# **Chapter 2 Molecular Representations**

# **Review of Concepts**

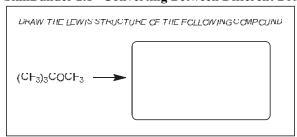
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 2. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

In <b>bond</b>	<b>l-line structures</b> , atoms and most atoms are not drawn.
Α	is a characteristic group of atoms/bonds that show a predictable behavior.
When a	carbon atom bears either a positive charge or a negative charge, it will have
rather th	nan four, bonds.
In bond	-line structures, a <b>wedge</b> represents a group coming the page, while a <b>dash</b>
represer	nts a group the page.
	<b>arrows</b> are tools for drawing resonance structures.
When d	rawing curved arrows for resonance structures, avoid breaking a bond and never
exceed	for second-row elements.
	owing rules can be used to identify the significance of resonance structures:
	The most significant resonance forms have the greatest number of filled
	The structure with fewer is more significant.
3.	Other things being equal, a structure with a negative charge on the more
	element will be more significant. Similarly, a positive charge will be more stable on the
	less element.
4.	Resonance forms that have equally good Lewis structures are described as
	and contribute equally to the resonance hybrid.
	lone pair participates in resonance and is said to occupy a orbital.
Α	lone pair does not participate in resonance.

# **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*.

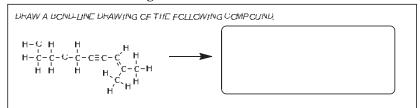
## SkillBuilder 2.1 Converting Between Different Drawing Styles



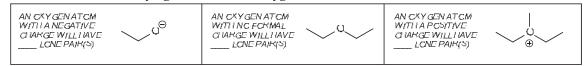
# SkillBuilder 2.2 Reading Bond-Line Structures



# SkillBuilder 2.3 Drawing Bond-Line Structures



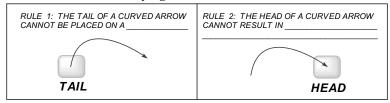
# SkillBuilder 2.4 Identifying Lone Pairs on Oxygen Atoms



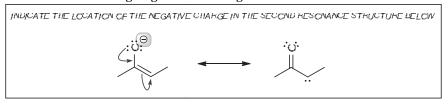
## SkillBuilder 2.5 Identifying Lone Pairs on Nitrogen Atoms



#### SkillBuilder 2.6 Identifying Valid Resonance Arrows

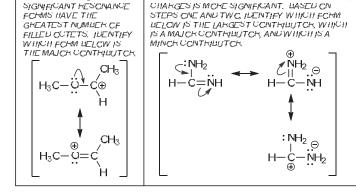


#### SkillBuilder 2.7 Assigning Formal Charges in Resonance Structures



STEP 2 THE STRUCTURE WITH FEWER FORMAL

# SkillBuilder 2.8 Ranking the Significance of Resonance Structures

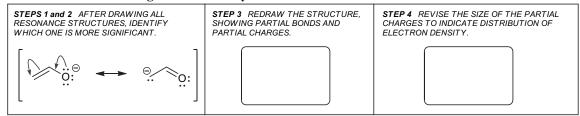


STEP 1 THE MOST

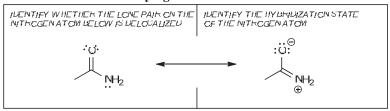
STEP 3 CONSIDER THE LOCATION OF THE FORMAL CHARGE(S), AND IDENTIFY THE MAJOR CONTRIBUTOR BELOW.

STEP 4 DETERMINE MAJOR AND MINOR
UCNTRIBUTORS, AND HANK RESONANCE FORMS.
AS A GENERAL RULE, IF ONE OR MORE OF THE
RESONANCE FORMS HAS ALL FILLED OUTETS,
THEN ANY RESONANCE FORM MISSING AN OUTET
WILL BE A MINOR CONTRIBUTOR.

## SkillBuilder 2.9 Drawing a Resonance Hybrid



### SkillBuilder 2.10 Identifying Localized and Delocalized Lone Pairs



# **Common Mistakes to Avoid**

When drawing a structure, make sure to avoid drawing a pentavalent carbon atom, or even a hexavalent or heptavalent carbon atom:



Carbon cannot have more than four bonds. Avoid drawing a carbon atom with more than four bonds, as that is one of the worst mistakes you can make as a student of organic chemistry.

Also, when drawing a structure, either draw all carbon atom labels (C) and all hydrogen atom labels (H), like this:

or don't draw any labels (except H attached to a heteroatom), like this:

That is, if you draw all C labels, then you should really draw all H labels also. Avoid drawings in which the C labels are drawn and the H labels are not, as shown here:

INCORRECT	INCORRECT
C-C-C-C-OH	C_C_C_OH

These types of drawings (where C labels are shown and H labels are not shown) should only be used when you are working on a scratch piece of paper and trying to draw constitutional isomers. For example, if you are considering all constitutional isomers with the molecular formula C<sub>3</sub>H<sub>8</sub>O, you might find it helpful to

use drawings like these as a form of "short-hand" so that you can identify all of the different ways of connecting three carbon atoms and one oxygen atom:

But your final structures should either show all C and H labels, or no labels at all. The latter is the more commonly used method:

# **Solutions**

#### 2.1.

(a) The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(b)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(c)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(d)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(e)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(f)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

$$\begin{array}{cccc} & & H & H \\ & & H - C & H \\ & & H - C & H \\ & & C = C \\ & & & C = C \\ & & & & H - C & H \\ & & & H - C & H \\ & & & H - C & H \\ & & & H - C & H \\ & & & H - C & H \\ & & & & H - C$$

**(g)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis

structure shows these connections more clearly, because every bond is drawn:

$$(CH_3)_3CCH_2CH_2OH \\ Condensed structure \\ H - C - C - C - C - O - H \\ H - C - H - H \\ H - H - H \\ Lewis structure$$

**(h)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

(i) The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

(j) The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

**(k)** The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis structure shows these connections more clearly, because every bond is drawn:

(I) The condensed structure indicates the constitution (how the atoms are connected to each other). The Lewis

structure shows these connections more clearly, because every bond is drawn:

**2.2.** Begin by drawing a Lewis structure for each isomer, so that the bonding of the carbon atoms is shown more clearly. Notice that in two of the isomers, a carbon atom is sharing a double bond with oxygen. Each of these carbon atoms is  $sp^2$  hybridized. All of the other carbon atoms exhibit four single bonds and are  $sp^3$  hybridized. These seven carbon atoms are highlighted, and thus the number of  $sp^3$ -hybridized carbons in the structures are two, three, and two, respectively:

2.3.

(a) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has six carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

**(b)** Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has twelve carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

$$=\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3}C \\ C \\ C \\ C \\ C \\ CH_{3} \end{array}$$

(c) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has six carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

(d) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

**(e)** Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

$$\ddot{\mathbf{v}} = \begin{bmatrix} \mathbf{v} & \mathbf{v} & \mathbf{v} & \mathbf{v} \\ \mathbf{v} & \mathbf{$$

**(f)** Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown:

**2.4.** Remember that each corner and each endpoint represents a carbon atom. This compound therefore has 16 carbon atoms, highlighted below:

Each carbon atom should have four bonds. We therefore draw enough hydrogen atoms in order to give each carbon atom a total of four bonds. Any carbon atoms that already have four bonds will not have any hydrogen atoms:

**2.5.** In each of the following structures, the carbon skeleton is drawn in a zig-zag format, in which carbon atoms represent each corner and endpoint. Hydrogen atoms are only drawn if they are connected to heteroatoms:

2.6. The carbon skeleton is drawn in a zig-zag format, in which carbon atoms represent each corner and endpoint.

2.7. The functional groups in the following compounds are highlighted and identified, using the terminology found in Table 2.1.

