** Why does fluorine, the element in the upper right corner of the Periodic Table, have the largest electronegativity of any element?

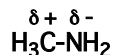
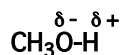
Electronegativity increases with increasing positive charge on the nucleus and with decreasing distance of the valence electrons from the nucleus. Fluorine is that element for which these two parameters lead to maximum electronegativity.

**Problem 1.35** Arrange the single covalent bonds within each set in order of increasing polarity.

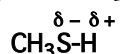
- (a) C-H, O-H, N-H      (b) C-H, B-H, O-H      (c) C-H, C-Cl, C-I  
**C-H < N-H < O-H**      **B-H < C-H < O-H**      **C-I < C-H < C-Cl**
- (d) C-S, C-O, C-N      (e) C-Li, C-B, C-Mg  
**C-S < C-N < C-O**      **C-B < C-Mg < C-Li**

**Problem 1.36** Using the values of electronegativity given in Table 1.5, predict which indicated bond in each set is the more polar and, using the symbols  $\delta^+$  and  $\delta^-$ , show the direction of its polarity

- (a) CH<sub>3</sub>-OH or CH<sub>3</sub>O-H      (b) CH<sub>3</sub>-NH<sub>2</sub> or CH<sub>3</sub>-PH<sub>2</sub>



- (c) CH<sub>3</sub>-SH or CH<sub>3</sub>S-H



- (d) CH<sub>3</sub>-F or H-F



**Problem 1.37** Identify the most polar bond in each molecule.

- (a) HSCH<sub>2</sub>CH<sub>2</sub>OH      (b) CHCl<sub>2</sub>F      (c) HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

**The O-H bond  
(1.4)**

**The C-F bond  
(1.5)**

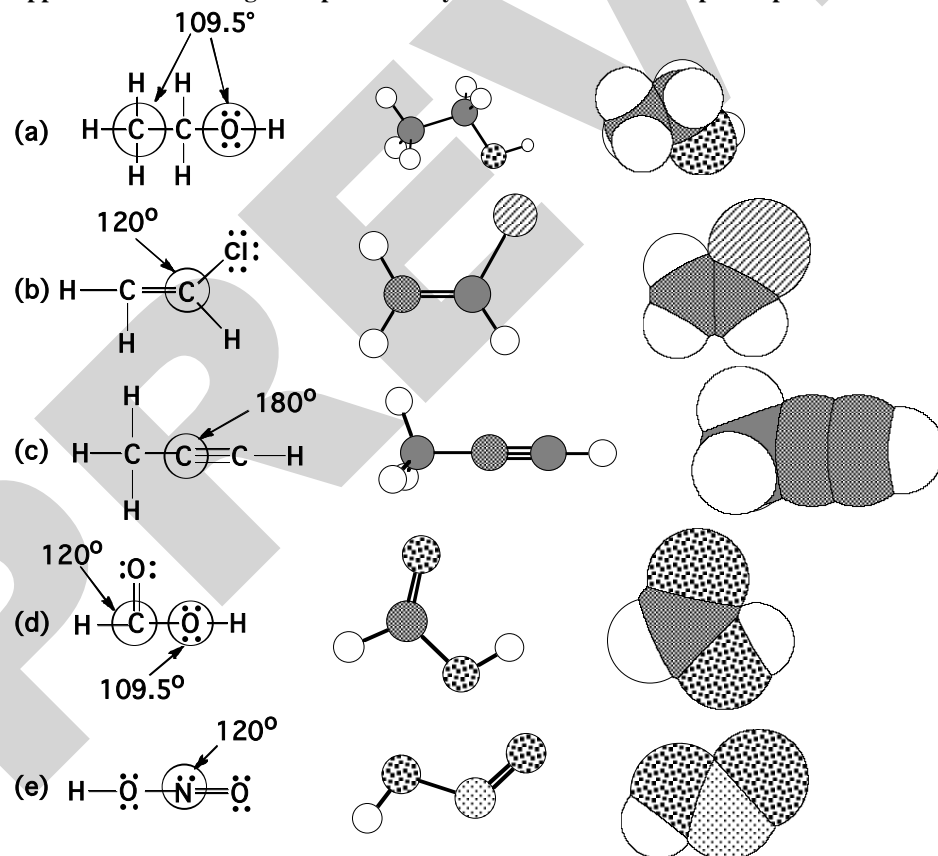
**The O-H bond  
(1.4)**

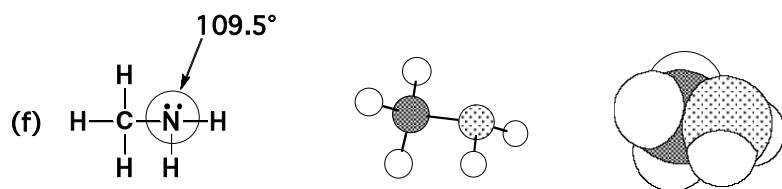
The difference in electronegativities is given in parentheses underneath each answer.

### Bond Angles and Shapes of Molecules

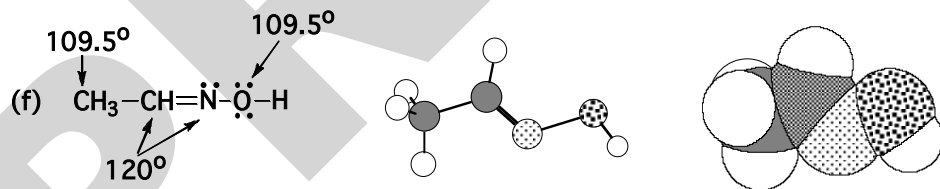
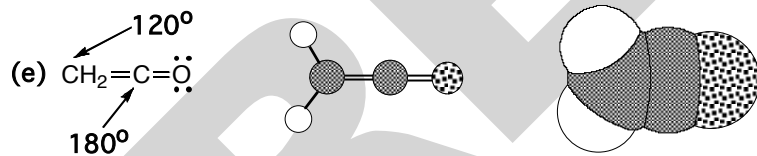
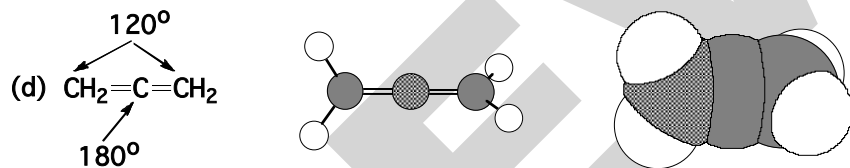
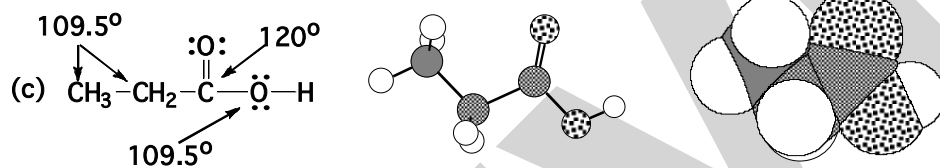
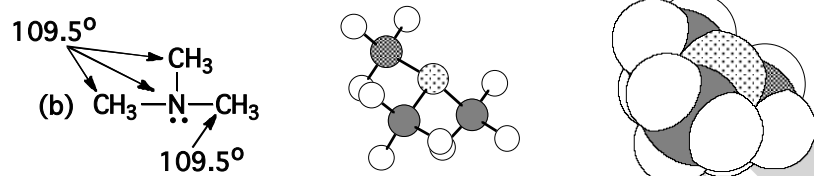
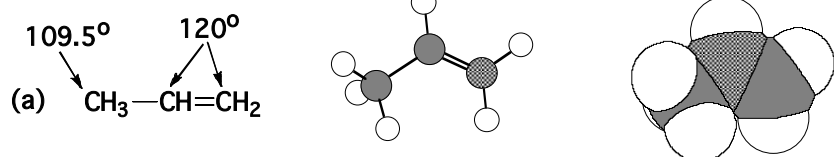
**Problem 1.38** Use VSEPR to predict bond angles about each highlighted atom.

Approximate bond angles as predicted by valence-shell electron-pair repulsion are as shown.



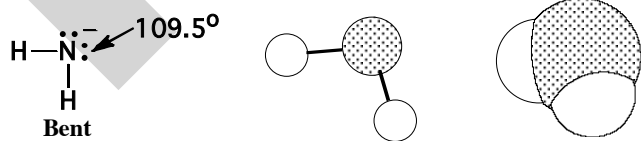


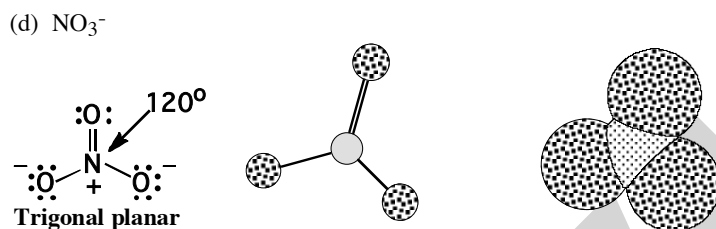
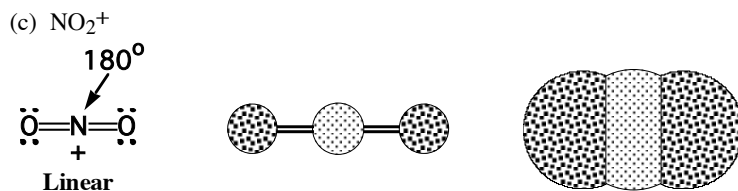
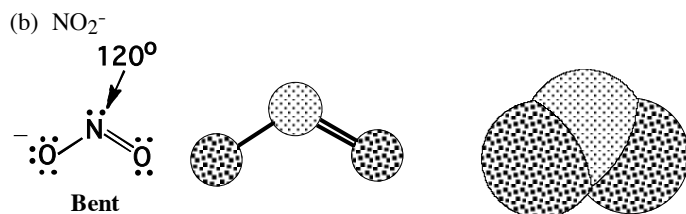
**Problem 1.39** Use VSEPR to predict bond angles about each atom of carbon, nitrogen, and oxygen in these molecules.



