Topic 5: Resonance

Note to students: This is a single chapter (or a portion of one) from a textbook that is under construction. Therefore you can ignore references to other textbook sections.

5.1 Why Should I Study This?

Your general chemistry instructor or textbook may not have emphasized resonance very much, leaving you with the impression that it is not a very important idea. The topic was not emphasized much because resonance is a phenomenon of (for the most part) hybrid orbitals. Many elements do not use hybrid orbitals when bonding, so in the overall broad scheme of your general chemistry studies, resonance was not emphasized. However, organic chemistry is all about carbon, and in organic molecules carbon always uses hybrid orbitals. It comes as no surprise to us then that we will encounter resonance as “electron accounting” time and time again. As we delve even deeper into organic chemistry we will discover that many chemical and physical properties of organic molecules, such as molecular geometry or acidity, are strongly influenced by presence (or absence!) of resonance. Therefore it is valuable for us to have an excellent command of resonance contributors.

Many students of introductory organic chemistry are mystified as to how one resonance contributor “becomes” another. Working together we will demystify this issue by helping you to recognize common resonance contributor patterns.

Before you begin this topic, you may find it useful to review the discussion of resonance in your general chemistry textbook.

5.2 What is Resonance?

Let us begin our work on resonance by looking at a molecule with more than one Lewis structure.
Think Ahead Question 5.1
Draw the Lewis structure for carbon monoxide, CO. Include all bonds, lone pairs and formal charges. Hint: There are actually two Lewis structures that can be drawn.

Answer: Working out the Lewis structure as we did previously (Topic 01), we discover that carbon monoxide must have a triple bond in order to have a full octet on oxygen and carbon. But these full octets can only be achieved if the carbon bears a +1 formal charge and the oxygen a –1 formal charge.

\[ \Theta: \equiv C \equiv O : \Theta \quad \text{or} \quad : C \equiv O : \]

Two structure choices - a quandary! In general chemistry, we learned the best Lewis structures have full octets on every atom and no formal charges. So our carbon monoxide structures are not perfect, but neither is completely wrong. Both are acceptable structures for this molecule.

There are many molecules that can be represented by more than one Lewis structure. This phenomenon is called resonance. Resonance is common for molecules containing carbon, and thus will be particularly important as we study organic chemistry. The separate Lewis structures are called resonance contributors. (Also called valence-bond isomers or canonical forms.)

Resonance contributors are just “alternate realities.” They are not in equilibrium. The fluxional electron pair of carbon monoxide is not a pi bond one moment then a lone pair the next. We use a double-headed arrow (\( \leftrightarrow \)) to indicate that Lewis structures are resonance contributors and not equilibrium structures.

\[ \Theta: \equiv C \equiv O : \Theta \quad \leftrightarrow \quad : C \equiv O : \]

Resonance: Correct
Equilibrium: Incorrect

Every molecule can be represented in different ways. Are all of these different representations resonance contributors?

Think Ahead Question 5.2
Are these structures resonance contributors?

\[ \Theta: \equiv C \equiv O : \Theta \quad \leftrightarrow \quad : \equiv C \equiv O : \]

Resonance
Answer: The definition of resonance given in the margin says that resonance contributors differ in positions of the electrons but not the nuclei. In this case a pair of electrons that is part of the vertical carbon-oxygen double bond shifts to become a lone pair on the top oxygen. At the same time a lone pair on the right hand oxygen shifts to become part of the C=O bond that point to the right. So the electron shift requirement is met, but what about the nuclei?

To explore this point, draw the first resonance contributor (with all lone pairs and formal charges) on a sheet of paper, dark enough so that it can be seen from the opposite side of the paper. Now change the positions of the nuclei in space by flipping the paper over. Compare the “flipped” structure with the second resonance contributor. Are they the same?

They certainly look the same! Does this mean the two structures are not resonance contributors? The double-headed arrow between the two structures means “these are resonance contributors,” and so by definition we cannot move the nuclei in any way.

The key idea here is that even though the two resonance contributors appear to differ in the positions of the nuclei, the resonance arrow tells us that they do not.

**Concept Focus Question 5.1**
Proteins are assembled from amino acids, of which glycine is the simplest example. Structure A is an accurate representation of glycine. Which of the other structures are also acceptable resonance contributors?