# 2.8.

(a) In this case, the oxygen atom has two bonds and no formal charge, so it must have two lone pairs (see Table

In this case, each of the oxygen atoms has two bonds and no formal charge, so each oxygen atom must have two lone pairs (see Table 2.2).

In this case, each of the oxygen atoms has two (c) bonds and no formal charge, so each oxygen atom must have two lone pairs (see Table 2.2).

(d) One of the oxygen atoms has two bonds and no formal charge, so that oxygen atom must have two lone pairs (see Table 2.2). The other oxygen atom has one bond and a negative charge, so that oxygen atom must have three lone pairs.

In this case, the oxygen atom has one bond and a negative charge, so it must have three lone pairs (see Table 2.2).

In this case, the oxygen atom has two bonds and no formal charge, so it must have two lone pairs (see Table 2.2).



(g) In this case, the oxygen atom has three bonds and a positive charge, so it must have one lone pair (see Table 2.2).

(h) In this case, the oxygen atom has three bonds and a positive charge, so it must have one lone pair (see Table 2.2).

From left to right, the first oxygen atom has two bonds and no formal charge, so it must have two lone pairs (see Table 2.2). The second oxygen atom has three bonds and a positive charge, so it must have one lone pair. Finally, the third oxygen atom has one bond and a negative charge, so it has three lone pairs.

(j) One of the oxygen atoms has two bonds and no formal charge, so that oxygen atom must have two lone pairs (see Table 2.2). The other oxygen atom has three bonds and a positive charge, so that oxygen atom must have one lone pair.

**2.9.** Each oxygen atom in hydroxymethylfurfural lacks a charge and has two bonds, so each oxygen atom must have two lone pairs.

#### 2.10.

(a) In this case, the nitrogen atom has three bonds and no formal charge, so it must have one lone pair (see Table 2.3).

**(b)** In this case, the nitrogen atom has three bonds and no formal charge, so it must have one lone pair (see Table 2.3).

**(c)** In this case, the nitrogen atom has three bonds and no formal charge, so it must have one lone pair (see Table 2.3).



(d) In this case, the nitrogen atom has four bonds and a positive charge, so it must have no lone pairs (see Table 2.3).



**(e)** In this case, the nitrogen atom has two bonds and a negative charge, so it must have two lone pairs (see Table 2.3).

**(f)** In this case, the nitrogen atom has three bonds and no formal charge, so it must have one lone pair (see Table 2.3).

(g) In this case, the nitrogen atom has four bonds and a positive charge, so it must have no lone pairs (see Table 2.3).

**(h)** One of the nitrogen atoms has four bonds and a positive charge, so it must have no lone pairs (see Table 2.3). The other nitrogen atom has three bonds and no formal charge, so it must have one lone pair.



**2.11.** Every uncharged nitrogen atom in this compound has three bonds and needs one lone pair of electrons to fill its octet. Every positively charged nitrogen atom has four bonds and no lone pairs.

#### 2.12.

- (a) This curved arrow violates the second rule by giving a fifth bond to a nitrogen atom.
- **(b)** This curved arrow does not violate either rule.
- (c) This curved arrow violates the second rule by giving five bonds to a carbon atom.
- **(d)** This curved arrow violates the second rule by giving three bonds and two lone pairs to an oxygen atom.
- **(e)** This curved arrow violates the second rule by giving five bonds to a carbon atom.
- **(f)** This curved arrow violates the second rule by giving five bonds to a carbon atom.
- **(g)** This curved arrow violates the first rule by breaking a single bond, and violates the second rule by giving five bonds to a carbon atom.
- **(h)** This curved arrow violates the first rule by breaking a single bond, and violates the second rule by giving five bonds to a carbon atom.
- (i) This curved arrow does not violate either rule.
- (j) This curved arrow does not violate either rule.
- **(k)** This curved arrow violates the second rule by giving five bonds to a carbon atom.
- (I) This curved arrow violates the second rule by giving five bonds to a carbon atom.
- **2.13.** The tail of the curved arrow must be placed on the double bond in order to avoid violating the first rule (avoid breaking a single bond).

#### 2.14.

- (a) This curved arrow violates the first rule (avoid breaking a single bond).
- **(b)** This curved arrow does not violate either rule.
- **(c)** This curved arrow violates the second rule (never exceed an octet for second-row elements) by giving five bonds to a carbon atom.
- **(d)** This curved arrow violates the second rule by giving five bonds to a carbon atom.

#### 2.15.

(a) The curved arrow indicates that we should draw a resonance structure in which the  $\pi$  bond has been pushed over. We then complete the resonance structure by assigning any formal charges. Notice that both resonance structures show a positive charge, but in different locations:

(b) The curved arrows indicate that we should draw a resonance structure in which the lone pair has been pushed to become a  $\pi$  bond, and the  $\pi$  bond has been pushed to become a lone pair. We then complete the resonance structure by assigning any formal charges. Notice that both resonance structures show a negative charge, but in different locations:

(c) The curved arrows indicate that we should draw a resonance structure in which a lone pair has been pushed

to become a  $\pi$  bond, and the  $\pi$  bond has been pushed to become a lone pair. We then complete the resonance structure by assigning any formal charges. Notice that both resonance structures have zero net charge:

(d) The curved arrows indicate that we should draw a resonance structure in which a lone pair has been pushed to become a  $\pi$  bond, and the  $\pi$  bond has been pushed to become a lone pair. We then complete the resonance structure by assigning any formal charges. Notice that both resonance structures show a negative charge, but in different locations:

**(e)** The curved arrows indicate that we should draw the following resonance structure. Notice that both resonance structures have zero net charge:

**(f)** The curved arrows indicate that we should draw the following resonance structure. Notice that both resonance structures have zero net charge:

(g) The curved arrows indicate that we should draw a resonance structure in which a lone pair has been pushed to become a  $\pi$  bond, and a  $\pi$  bond has been pushed to become a lone pair. We then complete the resonance structure by assigning any formal charges. Notice that both resonance structures have zero net charge, but they differ in the location of the negative charge:

**(h)** The curved arrows indicate that we should draw the following resonance structure. Notice that both resonance structures have zero net charge:

2.16.

(a) One curved arrow is required, showing the  $\pi$  bond being pushed to become a lone pair:

**(b)** Two curved arrows are required. One curved arrow shows the carbon-carbon  $\pi$  bond being pushed up, and the other curved arrow shows the carbon-oxygen  $\pi$  bond becoming a lone pair:

(c) Two curved arrows are required. One curved arrow shows a lone pair from the nitrogen atom becoming a  $\pi$  bond, and the other curved arrow shows the carbonoxygen  $\pi$  bond becoming a lone pair:

(d) One curved arrow is required, showing the  $\pi$  bond being pushed over:

2.17.

(a) Notice that there are two formal charges (positive and negative), but the positive charge is in the same locationi n all three resonance structures. Only the negative charge is spread out (over three locations). Two curved arrows are required to convert from resonance structure 2a to resonance structure 2b. One arrow shows that the lone pair on carbon can become a new carbon-nitrogen  $\pi$  bond while the other arrow shows that the electrons in

the original carbon-nitrogen  $\pi$  bond can become a lone pair on a different carbon atom.