**Problem 1.40** Use VSEPR to predict the geometry of these ions.

(a)  $\text{NH}_2^-$

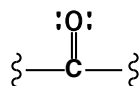




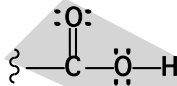
### Functional Groups

**Problem 1.41** Draw Lewis structures for these functional groups. Be certain to show all valence electrons on each.

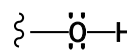
(a) Carbonyl group



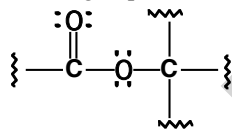
(b) Carboxyl group



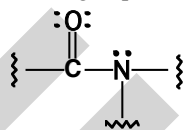
(c) Hydroxyl group



(d) Ester group



(e) Amide group



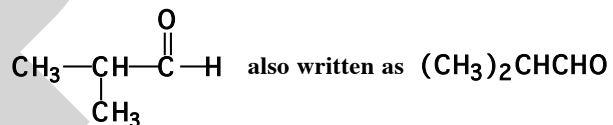
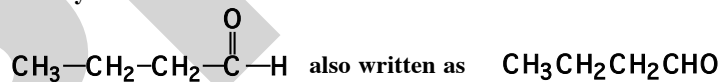
**Problem 1.42** Draw condensed structural formulas for all compounds with the molecular formula  $\text{C}_4\text{H}_8\text{O}$  that contain

(a) A carbonyl group (there are two aldehydes and one ketone).

#### Ketone

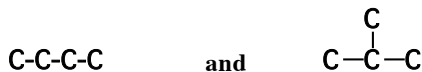


#### Aldehydes

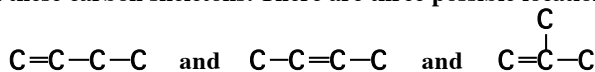


(b) A carbon-carbon double bond and a hydroxyl group (there are eight)

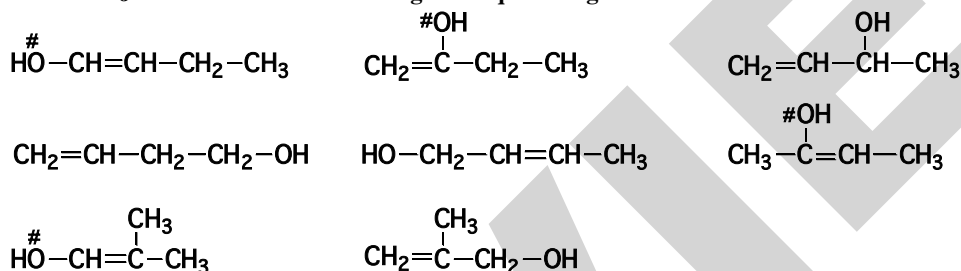
There are three separate but related things to build into this answer; the carbon skeleton (the order of attachment of carbon atoms), the location of the double bond, and the location of the -OH group. Here, as in other problems of this type, it is important to have a system and to follow it. As one way to proceed, first decide the number of different carbon skeletons that are possible. A little doodling with paper and pencil should convince you that there are only two.



Next locate the double bond on these carbon skeletons. There are three possible locations for it.

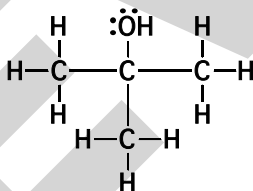


Finally, locate the -OH group and then add the remaining seven hydrogens to complete each structural formula. For the first carbon skeleton, there are four possible locations of the -OH group; for the second carbon skeleton there are two possible locations; and for the third, there are also two possible locations. Four of these compounds (marked by a # symbol) are not stable and are in equilibrium with a more stable aldehyde or ketone. You need not be concerned, however, with this now. Just concentrate on drawing the required eight condensed structural formulas.

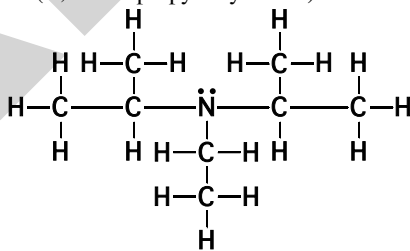


**Problem 1.43** What is the meaning of the term tertiary ( $3^\circ$ ) when it is used to classify alcohols? Draw a structural formula for the one tertiary ( $3^\circ$ ) alcohol with the molecular formula  $\text{C}_4\text{H}_{10}\text{O}$ .

A tertiary alcohol is one in which the -OH group is on a tertiary carbon atom. A tertiary carbon atom is one that is bonded to three other carbon atoms.

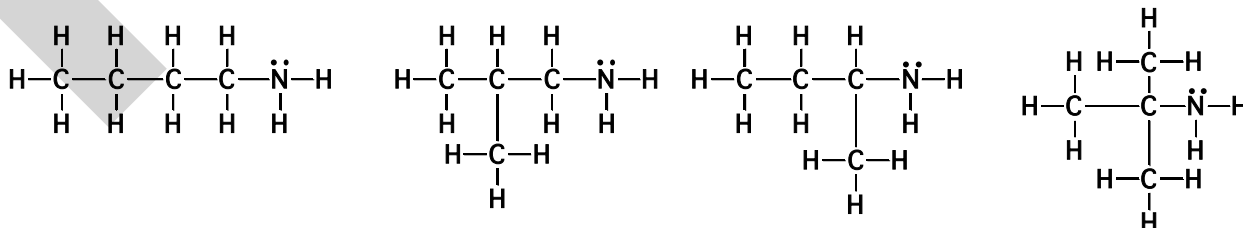


**Problem 1.44** What is the meaning of the term tertiary ( $3^\circ$ ) when it is used to classify amines? Draw a structural formula for the one tertiary ( $3^\circ$ ) amine known as Hunig's base (*N,N*-diisopropylethylamine).

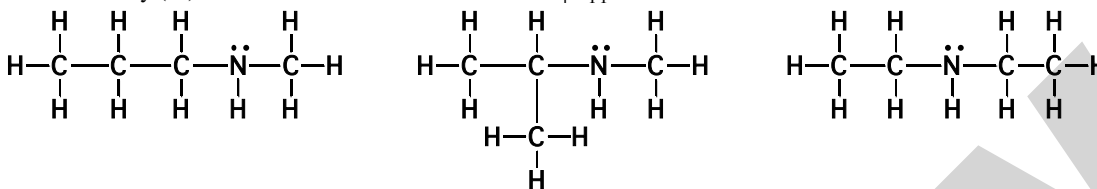


**Problem 1.45** Draw structural formulas for

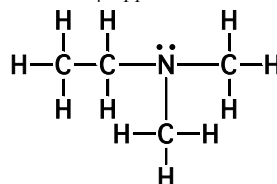
(a) The four primary ( $1^\circ$ ) amines with the molecular formula  $\text{C}_4\text{H}_{11}\text{N}$ .



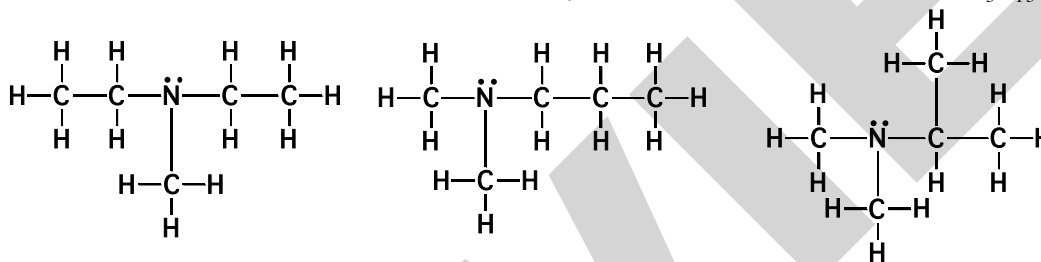
(b) The three secondary ( $2^\circ$ ) amines with the molecular formula  $C_4H_{11}N$ .



(c) The one tertiary ( $3^\circ$ ) amine with the molecular formula  $C_4H_{11}N$ .



**Problem 1.46** Draw structural formulas for the three tertiary ( $3^\circ$ ) amines with the molecular formula  $C_5H_{13}N$ .

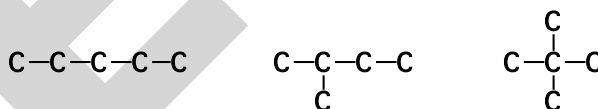


**Problem 1.47** Draw structural formulas for

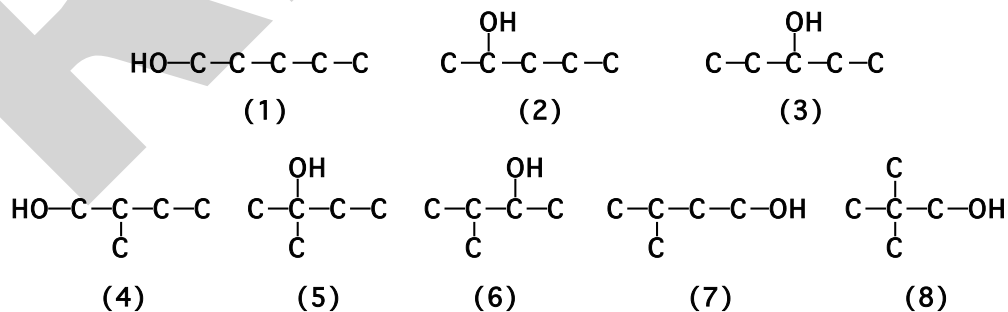
(a) The eight alcohols with the molecular formula  $C_5H_{12}O$ .