H\_3\text{N}\text{C}\text{H}\text{C}\text{O}\text{H} \quad \text{A}

H\_3\text{N}\text{C}\text{H}\text{C}\text{O}\text{H} \quad \text{B}

H\_3\text{N}\text{C}\text{H}\text{C}\text{O}\text{H} \quad \text{C}

H\_3\text{N}\text{C}\text{H}\text{C}\text{O}\text{H} \quad \text{D}

H\_3\text{N}\text{C}\text{H}\text{C}\text{O}\text{H} \quad \text{E}
5.3 The Resonance Hybrid

We saw in the previous section that some molecules can be represented by more than one valid Lewis structure. How do we know which one of these structures is the best representation of the actual molecular structure?

A. What is a Resonance Hybrid?

Think Ahead Question 5.3
1,2-Difluorobenzene has two resonance contributors as shown.

The distance between the two carbons with chlorines in 1,2-dichlorobenzene is 1.40 Å. An average carbon-carbon single bond is 1.53 Å long, and an average carbon-carbon double bond is 1.31 Å long. Based on these numbers, which of the two resonance contributors is the best representation of the molecule’s actual structure?

Answer: The actual bond length is intermediate between the two resonance contributors. Both of the individual contributors are off by the same amount. Neither contributor appears to be a good representation of reality. In fact, reality appears to be an average, or hybrid, of the two resonance contributors. How might this happen?

One idea is that the contributors are interconverting so quickly that we cannot tell them apart, and all we see is an average. This idea is no good because resonance contributors are not equilibrium structures.

What if, instead of rapidly switching back and forth, the molecule has a structure that is an average of the contributors? For example, the distance between the two carbons bearing the fluorine atoms would be intermediate between typical C-C and C=C bond lengths. In fact, all the carbon-carbon bond lengths would be longer than a typical single bond but shorter than a typical double bond.

The experimentally determined structure of 1,2-difluorobenzene agrees with these predictions.
A metaphor is very useful here. Imagine that during a break from your studies you take a walk in the woods. During this walk you photograph a large, horned animal with leathery skin that you’ve never seen before. You show the photograph to your friends who are biology majors. One says it must be a dragon because it has leathery skin. Another says it must be a unicorn because it has a horn. It is true that the unknown animal has some features that resemble a dragon, such as leathery skin, but it is not a dragon because it didn’t breathe fire. The unknown animal has some features that resemble a unicorn, such as the horn, but it isn’t a unicorn because the unknown animal didn’t have a horse’s tail. Maybe the unknown is a hybrid between a dragon and a unicorn? After some research you learn the unknown animal is a rhinoceros, an animal that appear to be a hybrid of a dragon and a unicorn. The rhinoceros has some dragon characteristics and some unicorn characteristics, but it isn’t switching back and forth between them.

Now back to reality! We say the actual structure of 1,2-difluorobenzene is a resonance hybrid, which has some characteristics of the individual resonance contributors. Like the rhinoceros, it is not rapidly flipping back and forth between the contributors. Also like the rhinoceros, the contributors are convenient things to thing about, but are just fantasy creatures, with no physical reality. (When is the last time you actually saw a dragon or unicorn?)

How much does each resonance contributor contribute to the hybrid? In the case of 1,2-difluorobenzene, the F-C-C-F bond length is almost half way between the corresponding bond lengths of the two contributors. This suggests that the resonance contributors contribute equally to the hybrid. If contributor A carried more weight than contributor B then the F-C-C-F bond length in 1,2-difluorobenzene would resemble a double bond more than a single bond.

**B. Drawing the Resonance Hybrid**

How can we draw the resonance hybrid? The hybrid has characteristics or features of all the resonance contributors, such as lone pairs, formal charges and double bonds. Features that are common to all of the resonance contributors are drawn differently in the hybrid than features that are not common. The procedure from drawing the hybrid is demonstrated here with formate, an ion we encountered earlier in this chapter.

**Step 1:** Draw the features that are common to all of the resonance contributors. For formate ion, we see that each contributor has a carbon that is bonded to a hydrogen and to two oxygens. The C-O
bonds change between single and double, but they always are at least single. The number of lone pairs on each oxygen atom can be two or three, but always at least two.

\[
\begin{align*}
\text{C} & \quad \text{H} & \quad \text{O} \\
\quad & \quad & \quad \text{O}
\end{align*}
\]

Step 2: Bonds that change between resonance contributors are drawn as dashed lines. Lone pairs that are sometimes lone pairs and sometimes bonds are not drawn, as these electrons are included in the dashed lines. (The dashed lines indicate the bond is more than a single bond but not a full double bond.) Atoms that have a negative charge in some, but not all, of the resonance contributors bear some extra electron density, so they are labeled with $\delta^-$. Atoms that are positive in some resonance contributors and neutral in others get a $\delta^+$. Our resonance hybrid is now complete.

\[
\begin{align*}
\text{C} & \quad \text{H} & \quad \text{O} \\
\quad & \quad & \quad \text{O}
\end{align*}
\]

Resonance hybrid of formate ion

**Concept Focus Question 5.2**

Draw the resonance hybrids for carbon monoxide (Think Ahead Question 5.1) and 1,2-difluorobenzene (Think Ahead Question 5.3).