(b) Two curved arrows are required to convert resonance structure 2a to resonance structure 2c. One arrow shows that the lone pair on carbon can become a carbon-carbon  $\pi$  bond while the other arrow shows that the electrons in the carbon-oxygen  $\pi$  bond can become a third lone pair on oxygen.

$$\begin{bmatrix} F_3C & & F_3C & &$$

#### 2.18.

(a) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

**(b)** This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(c) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(d) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(e) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(f) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(g) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(h) This pattern (lone pair next to a  $\pi$  bond) has two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

$$\begin{array}{c|c} & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

#### 2.19.

(a) This pattern has just one curved arrow, showing the  $\pi$  bond being pushed over:

(b) This pattern has just one curved arrow, showing the  $\pi$  bond being pushed over:

(c) This pattern has just one curved arrow, showing the  $\pi$  bond being pushed over. But when we draw the resulting resonance structure, we find that the same pattern can be applied again, giving another resonance structure, as shown:

(d) This pattern has just one curved arrow, showing the  $\pi$  bond being pushed over. But when we draw the resulting resonance structure, we find that the same pattern can be applied again, giving another resonance structure. This process continues several more times, and we can see that the positive charge is spread (via resonance) over all seven carbon atoms of the ring:

#### 2.20.

(a) This pattern has just one curved arrow, showing the lone pair becoming a  $\pi$  bond:

**(b)** This pattern has just one curved arrow, showing the lone pair becoming a  $\pi$  bond:

(c) This pattern has just one curved arrow, showing the lone pair becoming a  $\pi$  bond:

### 2.21.

(a) This pattern has just one curved arrow, showing the  $\pi$  bond becoming a lone pair:

(b) This pattern has just one curved arrow, showing the  $\pi$  bond becoming a lone pair:

(c) This pattern has just one curved arrow, showing the  $\pi$  bond becoming a lone pair:

**2.22.** This pattern has just one curved arrow, showing the  $\pi$  bond becoming a lone pair:

**2.23.** This pattern has just one curved arrow, showing the  $\pi$  bond becoming a lone pair:

**2.24.** This pattern has three curved arrows, showing the  $\pi$  bonds moving in a circle.

#### 2.25.

(a) We begin by looking for the five patterns. In this case, there is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge, so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond), shown here:

(b) The positive charge occupies an allylic position, so we draw the one curved arrow associated with that pattern (pushing over the  $\pi$  bond). The positive charge in the resulting resonance structure is again next to another  $\pi$  bond, so we draw one curved arrow and another resonance structure, as shown here:

(c) The lone pair (associated with the negative charge) occupies an allylic position, so we draw the two curved arrows associated with that pattern. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

(d) We begin by looking for one of the five patterns that employs just one curved arrow (in this case, there is another pattern that requires two curved arrows, but we will start with the pattern using just one curved arrow). There is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair adjacent to a positive charge, so we draw the curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

(e) This structure exhibits a lone pair that is adjacent to a positive charge, so we draw one curved arrow, showing a lone pair becoming a  $\pi$  bond:

(f) This compound exhibits a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge,

so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). The positive charge in the resulting resonance structure is next to another  $\pi$  bond, so we draw one more resonance structure, as shown here:

(g) This structure exhibits a lone pair that is adjacent to a positive charge, so we draw one curved arrow, showing a lone pair becoming a  $\pi$  bond:

(h) This compound exhibits a C=N bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair:

(i) We begin by looking for one of the five patterns that employs just one curved arrow (in this case, there is another pattern that requires two curved arrows, but we will start with the pattern using just one curved arrow). There is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair adjacent to a positive charge, so we draw the curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

(j) We begin by looking for one of the five patterns that employs just one curved arrow (in this case, there is another pattern that requires two curved arrows, but we will start with the pattern using just one curved arrow). There is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair adjacent to a positive charge, so we draw the curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

#### 2.26.

(a) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. None of the four structures have an atom with an incomplete octet, so they are all expected to be major contributors to the hybrid. The first resonance structure is the largest contributor because it has filled octets and the negative charge is on the more electronegative nitrogen atom. The other three resonance structures are approximately equivalent and they are less significant than the first structure because the negative charge is on the less electronegative carbon atom.

Equivalent and less important (#2)

**(b)** Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. Both resonance structures have filled octets and a negative charge on an oxygen atom. Both resonance structures are equivalent and equally significant.

(c) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. None of the three structures has an atom with an incomplete octet. The first resonance structure is the largest contributor because it has filled octets and no formal charges. The other two resonance structures are equivalent and less significant contributors because they contain formal charges.

(d) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. The first resonance structure is the only major contributor because it is the only one with filled octets. Recall that a structure with filled octets and no formal charges is an ideal Lewis structure. The other three resonance structures are approximately equivalent and minor contributors because each one is missing an octet (they also have formal charges, but that is a less significant feature to consider when ranking resonance forms).

Equivalent and minor contributors

(e) Using the skills developed in the previous SkillBuilders, we begin by drawing all significant resonance structures, shown below. Neither resonance structure has an incomplete octet so they are both expected to be major contributors to the hybrid. The second resonance structure is the more significant contributor because it has the negative charge on the more electronegative nitrogen atom. The first resonance structure is less significant because the negative charge is on the less electronegative carbon atom.

(f) This cation has two different resonance patterns that can be employed, using the lone pair or the  $\pi$  bond to fill the vacancy on carbon, giving a total of three resonance structures. The middle resonance structure is the only major contributor because it is the only one with filled octets. The other two structures are equivalent (missing one octet and

positive charge on carbon atom). They are minor and contribute equally to the hybrid. Note that the location of the charge  $(C^+ vs. N^+)$  is not as important in this problem, because filled octets are more important.

**2.27.** When looking for resonance in the first structure, we can begin with the carbonyl (C=O) group by relocating the  $\pi$  bond electrons to the more electronegative oxygen atom. This provides a resonance structure with an allylic C+ that can undergo allylic resonance throughout the ring, resulting in three more resonance structures. Be careful to use just one  $\pi$  bond at a time so you don't accidentally "jump" over a possible resonance structure.

$$\begin{bmatrix} \vdots \circ \vdots & \vdots \circ \vdots \circ & \vdots \circ \vdots \circ \\ \vdots \circ \vdots \circ & \vdots \circ \vdots \circ \end{bmatrix}$$

For the second compound, the allylic lone pair can be delocalized using one of the  $\pi$  bonds in the benzene ring, and this pattern can continue to use the remaining  $\pi$  bonds in the ring (again, one at a time!).

Overall, when we consider the contributions made by all resonance structures, we find that the ring in the first compound is electron-poor, with several electron-deficient sites on the ring, and the ring in the second compound is electron-rich, with several  $\delta$ - sites on the ring.

**2.28.** The benzene ring on the left has two oxygen atoms attached. Both oxygen atoms can *donate* electron density via allylic lone pair resonance, making this benzene ring electron-rich.

The benzene ring on the right is "connected" to the carbonyl (C=O) groups by a series of alternating  $\pi$  bonds, so the resonance of each carbonyl group extends into the benzene ring. The carbonyl groups withdraw electron density via allylic carbocation resonance, making this ring electron-deficient.

In summary, the benzene ring on the left is electron-rich due to resonance with the lone pairs of electrons on both attached oxygen atoms. The benzene ring on the left is electron-poor due to resonance with the carbonyl groups.

2 20

(a) Begin by drawing all significant resonance structures. In this case, there are two:

Both resonance structures are equally significant, so the resonance hybrid is the simple average of these two resonance structures. There are no formal charges, so only partial bonds need to be drawn.



Resonance hybrid

**(b)** Begin by drawing all significant resonance structures. In this case, there are two:

Both are equally significant, so the resonance hybrid is the simple average of these two resonance structures. Both partial bonds and partial charges are required, as shown:



#### Resonance hybrid

(c) Begin by drawing all significant resonance structures. In this case, there are two:

The left-hand structure is more significant because every atom has an octet. The resonance hybrid is a weighted average of these two resonance structures in which the oxygen atom has more of the charge than the carbon atom.

# Resonance hybrid

(d) Begin by drawing all significant resonance structures. In this case, there are two:

Both are equally significant, so the resonance hybrid is the simple average of these two resonance structures. Only the negative charge is delocalized, so partial charges are used for the negative charge but not for the positive charge.