To make it easier for you to see the patterns of carbon skeletons and functional groups, only carbon atoms and hydroxyl groups are shown in the following solutions. To complete these structural formulas, you need to supply enough hydrogen atoms to complete the tetravalence of each carbon.

There are three different carbon skeletons on which the -OH group can be placed:



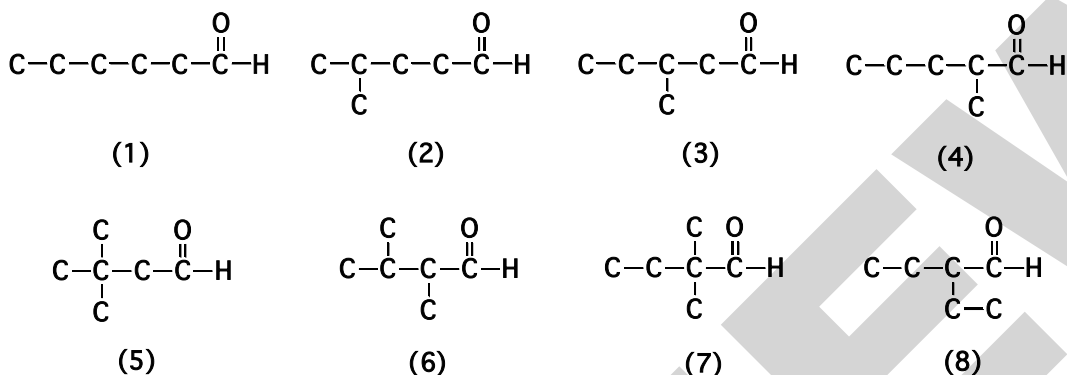
Three alcohols are possible from the first carbon skeleton, four from the second carbon skeleton, and one from the third carbon skeleton.





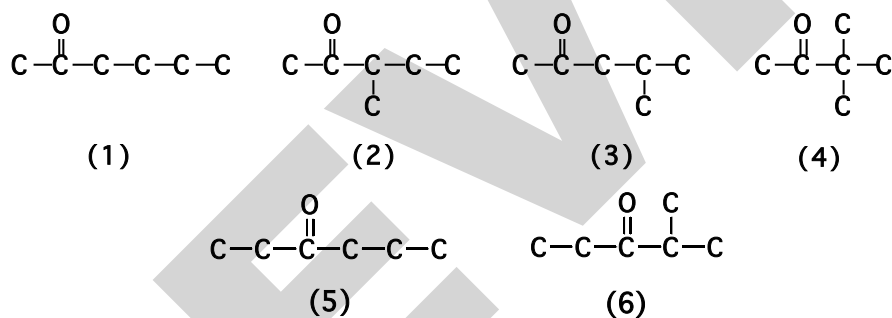
(b) The eight aldehydes with the molecular formula  $C_6H_{12}O$ .

Following are structural formulas for the eight aldehydes with the molecular formula  $C_6H_{12}O$ . They are drawn starting with the aldehyde group and then attaching the remaining five carbons in a chain (structure 1), then four carbons in a chain and one carbon as a branch on the chain (structures 2, 3, and 4) and finally three carbons in a chain and two carbons as branches (structures 5, 6, 7, and 8).



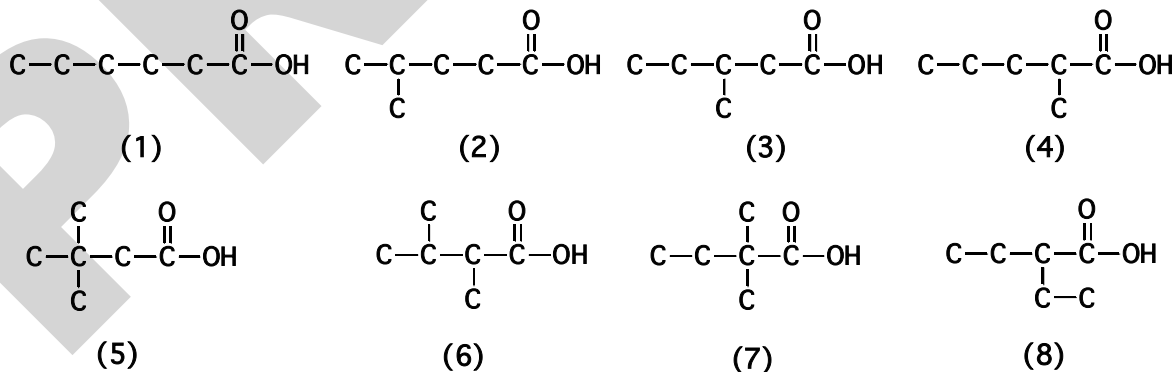
(c) The six ketones with the molecular formula  $C_6H_{12}O$ .

Following are structural formulas for the six ketones with the molecular formula  $C_6H_{12}O$ . They are drawn first with all combinations of one carbon to the left of the carbonyl group and four carbons to the right (structures 1, 2, 3, and 4) and then with two carbons to the left and three carbons to the right (structures 5 and 6).



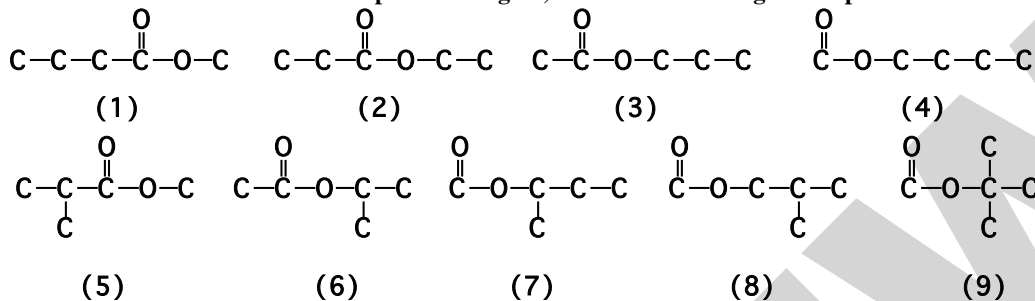
(d) The eight carboxylic acids with the molecular formula  $C_6H_{12}O_2$ .

There are eight carboxylic acids of molecular formula  $C_6H_{12}O_2$ . They have the same carbon skeletons as the eight aldehydes of molecular formula  $C_6H_{12}O$  shown in part (b) of this problem. In place of the aldehyde group, substitute a carboxyl group.

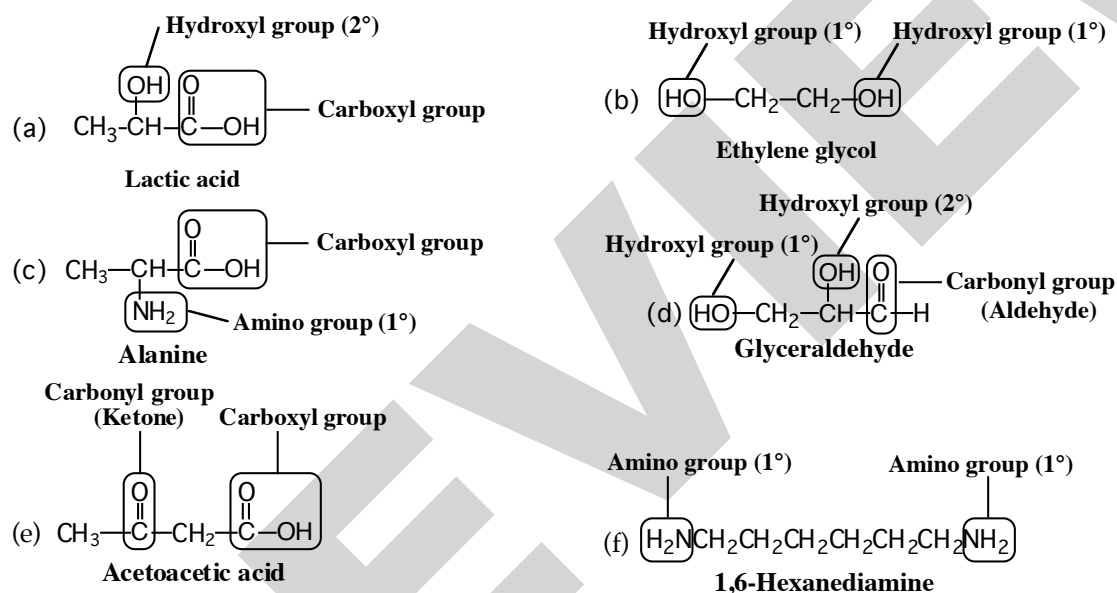


(e) The nine carboxylic esters with the molecular formula  $C_5H_{10}O_2$ .

Start with unbranched carbon chains of all possible lengths, then add branching to complete the set.



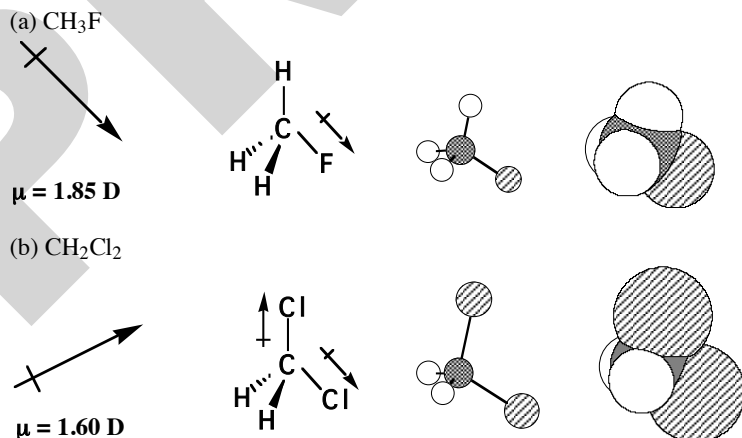
**Problem 1.48** Identify the functional groups in each compound.

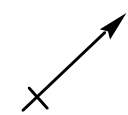


### Polar and Nonpolar Molecules

**Problem 1.49** Draw a three-dimensional representation for each molecule. Indicate which ones have a dipole moment and in what direction it is pointing.