Resonance hybrid

(e) Begin by drawing all significant resonance structures. In this case, there are two:

The structure on the right is more significant because every atom has an octet. The resonance hybrid is a weighted average of these two resonance structures in which the nitrogen atom has more of the charge than the carbon atom.

Resonance hybrid

**(f)** Begin by drawing all significant resonance structures. In this case, there are two:

The structure on the left is more significant because every atom has an octet and it has no formal charges. The resonance hybrid is a weighted average of these two resonance structures, although we do not denote that by making the partial charges different sizes. In this example, the charges are opposite in sign, but they must be equal in magnitude so that the overall charge will be zero.

Resonance hybrid

**(g)** Begin by drawing all significant resonance structures. In this case, there are three:

All three resonance structures are equally significant, so the resonance hybrid is the simple average of these three resonance structures, illustrating that the positive charge is delocalized over three carbon atoms.

Resonance hybrid

**(h)** Begin by drawing all significant resonance structures. In this case, there are three:

The structure on the left is most significant because every atom has an octet and it has no formal charge. The resonance hybrid is a weighted average of these three resonance structures. Since the partial positive charge is delocalized over two carbon atoms and the partial negative charge is localized on only one oxygen atom, the partial negative charge is drawn larger than each of the individual partial positive charges.

Resonance hybrid

**2.30.** Begin by drawing all significant resonance structures. In this case, there are four:

The first three resonance structures are the most significant, because all atoms have an octet in each of these three resonance structures. The fourth resonance structure (in which the carbon atom bears the positive charge) is the least significant because a carbon atom lacks an octet. If we compare the three most significant resonance structures, each has a positive charge on a nitrogen atom, so we expect these three resonance structures to contribute roughly equally to the resonance hybrid. To show this, we indicate  $\delta$ + at all three positions, with a smaller  $\delta$ + symbol at the central carbon atom (indicating the lower contribution of the fourth resonance structure). Also, if we compare the first three resonance structures, we find that the  $\pi$  bond is spread over three locations, and these locations are indicated with dashed lines in the resonance hybrid:

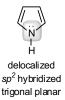
#### 2.31.

(a) Let's begin with the nitrogen atom on the left side of the structure. The lone pair on this nitrogen atom is delocalized by resonance (because it is next to a  $\pi$  bond). Therefore, this lone pair occupies a p orbital, which means that the nitrogen atom is  $sp^2$  hybridized. As a result, the geometry is trigonal planar.

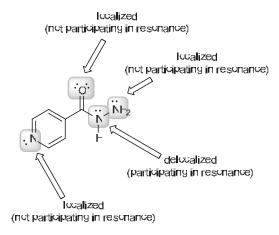
On the right side of the structure, there is a nitrogen atom with a localized lone pair (it does not participate in resonance). This nitrogen atom is therefore  $sp^3$  hybridized, with trigonal pyramidal geometry, just as expected for a nitrogen atom with  $\sigma$  sigma bonds and a localized lone pair.

(b) As we saw with pyridine, the lone pair on this nitrogen atom is not participating in resonance, because the nitrogen atom is already using a p orbital for the  $\pi$  bond. As a result, the lone pair cannot join in the conduit of overlapping p orbitals, and therefore, it cannot participate in resonance. In this case, the lone pair occupies an  $sp^2$  hybridized orbital, which is in the plane of the ring. Since this lone pair is not participating in resonance, it is localized. The nitrogen atom is  $sp^2$  hybridized, and the geometry is bent.

(c) The lone pair on this nitrogen atom is participating in resonance (it is next to a  $\pi$  bond), so it is delocalized via resonance. As such, the nitrogen atom is  $sp^2$  hybridized, with trigonal planar geometry.



- **2.32.** Each of these lone pairs is not participating in resonance. So each of these lone pairs is localized. Therefore, both lone pairs are expected to be reactive.
- **2.33.** Lone pairs that participate in resonance are delocalized, while those that do not participate in resonance are localized:



#### 2.34.

(a) Each corner and each endpoint represents a carbon atom (highlighted), so this compound has nine carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown. Each of the

oxygen atoms has two bonds and no formal charge, so each oxygen atom will have two lone pairs.

**(b)** Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has eight carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown. Each of the oxygen atoms has two bonds and no formal charge, so each oxygen atom will have two lone pairs. The nitrogen atom has three bonds and no formal charge, so it must have one lone pair of electrons.

(c) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has eight carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, as shown. Each of the oxygen atoms has two bonds and no formal charge, so each oxygen atom will have two lone pairs. Each nitrogen atom has three bonds and no formal charge, so each nitrogen atom must have one lone pair of electrons.

**2.35.** The molecular formula indicates that there are four carbon atoms. Recall that constitutional isomers are compounds that share the same molecular formula, but differ in constitution (the connectivity of atoms). So we are looking for different ways that four carbon atoms can be connected together. As described in the solution to Problem **1.1b**, the carbon atoms can be connected in a linear fashion (below left), or they can be connected with a branch (below right).

$$C_4$$
 $F_{10}$   $C_4$  $F_{10}$ 

These two compounds are the only constitutional isomers that have the molecular formula  $C_4H_{10}$ , because there are no other ways to connect four carbon atoms without changing the number of hydrogen atoms. For example, if we try to connect the carbon atoms into a ring, we find that the number of hydrogen atoms is reduced:

$$\begin{array}{ccc}
& & & \\
C_4 F_8 & & C_4 F_8
\end{array}$$

**2.36.** As described in the solution to Problem **1.1c**, there are only three constitutional isomers with the molecular formula  $C_5H_{12}$ , shown here again.

There are no other constitutional isomers with the molecular formula  $C_5H_{12}$ . The following two structures do NOT represent constitutional isomers, but are in fact two drawings of the same compound, as can be seen when the carbon skeletons are numbered, as shown:

Notice that in both drawings, the longest linear chain is four carbon atoms, and there is a  $CH_3$  group attached to the second carbon atom of the chain. As such, these two drawings represent the same compound. In contrast, we can see that all three constitutional isomers with the molecular formula  $C_5H_{12}$  exhibit different connectivity of the carbon atoms:

**2.37.** In each of the following structures, each corner and endpoint represents a carbon atom. Hydrogen atoms are only drawn if they are connected to heteroatoms (such as oxygen).

**2.38.** Each oxygen atom has two bonds and no formal charge. Therefore, each oxygen atom has two lone pairs, for a total of twelve lone pairs.

**2.39.** Carbon is in group **4A** of the periodic table, and it should therefore have four valence electrons. We are told that, in this case, the central carbon atom does not bear a formal charge.



Therefore, it must exhibit the appropriate number of valence electrons (four). This carbon atom already has two bonds (each of which requires one valence electron) and a lone pair (which represents two electrons), for a total of 1+1+2=4 valence electrons. This is the appropriate number of valence electrons, which means that this carbon atom does not have any bonds to hydrogen.

Notice that the carbon atom lacks an octet, so it should not be surprising that this structure is highly reactive and very short-lived.

**2.40.** An oxygen atom will bear a negative charge if it has one bond and three lone pairs, and it will bear a positive charge if it has three bonds and one lone pair (see Table 2.2). A nitrogen atom will bear a negative charge if it has two bonds and two lone pairs, and it will bear a positive charge if it has four bonds and no lone pairs (see Table 2.3).

**2.41.** This compound exhibits a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge, so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). This pattern continues, many more times, spreading the positive charge over many locations, as shown here:

**2.42.** Recall that constitutional isomers are compounds that share the same molecular formula, but differ in constitution (the connectivity of atoms). The problem statement shows a compound with the molecular formula  $C_5H_{12}$  and the following structure:

$$CF_3CF_2CF(CF_3)_2 \equiv$$

So we are looking for other compounds that also have the molecular formula  $C_5H_{12}$  but show a different connectivity of atoms. As seen in the solution to Problem 2.36, there are only two such compounds:

$$\sim$$

**2.43.** The following two compounds are constitutional isomers because they share the same molecular formula  $(C_5H_{12}O)$ . The third compound (not shown here) has a different molecular formula  $(C_4H_{10}O)$ .