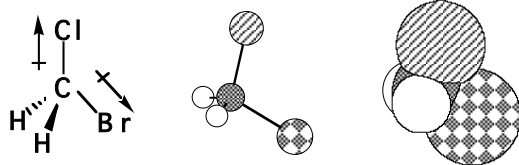
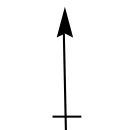
In the following diagrams, the C-H bond dipole moment has been left out because it is a nonpolar covalent bond. The listed dipole moments were looked up in the chemical literature and are only added for reference. You will not be expected to calculate these.



(c)  $\text{CH}_2\text{ClBr}$ 

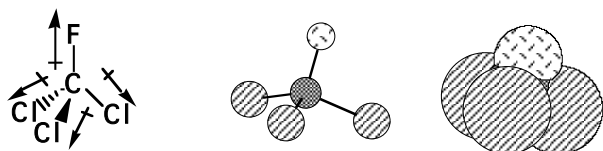
$$\mu = 1.50 \text{ D}$$

The bond dipole moment of the C-Cl bond dominates because chlorine is more electronegative than bromine.

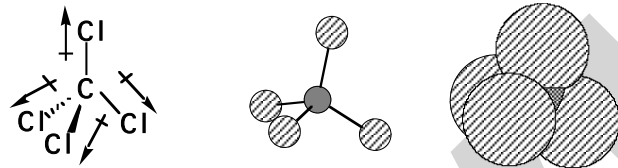
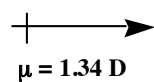
(d)  $\text{CFCl}_3$ 

$$\mu = 0.28 \text{ D}$$

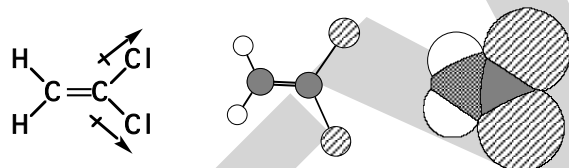
The bond dipole moment of the C-F bond dominates because of the higher electronegativity of fluorine.

(e)  $\text{CCl}_4$ 

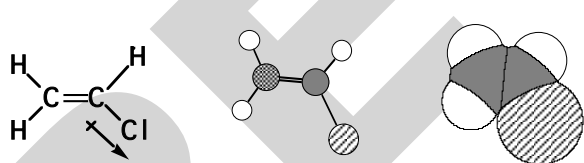
No molecular  
dipole moment

(f)  $\text{CH}_2=\text{CCl}_2$ 

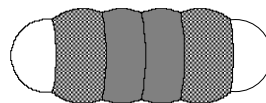
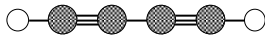
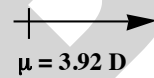
$$\mu = 1.34 \text{ D}$$

(g)  $\text{CH}_2=\text{CHCl}$ 

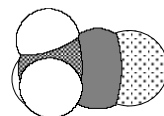
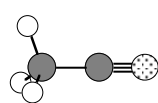
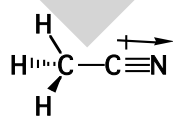
$$\mu = 1.45 \text{ D}$$

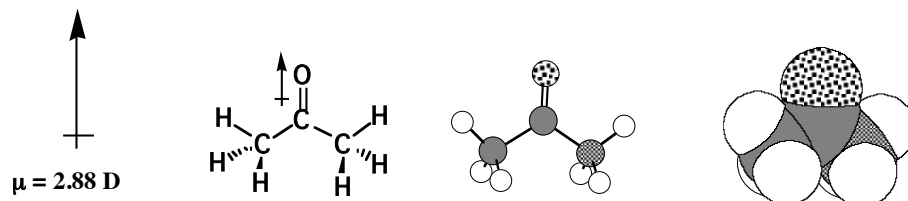
(h)  $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ 

No molecular  
dipole moment

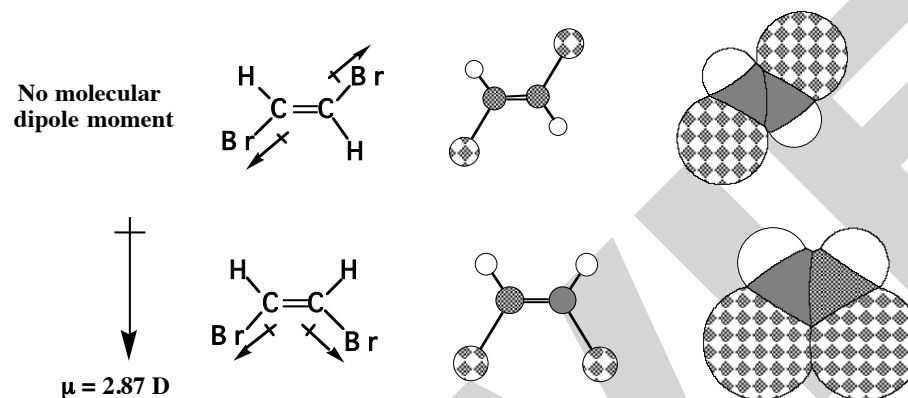
(i)  $\text{CH}_3\text{C}\equiv\text{N}$ 

$$\mu = 3.92 \text{ D}$$

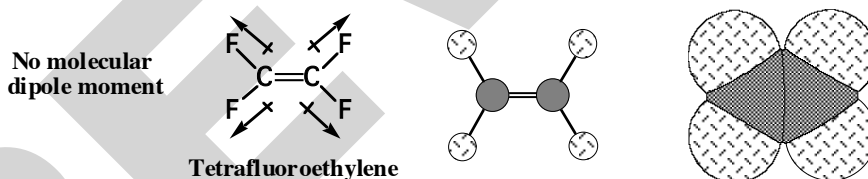


(j)  $(\text{CH}_3)_2\text{C}=\text{O}$ 

 (k)  $\text{BrCH}=\text{CHBr}$  (two answers)

The two bromine atoms can either be on opposite sides or on the same side of the double bond. Recall that double bonds do not rotate.



**Problem 1.50** Tetrafluoroethylene,  $\text{C}_2\text{F}_4$ , is the starting material for the synthesis of the polymer polytetrafluoroethylene (PTFE), one form of which is known as Teflon. Tetrafluoroethylene has a dipole moment of zero. Propose a structural formula for this molecule.



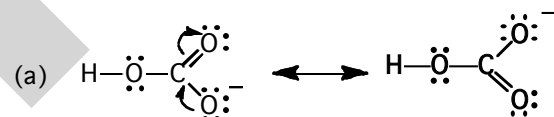
### Resonance and Contributing Structures

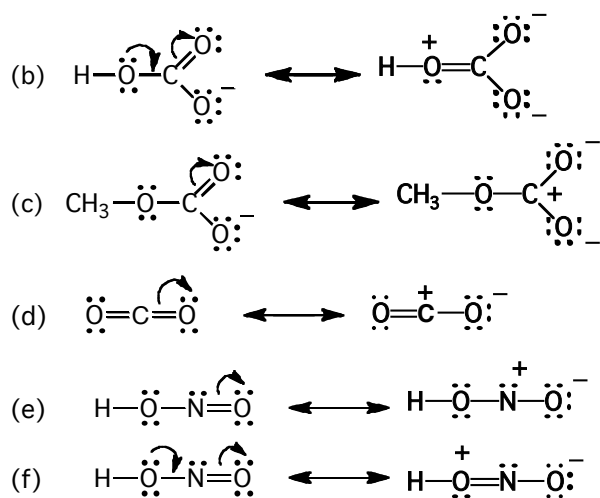
**Problem 1.51** Which statements are true about resonance contributing structures?

- All contributing structures must have the same number of valence electrons.
- All contributing structures must have the same arrangement of atoms.
- All atoms in a contributing structure must have complete valence shells.
- All bond angles in sets of contributing structures must be the same.

For sets of contributing structures, electrons (usually  $\pi$  electrons or lone pair electrons) move, but the atomic nuclei maintain the same arrangement in space. The atoms are arranged the same with the same bond angles among them, so statements (b) and (d) are true. In addition, the total number of electrons, valence and inner shell electrons, in each contributing structure must be the same, so statement (a) is also true. However, the movement of electrons often leaves one or more atoms without a filled valence shell in a given contributing structure, so statement (c) is false.

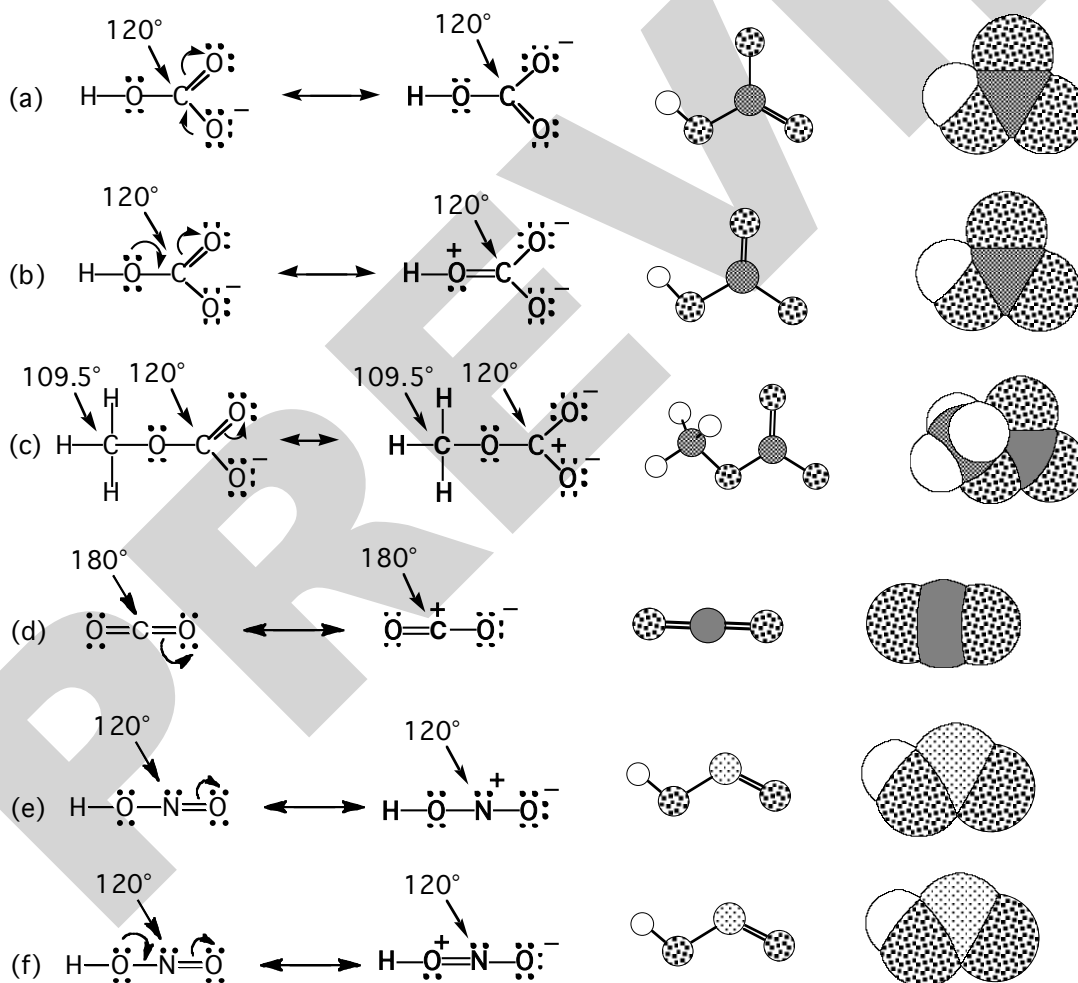
**Problem 1.52** Draw the contributing structure indicated by the curved arrow(s). Assign formal charges as appropriate.





**Problem 1.53** Using VSEPR, predict the bond angles about the carbon and nitrogen atoms in each pair of contributing structures in problem 1.52. In what way do these bond angles change from one contributing structure to the other?

As stated in the answer to Problem 1.51, bond angles do not change from one contributing structure to another.

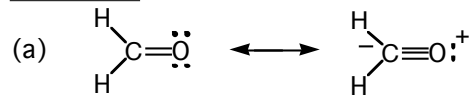


**Problem 1.54** In the Problem 1.52 you were given one contributing structure and asked to draw another. Label pairs of contributing structures that are equivalent. For those sets in which the contributing structures are not equivalent, label the more important contributing structure.

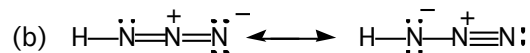
(a) The two structures are equivalent because each involves a similar separation of charge.

(b, c, d, e, f) The first structure is more important, because the second involves creation and separation of unlike charges.

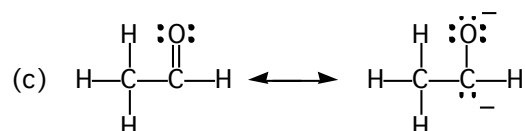
**Problem 1.55** Are the structures in each set valid contributing structures?



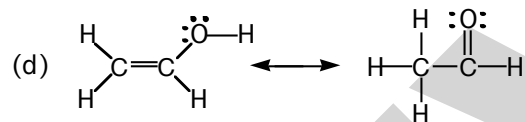
The structure on the right is not a valid contributing structure because there are 10 electrons in the valence shell of the carbon atom.



Both of these are valid contributing structures.



The structure on the right is not a valid contributing structure because there are two extra electrons and thus it is a completely different species.

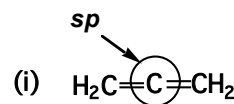
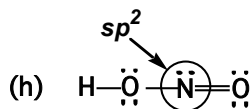
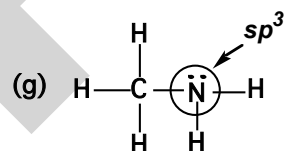
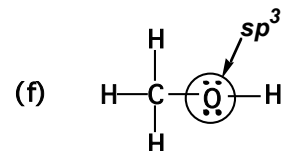
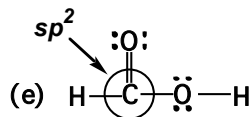
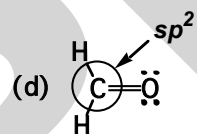
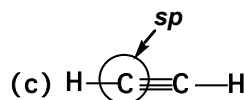
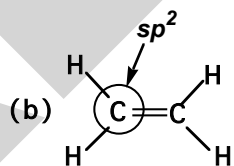
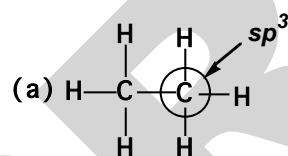


Although each is a valid Lewis structure, they are not valid contributing structures for the same resonance hybrid. An atomic nucleus, namely a hydrogen, has changed position. Later you will learn that these two molecules are related to each other and are called tautomers.

### Valence Bond Theory

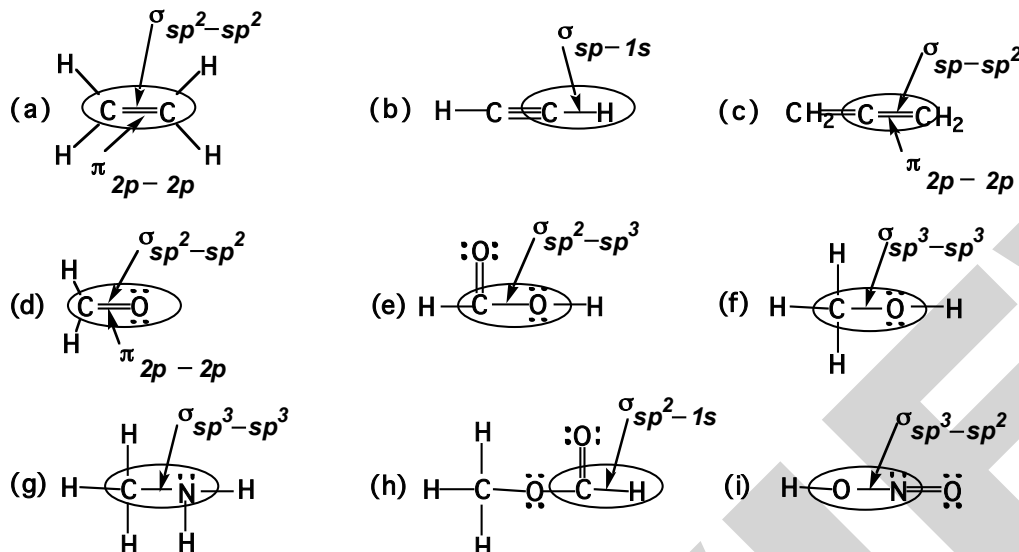
**Problem 1.56** State the orbital hybridization of each highlighted atom.

Each circled atom is either  $sp$ ,  $sp^2$ , or  $sp^3$  hybridized.

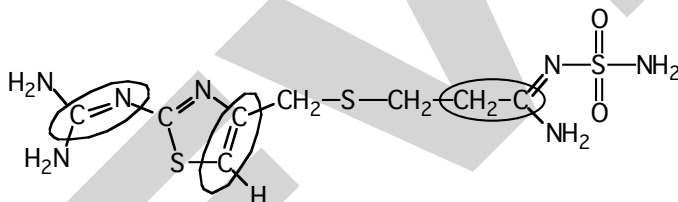


**Problem 1.57** Describe each highlighted bond in terms of the overlap of atomic orbitals.

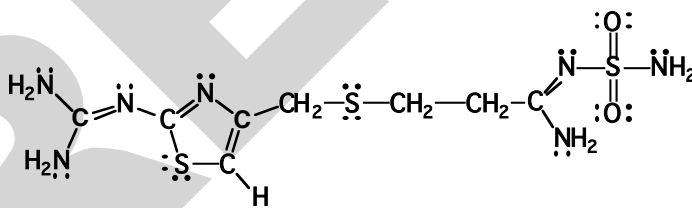
Shown is whether the bond is  $\sigma$  or  $\pi$ , as well as the orbitals used to form it.



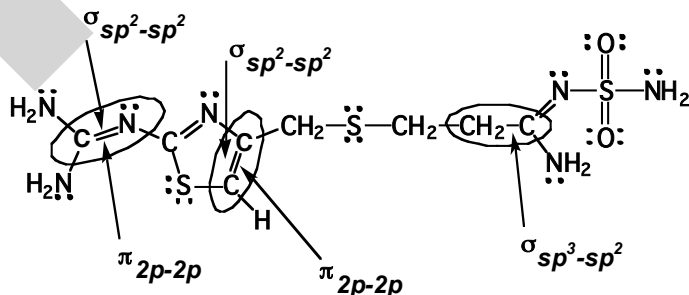
**Problem 1.58** Following is a structural formula of the prescription drug famotidine marketed by by McNeil Consumer Pharmaceuticals Co. under the name Pepcid. The primary clinical use of Pepcid is for the treatment of active duodenal ulcers and benign gastric ulcers. Pepcid is a competitive inhibitor of histamine  $H_2$  receptors and reduces both gastric acid concentration and the volume of gastric secretions.