**2.44.** Begin by drawing a Lewis structure, so that the bonding of each carbon atom is shown more clearly:

$$(CF_3)_2C=CFC(CF_3)_3 \qquad C=C \qquad C=C \qquad C=C \qquad F$$

$$C=C \qquad C=C \qquad C=C \qquad F$$

$$C=C \qquad C=C \qquad C=C \qquad F$$

$$C=C \qquad F$$

Lewis structure

Notice that two of the carbon atoms are sharing a double bond. These two atoms are  $sp^2$  hybridized. Each of the other six carbon atoms exhibits four single bonds, and as

such, each of these six carbon atoms (highlighted) is  $sp^3$  hybridized.

**2.45.** One of the oxygen atoms has two bonds and no formal charge, so that oxygen atom must have two lone pairs (see Table 2.2). The other oxygen atom has one bond and a negative charge, so that oxygen atom must have three lone pairs. The nitrogen atom has four bonds and a positive charge, so it does not have any lone pairs (see Table 2.3). Therefore, there are a total of five lone pairs in this structure.

#### 2.46.

(a) In order for the lone pair to participate in resonance, it must occupy a *p* orbital, which would render the nitrogen atom *sp* hybridizxed. With *sp* hybridization, the geometry of the nitrogen atom should be linear, which cannot be accommodated in a six-membered ring.

**(b)** There is a lone pair associated with the negative charge, and this lone pair is delocalized via resonance (the lone pair is allylic):

As such, the lone pair must occupy a p orbital.

**(c)** The nitrogen atom has a lone pair, which is delocalized via resonance (there is an adjacent positive charge):

As such, the lone pair must occupy a p orbital.

#### 2.47.

(a) This structure exhibits a lone pair that is adjacent to a positive charge. In fact, there are two such lone pairs (on the nitrogen and oxygen atoms). We will begin with a lone pair on the oxygen atom, although we would have arrived at the same solution either way (we will draw a total of three resonance structures, below, and it is just a matter of the order in which we draw them). We draw one curved arrow, showing a lone pair on the oxygen atom becoming a  $\pi$  bond. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair next to a  $\pi$  bond, so we draw the two curved arrows associated with that pattern. The first curved arrow is drawn showing a lone pair on the nitrogen atom becoming a  $\pi$ bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair on the oxygen atom:

(b) This structure exhibits an allylic positive charge, so we draw one curved arrow showing the  $\pi$  bond being pushed over. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the positive charge is adjacent to a lone pair, so we draw the curved arrow associated with that pattern (the lone pair is shown becoming a  $\pi$  bond):

(c) This structure exhibits an allylic positive charge, so we draw one curved arrow showing the  $\pi$  bond being pushed over. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the positive charge is again next to a  $\pi$  bond, so again, we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond again). The resulting resonance structure has the positive charge next to yet another  $\pi$  bond, so we draw a curved arrow showing the  $\pi$  bond being pushed over one more time to give our final resonance structure:

#### 2.48.

(a) In a condensed structure, single bonds are not drawn. Instead, groups of atoms are clustered together, as shown here:

 $(CH_3)_3CCH_2CH_2CH(CH_3)_2$ 

**(b)** In a condensed structure, single bonds are not drawn. Instead, groups of atoms are clustered together, as shown here:

**(c)** In a condensed structure, single bonds are not drawn. Instead, groups of atoms are clustered together, as shown here:

 $CH_3CH_2CH=C(CH_2CH_3)_2$ 

#### 2.49.

(a) Each corner and each endpoint represents a carbon atom, so this compound has nine carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, giving a total of twenty hydrogen atoms. So the molecular formula is C<sub>9</sub>H<sub>20</sub>.

(b) Each corner and each endpoint represents a carbon atom, so this compound has six carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, giving a total of fourteen hydrogen atoms. So the molecular formula is  $C_6H_{14}O$ .

(c) Each corner and each endpoint represents a carbon atom, so this compound has eight carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, giving a total of sixteen hydrogen atoms. So the molecular formula is C<sub>8</sub>H<sub>16</sub>.

**2.50.** Each corner and each endpoint represents a carbon atom, so this compound has fifteen carbon atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds, giving a total of eighteen hydrogen atoms, as shown here:

**2.51.** As seen in the solution to Problem 2.35, there are only two ways to connect four carbon atoms in a compound with the molecular formula C<sub>4</sub>H<sub>10</sub>:

In our case, the molecular formula is  $C_4H_9Cl$ , which is similar to  $C_4H_{10}$ , but one H has been replaced with a chlorine atom. So, we must explore all of the different locations where a chlorine atom can be placed on each of the carbon skeletons above (the linear skeleton and the branched skeleton).

Let's begin with the linear skeleton. There are two distinctly different locations where a chlorine atom can be placed on this skeleton: either at position 1 or position 2, shown here.

$$CI$$
 $2$ 
 $4$ 
 $2$ 
 $CI$ 
 $4$ 

Placing the chlorine atom at position 3 would be the same as placing it at position 2; and placing the chlorine atom at position 4 would be the same as it as position 1:

Next, we move on to the other carbon skeleton, containing a branch. Once again, there are two distinctly different locations where a chlorine atom can be placed: either at position 1 or position 2, shown here.

Placing the chlorine atom on any of the peripheral carbon atoms will lead to the same compound:

In summary, there are a total of four constitutional isomers with the molecular formula C<sub>4</sub>H<sub>9</sub>Cl:

#### 2.52.

(a) This compound exhibits a lone pair next to a  $\pi$  bond, so we draw the two curved arrows associated with that pattern. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

**(b)** This structure exhibits a lone pair that is adjacent to a positive charge, so we draw one curved arrow, showing a lone pair becoming a  $\pi$  bond:

(c) This structure exhibits an allylic positive charge, so we draw one curved arrow showing the  $\pi$  bond being pushed over.

(d) This compound exhibits a C=N bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair.

(e) This compound exhibits a lone pair next to a  $\pi$  bond, so we draw two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the lone pair is now next to another  $\pi$  bond, so once again, we draw the two curved arrows associated with that pattern. The resulting resonance structure again exhibits a lone pair next to a  $\pi$  bond. This pattern continues again, thereby spreading a negative charge over many locations, as shown here:

(f) This structure exhibits a lone pair next to a  $\pi$  bond, so we draw two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the lone pair is now next to another  $\pi$  bond, so once again, we draw the two curved arrows associated with that pattern. The resulting resonance structure again exhibits a lone pair next to a  $\pi$  bond, so we draw one more resonance structure, as shown here:

(g) This compound exhibits a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge, so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). This pattern continues, many more times, spreading the positive charge over many locations, as shown here:

(h) We begin by looking for one of the five patterns that employs just one curved arrow (in this case, there is another pattern that requires two curved arrows, but we will start with the pattern using just one curved arrow). There is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair adjacent to a positive charge, so we draw the curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

(i) This structure exhibits an allylic positive charge, so we draw one curved arrow showing the  $\pi$  bond being pushed over. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the positive charge is again next to a  $\pi$  bond, so again, we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). The resulting resonance structure has a positive charge adjacent to a lone pair, so we draw the one curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

(j) This structure exhibits an allylic positive charge, so we draw one curved arrow showing the  $\pi$  bond being pushed over. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the positive charge is again next to a  $\pi$  bond, so again, we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). The resulting resonance structure again has a positive charge next to a  $\pi$  bond, so again, we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond). The resulting resonance structure has a positive charge adjacent to a lone pair, so we draw the one curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here.