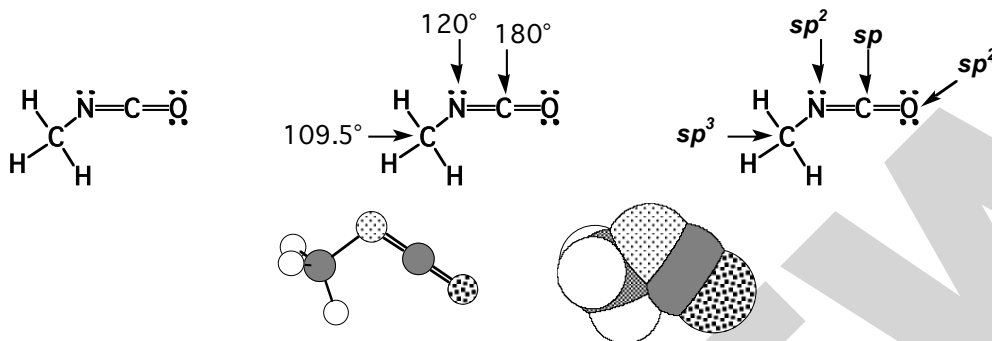
(a) Complete the Lewis structure of famotidine showing all valence electrons and any positive or negative charges.



(b) Describe each circled bond in terms of the overlap of atomic orbitals.

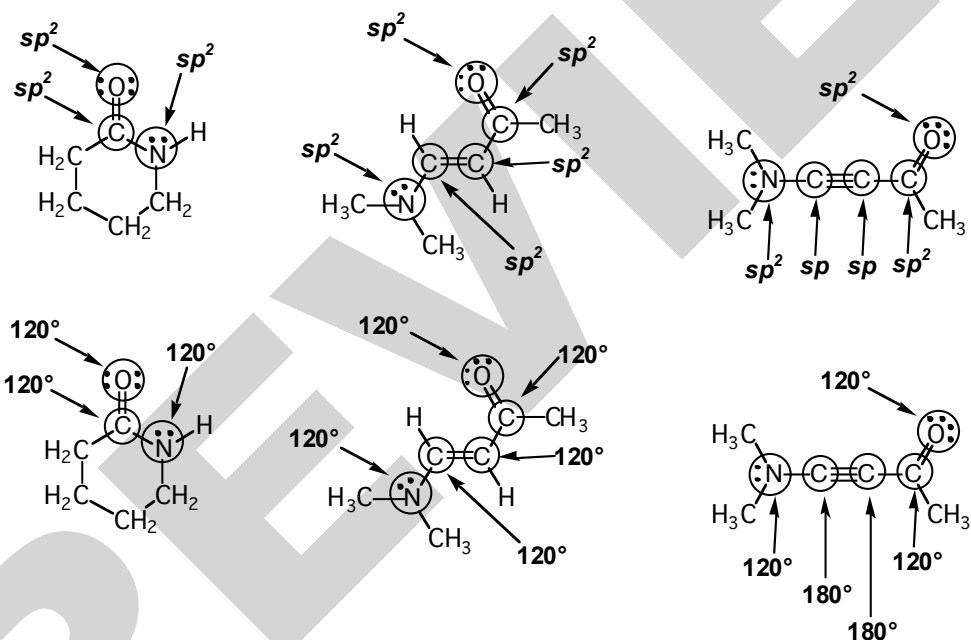


**Problem 1.59** Draw a Lewis structure for methyl isocyanate,  $\text{CH}_3\text{NCO}$ , showing all valence electrons. Predict all bond angles in this molecule and the hybridization of each atom C, N, and O.

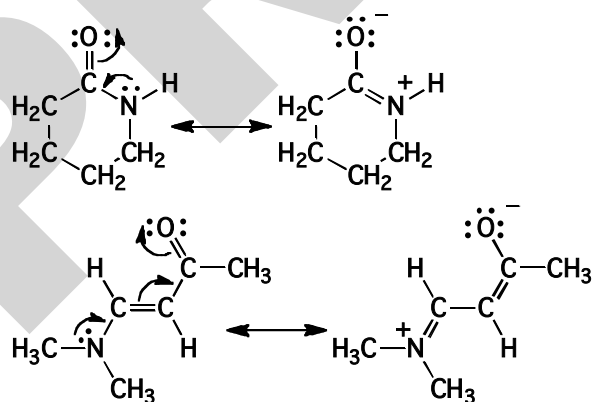


### Combined MO/VB Theory

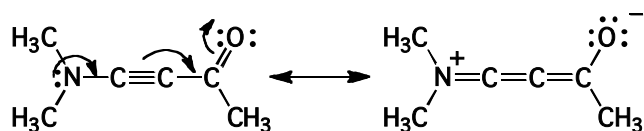
**Problem 1.60** What is the hybridization of the highlighted atoms in the following structures, and what are your estimates for the bond angles around these highlighted atoms? In each case, in what kind of orbital does the lone pair of electrons on the nitrogen reside.



In each case there are significant contributing structures that have a  $\pi$  bond involving nitrogen.

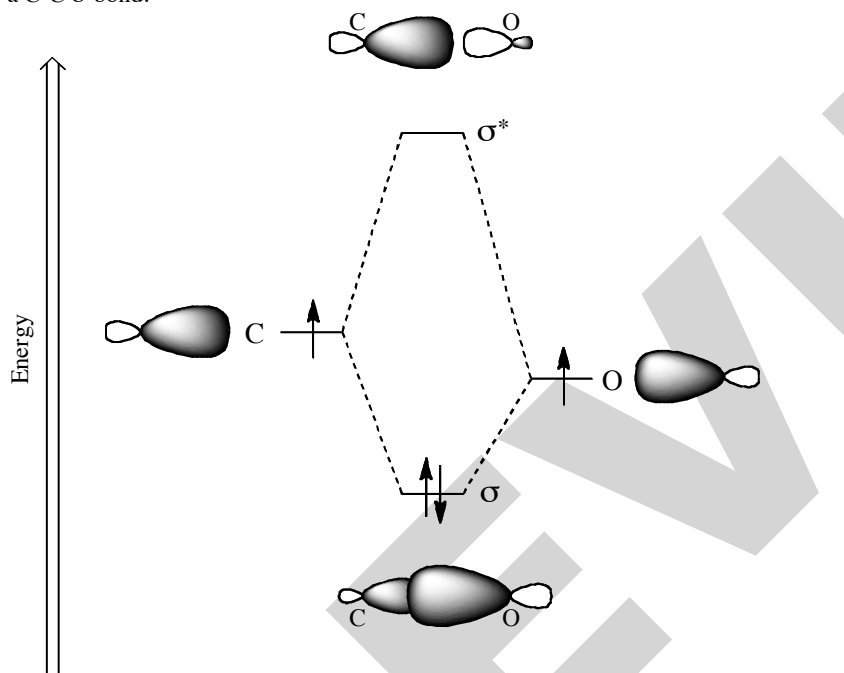






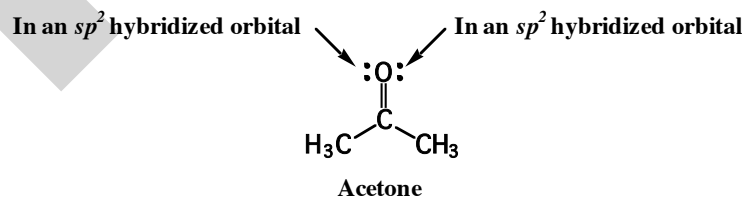
These are examples of nitrogen lone pairs delocalizing into adjacent  $\pi$  bonds, a common feature of many organic molecules you will come across. For this to happen, the nitrogen atoms must be  $sp^2$  hybridized, so the lone pairs on nitrogen are best thought of as being in  $2p$  orbitals. Such delocalization of electron density in  $\pi$  orbitals is stabilizing and therefore favorable, a phenomenon that is best explained using quantum mechanical arguments (beyond the scope of this text).

**Problem 1.61** Using cartoon representations, draw a molecular orbital mixing diagram for a C-O  $\sigma$ -bond. In your picture, consider the relative energies of C and O, and how this changes the resulting bonding and antibonding molecular orbitals relative to a C-C  $\sigma$ -bond.



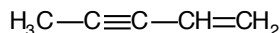
The O atom, being more electronegative, is of lower energy than the C atom. This means the O orbital makes a larger contribution to the  $\sigma$ -bonding orbital, while the C atom makes a larger contribution to the  $\sigma^*$ -antibonding orbital. For a  $\sigma$ -bonding orbital formed from two C atoms of the same hybridization, both C orbitals make equal contributions.

**Problem 1.62** In what kind of orbitals do the lone-pair electrons on the oxygen of acetone reside, and are they in the same plane as the methyl  $-CH_3$  groups or are they perpendicular to the methyl  $-CH_3$  groups?

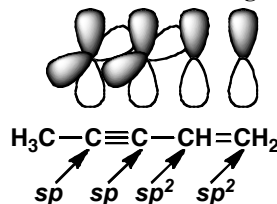


In acetone, both lone pairs reside in  $sp^2$  hybridized orbitals, so they are in the same plane as the two methyl groups.

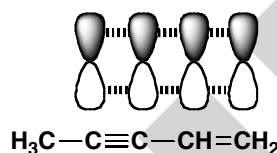
**Problem 1.63** Draw the delocalized molecular orbitals for the following molecule. Are both  $\pi$ -bonds of the triple bond involved in the delocalized orbitals?



Shown below are the  $2p$  orbitals involved with delocalized  $\pi$ -bonding.



The delocalized molecular orbital involves only the four parallel  $2p$  orbitals as shown below. The perpendicular  $2p$  orbitals of the two  $sp$  hybridized carbons only overlap with each other, so they are not involved with delocalized bonding.



#### Additional Problems

**Problem 1.64** Why are the following molecular formulas impossible?

(a)  $\text{CH}_5$

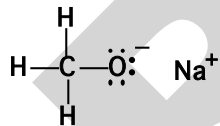
Carbon atoms can only accommodate 8 electrons in their valence shell, and each hydrogen atom can only accommodate one bond. Thus, there is no way for a stable bonding arrangement to be created that utilizes one carbon atom and all five hydrogen atoms.

(b)  $\text{C}_2\text{H}_7$

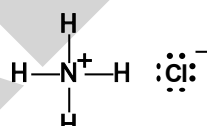
Because hydrogen atoms can only accommodate one bond each, no single hydrogen atom can make stable bonds to both carbon atoms. Thus, the two carbon atoms must be bonded to each other. This means that each of the bonded carbon atoms can accommodate only three more bonds. Therefore, only six hydrogen atoms can be bonded to the carbon atoms, not seven hydrogen atoms.

**Problem 1.65** Each compound contains both ions and covalent bonds. Draw the Lewis structure for each compound, and show by dashes which are covalent bonds and show by charges which are ions.

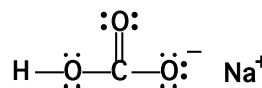
(a)  $\text{CH}_3\text{ONa}$   
Sodium methoxide



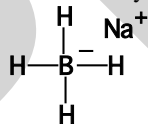
(b)  $\text{NH}_4\text{Cl}$   
Ammonium chloride



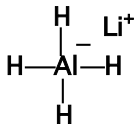
(c)  $\text{NaHCO}_3$   
Sodium bicarbonate



(d)  $\text{NaBH}_4$   
Sodium borohydride

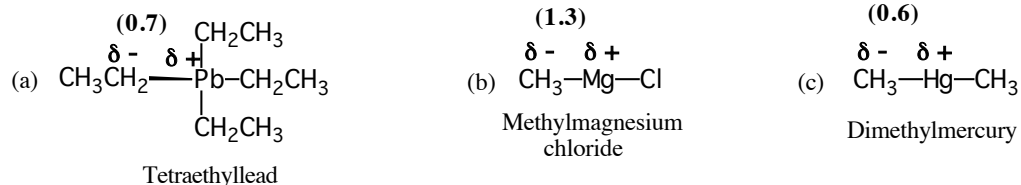


(e)  $\text{LiAlH}_4$   
Lithium aluminum hydride



In naming these compounds, the cation is named first followed by the name of the anion.

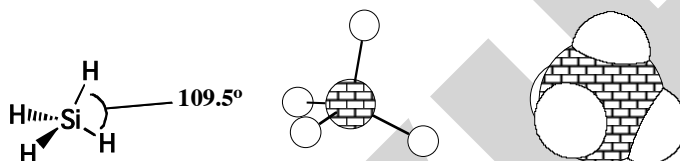
**Problem 1.66** Predict whether the carbon-metal bond in these organometallic compounds is nonpolar covalent, polar covalent, or ionic. For each polar covalent bond, show the direction of its polarity by the symbols  $\delta+$  and  $\delta-$ .



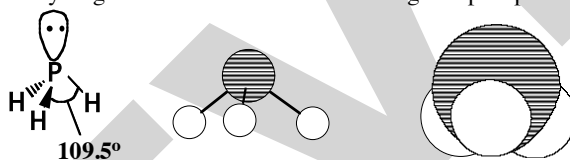
All of these carbon-metal bonds are polar covalent because the difference in electronegativities is between 0.5 and 1.9. In each case, carbon is the more electronegative element so it has the partial negative charge. The difference in electronegativities is given above the carbon-metal bond in each answer.

**Problem 1.67** Silicon is immediately under carbon in the Periodic Table. Predict the geometry of silane,  $\text{SiH}_4$ .

Silicon is in Group 4 of the Periodic Table, and like carbon, has four valence electrons. In silane,  $\text{SiH}_4$ , silicon is surrounded by four regions of electron density. Therefore, you should predict all H-Si-H bond angles to be  $109.5^\circ$ , so the molecule is tetrahedral around Si.



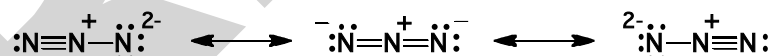
**Problem 1.68** Phosphorus is immediately under nitrogen in the Periodic Table. Predict the molecular formula for phosphine, the compound formed by phosphorus and hydrogen. Predict the H-P-H bond angle in phosphine.



Like nitrogen, phosphorus has five valence electrons, so you should predict that phosphine has the molecular formula of  $\text{PH}_3$  in analogy to ammonia,  $\text{NH}_3$ . In phosphine, the phosphorus atom is surrounded by four regions of electron density; one lone pair of electrons and single bonds to three hydrogens. Therefore, predict all H-P-H bond angles to be roughly  $109.5^\circ$ , meaning the molecule is pyramidal.

**Problem 1.69** Draw a Lewis structure for the azide ion,  $\text{N}_3^-$ . (The order of attachment is N-N-N and they do not form a ring). How does the resonance model account for the fact that the lengths of the N-N bonds in this ion are identical.

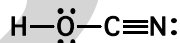
It is not possible to draw a single Lewis structure that adequately describes the azide ion. Rather, it can be drawn as the hybrid of three contributing structures.



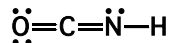
Taken together, the three contributing structures present a symmetric picture of azide ion bonding, thus explaining why both N-N bonds are identical.

**Problem 1.70** Cyanic acid,  $\text{HOCN}$ , and isocyanic acid,  $\text{HNCO}$ , dissolve in water to yield the same anion on loss of  $\text{H}^+$ .

(a) Write a Lewis structure for cyanic acid.

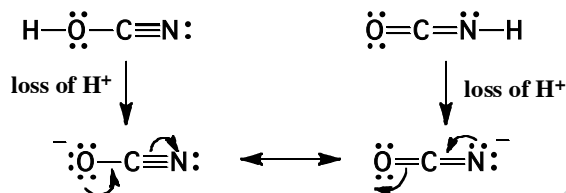


(b) Write a Lewis structure for isocyanic acid.



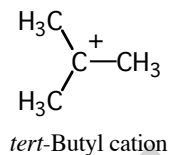
(c) Account for the fact that each acid gives the same anion on loss of  $H^+$ .

Loss of an  $H^+$  from the two different acids gives the same anion that can best be described by drawing the following two contributing structures.



### Looking Ahead

**Problem 1.71** In Chapter 6, we study a group of organic cations called carbocations. Following is the structure of one such carbocation, the *tert*-butyl cation.

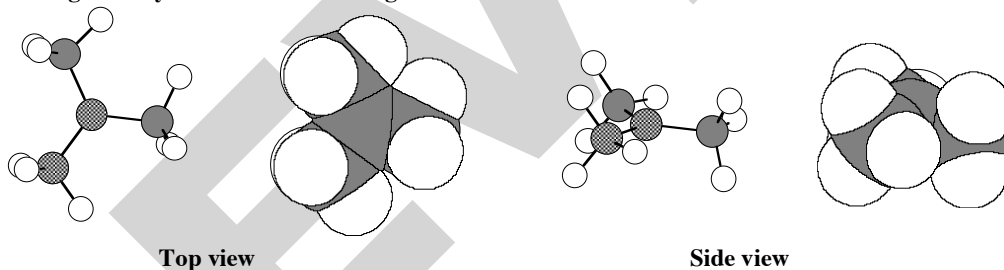


(a) How many electrons are in the valence shell of the carbon bearing the positive charge?

There are six valence shell electrons on the carbon atom bearing the positive charge, two contained in each of the three single bonds.

(b) Using VSEPR predict the bond angles about this carbon.

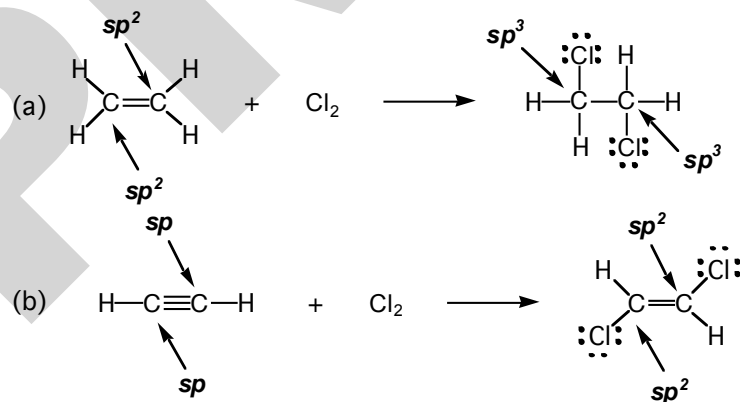
According to VSEPR, there are three regions of electron density around the central carbon atom, so you should predict a trigonal planar geometry and C-C-C bond angles of  $120^\circ$ .

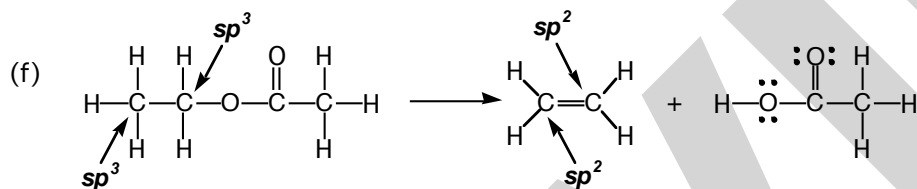
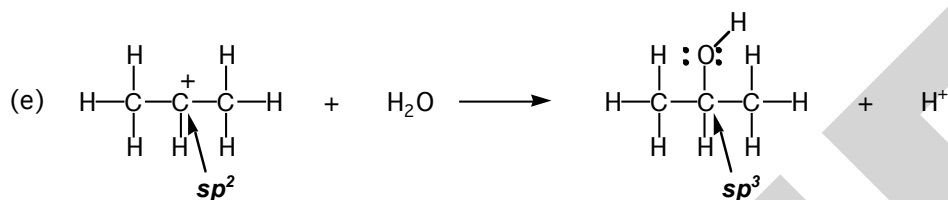
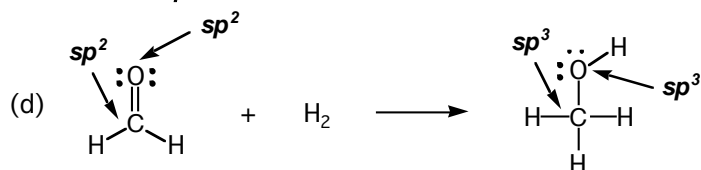
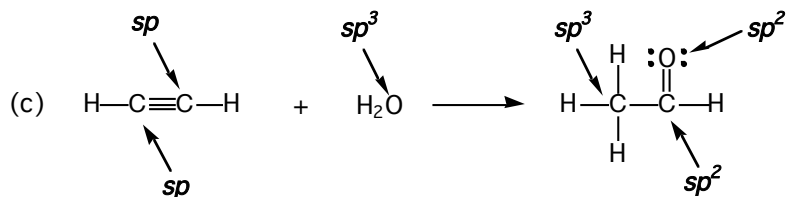


(c) Given the bond angle you predicted in (b), what hybridization do you predict for this carbon?