**2.53.** These structures do not differ in their connectivity of atoms. They differ only in the placement of electrons.

Therefore, these structures are resonance structures, as shown here:

#### 2.54.

- (a) These compounds both have the same molecular formula  $(C_7H_{12})$ , but they differ in their connectivity of atoms, or constitution. Therefore, they are constitutional isomers.
- **(b)** These structures have the same molecular formula  $(C_7H_{16})$ , AND they have the same constitution (connectivity of atoms), so they represent the same compound.
- (c) The first compound has the molecular formula  $C_5H_{10}$ , while the second compound has the molecular formula  $C_5H_8$ . As such, they are different compounds that are not isomeric.
- (d) These compounds both have the same molecular formula (C<sub>5</sub>H<sub>8</sub>), but they differ in their connectivity of atoms, or constitution. Therefore, they are constitutional isomers.

## 2.55.

(a) The condensed structure (shown in the problem statement) indicates the constitution (how the atoms are connected to each other). In the bond-line structure, hydrogen atoms are not drawn (they are implied). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

**(b)** The condensed structure indicates how the atoms are connected to each other. In the bond-line structure, hydrogen atoms are not drawn (they are implied), except for the hydrogen atom attached to the oxygen atom (hydrogen atoms must be drawn if they are connected to a heteroatom, such as oxygen). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

(c) The condensed structure indicates how the atoms are connected to each other. In the bond-line structure,

hydrogen atoms are not drawn (they are implied). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

(d) The condensed structure indicates how the atoms are connected to each other. In the bond-line structure, hydrogen atoms are not drawn (they are implied). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

**(e)** The condensed structure indicates how the atoms are connected to each other. In the bond-line structure, hydrogen atoms are not drawn (they are implied). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

**(f)** The condensed structure indicates how the atoms are connected to each other. In the bond-line structure, hydrogen atoms are not drawn (they are implied). Each corner and each endpoint represents a carbon atom, so the carbon skeleton is shown more clearly.

Bond-line structure

- **2.56.** 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 be significant resonance structures.
- **2.57.** The negatively charged oxygen atom has three lone pairs, while the positively charged oxygen atom has one lone pair (see Table 2.2). Notice that this compound exhibits a lone pair that is next to a  $\pi$  bond, so we must draw two curved arrows associated with that pattern. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair:

There are no other valid resonance structures that are significant.

**2.58.** Each nitrogen atom has a lone pair that is delocalized via resonance. In order to be delocalized via resonance, the lone pair must occupy a p orbital, and therefore, each nitrogen atom must be  $sp^2$  hybridized. As such, each nitrogen atom is trigonal planar.

#### 2.59.

(a) This compound exhibits a lone pair next to a  $\pi$  bond, so we draw two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, the lone pair is next to another  $\pi$  bond, so once again, we draw the two curved arrows associated with that pattern. The resulting resonance structure again exhibits a lone pair next to a  $\pi$  bond, so again we draw two curved arrows and the resulting resonance structure. Once again, there is a lone pair next to a  $\pi$  bond, which requires that we draw one final resonance structure, shown below. This last resonance structure is not the same as the original resonance structure, because of the locations in which the  $\pi$  bonds are drawn.

(b) The following compound exhibits a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge, so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond), shown here:

**2.60.** This compound exhibits a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is an allylic positive charge, so we draw the curved arrow associated with that pattern (pushing over the  $\pi$  bond), shown here. This pattern continues, many more times, spreading the positive charge over many locations:

By considering the significant resonance structures (drawn above), we can determine the positions that are electron deficient  $(\delta+)$ . This information is summarized here.

**2.61.** This compound exhibits a lone pair next to a  $\pi$  bond, so we draw two curved arrows. The first curved arrow is drawn showing a lone pair becoming a  $\pi$  bond, while the second curved arrow shows a  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair next to a  $\pi$  bond, so once again, we draw the two curved arrows associated with that pattern. The resulting resonance structure again exhibits a lone pair next to a  $\pi$  bond. This pattern continues, many more times, spreading a negative charge over many locations:

By considering the significant resonance structures (drawn above), we can determine the positions that are electron rich ( $\delta$ -). This information is summarized here.

**2.62.** Two patterns of resonance can be identified on the given structure: carbonyl resonance and allylic lone pair resonance (involving either the oxygen or nitrogen lone pairs). All three of these options will be used. Since it is possible to start with any one of the three, you may have developed the resonance forms in a different order than presented here, but you still should have found four reasonable resonance forms. Only one of the four structures has an atom with an incomplete octet (the last resonance structure shown), so that is identified as the only minor contributor to the hybrid. The first resonance form is the largest contributor because it has filled octets and no formal charges. The middle two resonance structures both have filled octets and a negative charge on an oxygen atom, so they are ranked according to their only difference: the location of the positive charge. The third structure is the 2<sup>nd</sup> most significant resonance form because it has the positive charge on the less electronegative nitrogen atom. Note it is better to place a

negative charge on a more electronegative atom, and it is better to place a positive charge on a less electronegative atom.

**2.63.** The only resonance pattern evident in the enamine is an allylic lone pair. After that pattern is applied, however, another allylic lone pair results so the resonance can ultimately involve both  $\pi$  bonds. There are a total of three major resonance forms that all have filled octets. Consideration of the hybrid of these resonance forms predicts two electronrich sites.

Did you draw the following additional structure (or something similar, with C+ and C-) and wonder why it was not shown in this solution?

Insignificant

This resonance form suffers from two major deficiencies: 1) it does not have filled octets, while the other resonance forms shown above all have filled octets, and 2) it has a negative charge on a carbon atom (which is not an electronegative atom). Either of these deficiencies alone would render the resonance form a minor contributor. But with both deficiencies together (C+ and C-), this resonance form is insignificant. The same is true for any resonance form that has both C+ and C-. Such a resonance form will generally be insignificant (there are very few exceptions, one of which will be seen in Chapter 17).

Also, note that the  $\pi$  bonds cannot be moved to other parts of the six-membered ring since the CH<sub>2</sub> groups are  $sp^3$  hybridized. These carbon atoms cannot accommodate an additional bond without violating the octet rule.

# 2.64.

- (a) The molecular formula is C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>.
- **(b)** Each of the highlighted carbon atoms (below) has four sigma bonds (the bonds to hydrogen are not shown). As such, these two carbon atoms are  $sp^3$  hybridized.

(c) There is one carbon atom that is using a p orbital to form a  $\pi$  bond. As such, this carbon atom (highlighted) is  $sp^2$  hybridized.

- (d) There are no sp hybridized carbon atoms in this structure.
- (e) There are six lone pairs (each nitrogen atom has one lone pair and each oxygen atom has two lone pairs):

**(f)** Only the lone pair on one of the nitrogen atoms is delocalized via resonance (to see why it is delocalized, see the solution to 2.64h). The other lone pairs are all localized.

**(g)** The geometry of each atom is shown below (see SkillBuilder 1.8):

(h) We begin by looking for one of the five patterns that employs just one curved arrow (in this case, there is another pattern that requires two curved arrows, but we will start with the pattern using just one curved arrow). There is a C=O bond (a  $\pi$  bond between two atoms of differing electronegativity), so we draw one curved arrow showing the  $\pi$  bond becoming a lone pair. We then draw the resulting resonance structure and assess whether it exhibits one of the five patterns. In this case, there is a lone pair adjacent to a positive charge, so we draw the curved arrow associated with that pattern (showing the lone pair becoming a  $\pi$  bond), shown here:

#### 2.65.

- (a) The molecular formula is  $C_{16}H_{21}NO_2$ .
- **(b)** Each of the highlighted carbon atoms (below) has four sigma bonds (the bonds to hydrogen are not shown). As such, these nine carbon atoms are  $sp^3$  hybridized.