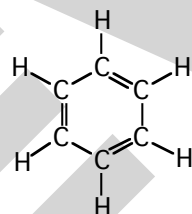
Given the trigonal planar geometry predicted in (b), so you should predict  $sp^2$  hybridization of this carbon atom.

**Problem 1.72** Many reactions involve a change in hybridization of one or more atoms in the starting material. In each reaction, identify the atoms in the organic starting material that change hybridization and indicate what the change is. We examine these reactions in more detail later in the course.





**Problem 1.73** Following is a structural formula of benzene,  $\text{C}_6\text{H}_6$ , which we study in Chapter 21



(a) Using VSEPR, predict each H-C-C and C-C-C bond angle in benzene.

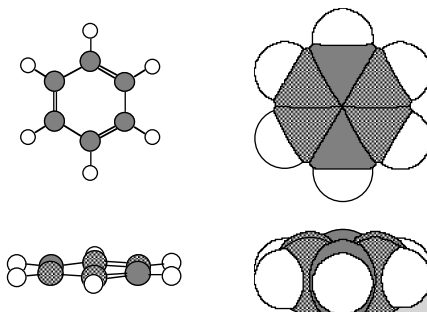
**Each carbon atom in benzene has three regions of electron density around it, so according to VSEPR, the carbon atoms are trigonal planar. You should predict each H-C-C bond angle to be  $120^\circ$  and each C-C-C bond angle to be  $120^\circ$ .**

(b) State the hybridization of each carbon atom in benzene.

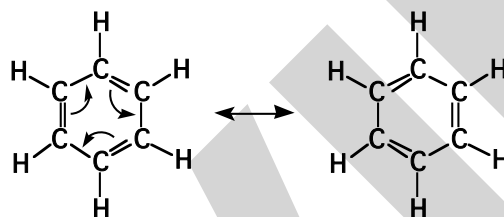
**Each carbon atom is  $sp^2$  hybridized because each one makes three  $\sigma$  bonds and one  $\pi$  bond.**

(c) Predict the shape of a benzene molecule.

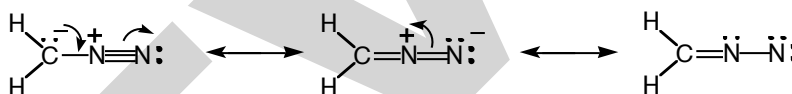
Because all of the carbon atoms in the ring are  $sp^2$  hybridized and thus trigonal planar, predict carbon atoms in benzene to form a flat hexagon in shape, with the hydrogen atoms in the same plane as the carbon atoms.



(d) Draw important resonance contributing structures.



**Problem 1.74** Following are three contributing structures for diazomethane,  $\text{CH}_2\text{N}_2$ . This molecule is used to make methyl esters from carboxylic acids (Section 17.7C).



(a) Using curved arrows, show how each contributing structure is converted to the one on its right.

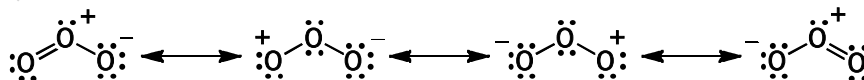
The arrows are indicated on the above structures.

(b) Which contributing structure makes the largest contribution to the hybrid?

The middle and left structures have filled valence shells, so these will make a larger contribution to the hybrid than the structure on the right, in which the terminal nitrogen atom has an unfilled valence shell. The structure in the middle has the negative charge on the more electronegative atom, N, compared with the structure on the left (negative charge on C), so the structure in the middle will make the largest contribution to the resonance hybrid.

**Problem 1.75** Draw a Lewis structure for the ozone molecule,  $\text{O}_3$ . (The order of atom attachment is O-O-O and they do not form a ring). How does the resonance model account for the fact that the length of each O-O bond in ozone (128 pm) is shorter than the O-O single bond in hydrogen peroxide (HOOH 147 pm), but longer than the O-O double bond in the oxygen molecule (123 pm).

It is not possible to draw a single Lewis structure that adequately describes the ozone molecule. Rather, it is better to draw ozone as a hybrid of four contributing structures, each with a separation of charges.



Taken together, the four contributing structures present a symmetric picture of the bonding in which each O-O bond is intermediate between a single bond and a double bond. Recall that bonds become shorter as bond order increases. As a result, the bonds in ozone are shorter than the single O-O bond in HOOH, but longer than the O=O double bond in the oxygen molecule.

### Molecular Orbitals

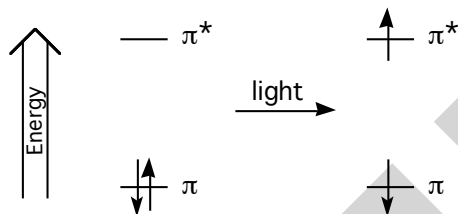
**Problem 1.76** The following two compounds are isomers; that is, they are different compounds with the same molecular formula. We discuss this type of isomerism in Chapter 5.



(a) Why are these different molecules that do not interconvert?

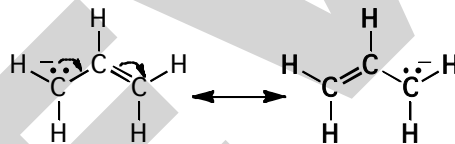
**Interconversion of the two isomers involves rotation about the carbon-carbon double bond. This cannot occur without breaking the  $\pi$  bond. The  $\pi$  bond is strong enough so that this does not happen spontaneously at room temperature and the isomers do not interconvert.**

(b) Absorption of light by a double bond in a molecule excites one electron from a  $\pi$  molecular orbital to a  $\pi^*$  molecular orbital. Explain how this absorption can lead to interconversion of the two isomers.



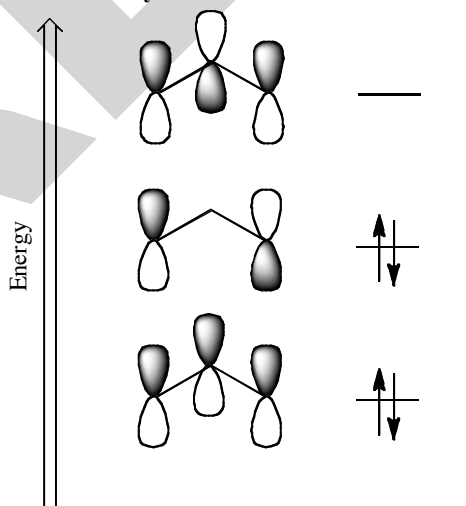
**Putting electron density into an antibonding (\*) orbital of a bond weakens that bond. Excitation of the electron from the  $\pi$  bond to the  $\pi^*$  orbital upon absorption of light weakens the  $\pi$  bond, allowing the molecule to rotate about the carbon-carbon bond. This rotation interconverts the two isomers. A similar alkene rotation reaction is responsible for the mammalian photoreceptor molecules that allow us to see visible light.**

**Problem 1.77** In future chapters we will encounter carbanions—ions in which a carbon atom has three bonds and a lone pair of electrons and bears a negative charge. Draw another contributing structure for the allyl anion. Now using cartoon representations, draw the three orbitals that represent the delocalized  $\pi$  system (look at Figure 1.26 for a hint). Which of the three orbitals are populated with electrons?



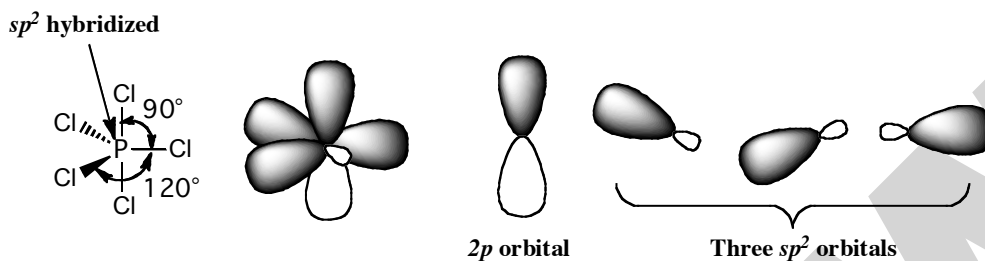
Allyl anion

Below is drawn a cartoon representation of the allyl anion  $\pi$  molecular orbitals.



The lowest two molecular orbitals are filled with a pair of electrons each. Notice that filling of the middle orbital, with lobes on only the two terminal carbon atoms, indicates the negative charge will be found on these two atoms consistent with the contributing structures.

**Problem 1.78** Describe the bonding in  $\text{PCl}_5$  without using  $d$  orbitals. As a hint, the geometry of  $\text{PCl}_5$  is as shown:



Based on the bond angles, the bonding in  $\text{PCl}_5$  can be explained if the P atom is  $sp^2$  hybridized. The three  $sp^2$  hybridized orbitals would overlap with Cl orbitals to form the three "equatorial"  $\sigma$  bonds spaced at  $120^\circ$ , while the unhybridized  $2p$  orbital would overlap with Cl orbitals to form the two "axial"  $\sigma$  bonds.



Gray reef shark *Carcharhinus ambyrhynchus*  
Rangiroa, French Polynesia