(c) There are seven carbon atoms that are each using a p orbital to form a  $\pi$  bond. As such, these seven carbon atoms (highlighted) are  $sp^2$  hybridized.

- (d) There are no sp hybridized carbon atoms in this structure
- **(e)** 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 via resonance. The lone pair on the nitrogen atom is delocalized via resonance.
- (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 (see SkillBuilder 1.8).

#### 2.66.

(a) In Section 1.5, we discussed inductive effects and we learned how to identify polar covalent bonds. In this case, there are two carbon atoms that participate in polar covalent bonds (the C–Br bond and the C–O bond). Each of these carbon atoms will be poor in electron density  $(\delta+)$  because oxygen and bromine are each more electronegative than carbon:

**(b)** There are two carbon atoms that are adjacent to oxygen atoms. These carbon atoms will be poor in

electron density ( $\delta$ +), because oxygen is more electronegative than carbon:

The carbon atom of the carbonyl (C=O) group is especially electron deficient, as a result of resonance.

(c) There are two carbon atoms that are adjacent to electronegative atoms. These carbon atoms will be poor in electron density  $(\delta+)$ , because oxygen and chlorine are each more electronegative than carbon:

The carbon atom of the carbonyl (C=O) group is especially electron deficient, as a result of resonance.

**2.67.** We begin by drawing all significant resonance structures, and then considering the placement of the formal charges in each of those resonance structures (highlighted below)

A position that bears a positive charge is expected to be electron deficient ( $\delta$ +), while a position that bears a negative charge is expected to be electron rich ( $\delta$ -). The following is a summary of the electron-deficient positions and the electron-poor positions, as indicated by the resonance structures above.

#### 2.68.

(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 significant 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:

#### 2.69.

(a) The following group is introduced, and it contains five carbon atoms:

**(b)** The following highlighted carbon atom is involved in the reaction:

(c) Compound 1 has three significant resonance structures, shown here:

The structure on the left is the most significant, because every atom has an octet and it has no formal charges. The resonance hybrid is a weighted average of these three resonance structures. Since the partial positive charge is delocalized onto two carbon atoms and the partial negative charge is localized on only one oxygen atom, the partial negative charge is drawn larger than each of the individual partial positive charges.

(d) The reactive site has partial positive character, which means that it is electron deficient. This is what makes it reactive. In the actual synthesis, this compound is treated with a carbanion (a structure containing a carbon atom with a negative charge). The reaction causes formation of a bond between the electron-deficient carbon atom and the electron-rich carbon atom. We will learn that reaction in Chapter 21.

**2.70.** We will need to draw two resonance hybrids, one for each of the highlighted carbon atoms. One highlighted position is part of an aromatic ring, and we will begin by focusing on that position. In doing so, we can save time by redrawing only the relevant portion of the molecule, like this:

$$= \begin{array}{c} RO \\ OR \end{array}$$

This aromatic ring has eight significant resonance structures, shown below:

The resonance hybrid is a weighted average of these eight resonance structures. Resonance structures 1 and 2 are equally most significant because all atoms have an octet AND there are no formal charges. Resonance structures 3-8 are less significant than 1 and 2 but equally significant to each other because every atom has a full octet with a positive charge on an oxygen atom and a negative charge on a carbon atom. Since the partial negative charge is delocalized onto three carbon atoms and the partial positive charge is delocalized onto only two oxygen atoms, the partial positive charges are drawn slightly larger than the partial negative charges. The analysis allows us to draw the resonance hybrid for this portion of the molecule, and it demonstrates that the highlighted carbon atom is  $\delta$ -.

Now let's focus on our attention on the other highlighted carbon atom (the one that is part of a carboxylic acid group). Just as we did before, we will draw only the portion of the molecule that is of interest:

This portion of the molecule has four significant resonance structures, shown below:

The resonance hybrid is a weighted average of these four resonance structures. Resonance structure 1 is most significant because all atoms have an octet AND there are no formal charges. Resonance structure 3 is the next most significant because there are formal charges, yet every atom has a full octet. Since the partial negative charge is localized on one oxygen atom, this partial charge is the largest. The partial positive charge is delocalized over three atoms, but it is larger on the oxygen (relative to either of the carbon atoms). The resonance hybrid demonstrates that this carbon atom is  $\delta$ +.

## 2.71.

- (a) The molecular formula for CL-20 is C<sub>6</sub>H<sub>6</sub>N<sub>12</sub>O<sub>12</sub>. The molecular formula for HMX is C<sub>4</sub>H<sub>8</sub>N<sub>8</sub>O<sub>8</sub>.
- **(b)** The lone pair is delocalized (see resonance structures below).

#### 2.72.

This intermediate is highly stabilized by resonance. The positive charge is spread over one carbon atom and three oxygen atoms.

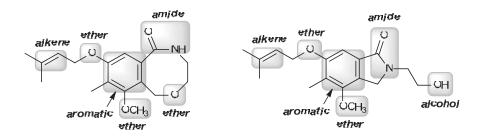
#### 2.73.

(a) Both molecules have identical functional groups (alcohol + alkene).

The structure on the left exhibits two six-membered rings and two five-membered rings, while the structure on the right has three six-membered rings and only one five-membered ring.

The long alkane group is apparently located in the wrong position on the five-membered ring of the incorrect structure.

**(b)** Both structures contain an alkene group, an aromatic ring, an amide group, and two ether functional groups. But the incorrect structure has a third ether functional group (in the eight-membered ring), while the correct structure has an alcohol functional group. The incorrect structure has an eight-membered ring, while the correct structure has a five-membered ring. The two carbon atoms and oxygen atom in the ring of the incorrect structure are not part of the ring for the correct structure.



# 2.74.

(a) The positive charge in basic green 4 is resonance-stabilized (delocalized) over twelve positions (two nitrogen atoms and ten carbon atoms), as seen in the following resonance structures.

**(b)** The positive charge in basic violet 4 is expected to be more stabilized than the positive charge in basic green 4, because the former is delocalized over thirteen positions, rather than twelve. Specifically, basic violet 4 has an additional resonance structure that basic green 4 lacks, shown below:

In basic violet 4, the positive charge is spread over *three* nitrogen atoms and ten carbon atoms.

**2.75.** Polymer 2 contains only ester groups, so the IR spectrum of polymer **2** is expected to exhibit a signal near 1740 cm<sup>-1</sup> (typical for esters), associated with vibrational excitation (stretching) of the C=O bond. Polymer **4** lacks any ester groups, so the signal near 1740 cm<sup>-1</sup> is expected to be absent in the IR spectrum of polymer **4**. Instead, polymer **4** has OH groups, which are expected to produce a broad signal in the range 3200-3600 cm<sup>-1</sup>. Polymer **3** has both functional groups (alcohol group and ester group), so an IR spectrum of polymer **3** is expected to exhibit both characteristic signals. When polymer **3** is converted to polymer **4**, the signal near 1740 cm<sup>-1</sup> is expected to vanish, which would indicate complete hydrolysis of polymer **3**.

In practice, the signal for the C=O stretch in polymer 2 appears at 1733 cm<sup>-1</sup>, which is very close to our estimated value of 1740 cm<sup>-1</sup>.

**2.76.** Compound **1** has an OH group, which is absent in compound **2**. Therefore, the IR spectrum of **1** should exhibit a broad signal in the range 3200-3600 cm<sup>-1</sup> (associated with O-H stretching), while the IR spectrum of **2** would be expected to lack such a signal. The conversion of **1** to **2** could therefore be confirmed with the disappearance of the signal corresponding with excitation of the O-H bond.

Another way to monitor the conversion of 1 to 2 is to focus on the C-H bond of the aldehyde group in compound 1, which is expected to produce a signal in the range 2750-2850 cm<sup>-1</sup>. Since the aldehyde group is not present in compound 2, we expect this signal to vanish when 1 is converted to 2.

There is yet another way to monitor this reaction with IR spectroscopy. Compound 1 possesses only one C=O bond, while compound 2 has two C=O bonds. As such, the latter should exhibit two C=O signals. One signal is expected to be near 1680 cm<sup>-1</sup> (for the conjugated

ketone), and the other signal should be near 1700 cm<sup>-1</sup> (corresponding to the conjugated ester). In contrast compound 1 has only one C=O bond, which is expected to produce a signal near 1680 cm<sup>-1</sup> (for the conjugated aldehyde). Therefore, the conversion of 1 to 2 can be monitored by the appearance of a signal near 1700 cm<sup>-1</sup>.

**2.77.** Structures (a), (b) and (d) are all significant resonance structures, as shown:

Structure (c) is not a resonance form at all. To see this more clearly, notice that the benzyl carbocation does not have any CH<sub>2</sub> groups in the ring, but structure (c) does have a CH<sub>2</sub> group in the ring:

Resonance structures differ only in the placement of electrons. Since structure (c) differs in the connectivity of atoms, it cannot be considered a resonance structure of the benzyl carbocation. Therefore, the answer is (c).

**2.78.** The atoms in all four structures have complete octets. So we must consider the location of the negative charge. Structure (a) has a negative charge on an electronegative atom (oxygen). A negative charge is more stable on the more electronegative atom (oxygen) than it is on a nitrogen atom or a carbon atom. Therefore, structure (a) will contribute the most character to the resonance hybrid:

**2.79.** The nitrogen atom in structure (a) is delocalized by resonance, and is therefore  $sp^2$  hybridized:

The nitrogen atom in structure (b) is also delocalized, so it is  $sp^2$  hybridized as well:

The nitrogen atom in structure (c) is also  $sp^2$  hybridized, because this nitrogen atom must be using a p orbital to participate in  $\pi$  bonding (C=N). The nitrogen atom in structure (d) has three  $\sigma$  bonds, and its lone pair is localized. Therefore, this nitrogen atom is  $sp^3$  hybridized:

**2.80.** We begin by considering all bonds in the compound, which is easier to do if we redraw the compound as shown:

$$(CH_3)_2 CHCH_2 UC (CH_3)_3 \quad \equiv \quad \begin{array}{cccc} & H_3 C & H & CH_3 \\ & 1 & 1 & 1 \\ & H-C-C-U-C-CH_3 \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & &$$

This compound corresponds to structure (c):

#### 2.81.

(a) This compound contains the following functional groups:

ether 
$$O(CF_2)_{11}CF_3$$
 amide  $O(CF_3)_{11}O(CF_3)_{$ 

**(b)** The nitrogen atom has a lone pair that is delocalized via resonance:

In the second resonance structure shown, the C-N bond is drawn as a double bond, indicating partial double-bond character. This bond is thus a hybrid between a single and double bond; the partial double bond character results in

partially restricted rotation around this bond. In contrast, the C-N bond on the left experiences free rotation because that bond has only single-bond character.

#### 2.82.

(a) For each of the four reactions (i–iv), the product should have two imine groups, resulting from the reaction between a compound with two amino groups ( $\mathbf{B}$  or  $\mathbf{C}$ ) with two equivalents of an aldehyde ( $\mathbf{A}$  or  $\mathbf{D}$ ).

**(b)** The products of reactions iii and iv are constitutional isomers of each other. These products have the same molecular formula, but differ in their relative connectivity on the two central aromatic rings.

#### 2.83.

(a) Each of the four amides can be represented as a resonance hybrid (one example shown below). The charge-separated resonance structure indicates that there is a  $\delta$ + on the amide nitrogen, which thus pulls the electrons in the N-H bond closer to the nitrogen atom, leaving the hydrogen atom with a greater  $\delta$ +. This resonance effect is not present in the N-H bond of the amines. Thus, the  $\delta$ + on an amide H is greater than that on an amine H, leading to a stronger hydrogen bond.

**(b)** The following intermolecular hydrogen bonds are formed during self-assembly:

# 2.84.

(a) Anion 2 is highly stabilized by resonance (the negative charge is delocalized over two oxygen atoms and three carbon atoms). The resonance structures for 2 are as follows:

Cation 3 is highly stabilized by resonance (the positive charge is delocalized over two oxygen atoms and four carbon atoms). The resonance structures of 3 are as follows:

**(b)** Double bonds are shorter in length than single bonds (see Table 1.2). As such, the C-C bonds in compound 1 will alternate in length (double, single, double, etc.):

The double bonds do have some single-bond character as a result of resonance, as can be seen in resonance structure 1c:

Similarly, the single bonds have some double-bond character, also because of resonance. However, this effect is relatively small, because there is only one resonance structure (1a above) in which all atoms have an octet AND there are no formal charges. Therefore, it is the greatest contributor to the overall resonance hybrid. As such, the double bonds have only a small

amount of single-bond character, and the single bonds have only a small amount of double-bond character.

In contrast, anion 2 does not have a resonance structure that lacks charges. All resonance structures of 2 bear a negative charge. Among the resonance structures, two of them (2a and 2e) contribute the most character to the overall resonance hybrid, because the negative charge is on an electronegative oxygen atom (rather than carbon).

In fact, these two resonance contributors will contribute equally to the overall resonance hybrid. As such, the bonds of the ring will be very similar in length, because they have both single-bond character and double-bond character in equal amounts. A similar argument can be made for compound 3.

(c) In compound 1, a hydrogen bonding interaction occurs between the proton of the OH group and the oxygen atom of the C=O bond:

This interaction is the result of the attraction between partial charges ( $\delta$ + and  $\delta$ -). However, in cation 3, a similar type of interaction is less effective because the O of the C=O bond is now poor in electron density, and

therefore less capable of forming a hydrogen bonding interaction, as can be seen in resonance structure **3a**.

The other oxygen atom is also ineffective at forming an intramolecular hydrogen bond because it too is poor in electron density, as can be seen in resonance structure **3f**:

**2.85.** In order for all four rings to participate in resonance stabilization of the positive charge, the p orbitals in the four rings must all lie in the same plane (to achieve effective overlap). In the following drawing, the four rings are labeled A-D. Notice that the D ring bears a large substituent (highlighted) which is trying to occupy the same space as a portion of the C ring:

This type of interaction, called a steric interaction, forces the D ring to twist out of plane with respect to the other three rings, like this:

In this way, the overlap between the p orbitals of the D ring and the p orbitals of the other three rings is expected to be less effective. As such, participation of the D ring in resonance stabilization is expected to be diminished with respect to the participation of the other three rings.

# Chapter 3 Acids and Bases

# **Review of Concepts**

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 3. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

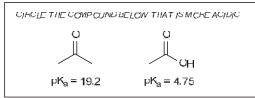
A Brønsted-Lowry acid is a proton, while a Brønsted-Lowry base	is a proton
A reaction mechanism utilizes curved arrows to show the flow of	that account
for a chemical reaction.	
The mechanism of <b>proton transfer</b> always involves at least curved arro	ws.
A strong acid has a $pK_a$ , while a weak acid has a $pK_a$ .	
There are four factors to consider when comparing the of conjugations o	ate bases.
The equilibrium of an acid-base reaction always favors the more	_ negative charge.
A Lewis acid is an electron-pair while a Lewis base is an electron-	on-pair

# **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 3. The answers appear in the section entitled *SkillBuilder Review*.

## SkillBuilder 3.1 Drawing the Mechanism of a Proton Transfer

# SkillBuilder 3.2 Using pKa Values to Compare Acids



# SkillBuilder 3.3 Using pK<sub>a</sub> Values to Compare Basicity

## SkillBuilder 3.4 Using pKa Values to Predict the Position of Equilibrium