### 5. 4 Learning to Recognize Two-Electron Resonance Patterns

Resonance is a common feature in many organic molecules so it very important to determine if it is present, and if so, to draw the appropriate resonance contributors. How can we quickly recognize these resonance contributors?

**Think Ahead Question 5.4**

Examine each pair of resonance contributors shown below. Write a one-sentence description of the single “electron accounting” change they have in common. You may find it easier to see the patterns if you include curved arrows (Topic 4) to indicate electron shifts.
Acetone enolate: \[
\begin{align*}
\text{H & C & C & H} & \quad \text{H & C & C & H} \\
\text{H & O:} & \quad \text{H & O:} \\
\end{align*}
\]

Amide: \[
\begin{align*}
\text{H & C & N & H} & \quad \text{H & C & N & H} \\
\text{H & O:} & \quad \text{H & O:} \\
\end{align*}
\]

Allyl carbanion: \[
\begin{align*}
\text{H & C & \text{=C} & \text{H}} & \quad \text{H & C & \text{=C} & \text{H}} \\
\text{H & O:} & \quad \text{H & O:} \\
\end{align*}
\]

Answer: This is a good place to introduce some useful terms to aid in our exploration of these molecules. A molecule bearing a negative charge on the carbon atom next to a carbonyl group (C=O) is called an enolate. A carbanion is a molecule with a carbon atom that bears a formal negative charge. The term is a contraction of carbon anion. A carbon directly attached to an alkene is called an allylic carbon. The simplest carbanion carrying its negative charge on an allylic carbon is called the allyl carbanion.

So what is similar about acetone enolate, amide and allyl carbanion resonance structures? Each structure differs by the position of a lone pair and a pi bond. The lone pair electrons become a pi bond between the atom where the lone pair used to reside and an adjacent atom that used to be part of a pi bond. The electrons that used to be the pi bond become the sole property of the “far end” of the pi bond. We can illustrate this “electron shift” by using curved arrows. The arrow starts at the source of the electrons and points to where they end up. For example, in the first acetone enolate resonance contributor shown below, a curved arrow points away from the carbon lone pair (the electron source) and points to the space between the two carbon atoms (indicating it is shared by those two carbon atoms to form a pi bond).

\[
\begin{align*}
\text{H & C & C & H} & \quad \text{H & C & C & H} \\
\text{H & O:} & \quad \text{H & O:} \\
\end{align*}
\]

It is not necessary to draw curved arrows for every resonance contributor, but they can clarify the electron accounting process, especially when your mastery of resonance is not yet perfect. For more on the curved arrow notation read Topic 4.
Concept Focus Question 5.3
Draw curved arrows that show the electron shifts between the amide and allyl anion resonance contributors in the previous Think Ahead Question.

Concept Focus Question 5.4
Draw one more significant resonance contributor for each structure shown. Include the curved arrows.

(a) \( \begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \quad \text{C} \quad \text{O} \\
&\text{H} \quad \text{H} \\
&\text{O} \\
\end{align*} \)

(b) \( \begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \quad \text{C} \quad \text{N} \\
&\text{H} \quad \text{H} \\
&\text{O} \\
\end{align*} \)

(c) \( \begin{align*}
&\text{N} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{O} \\
\end{align*} \)

(d) \( \begin{align*}
&\text{N} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{O} \\
\end{align*} \)

Concept Focus Question 5.5
Draw three more resonance contributors for this anion, called the benzyl carbanion. Try this one without drawing the curved arrows.

Now we examine another, related resonance pattern.

Think Ahead Question 5.5
Examine each pair of resonance contributors shown below. Write a one-sentence description of the single “electron accounting” change they have in common.

Allyl carbocation:
\( \begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \quad \text{C} \quad \text{CH}_2 \\
&\text{C} \quad \text{CH}_2 \\
&\text{H} \\
&\text{H} \\
\end{align*} \)

Benzyl carbocation:
\( \begin{align*}
&\text{C} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \\
&\text{CH}_2 \\
&\text{CH}_2 \\
&\text{C} \\
&\text{H} \\
\end{align*} \)

Vinyl borane:
\( \begin{align*}
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{H} \\
&\text{C} \\
&\text{C} \\
&\text{BH}_2 \\
&\text{BH}_2 \\
\end{align*} \)

A carbon directly attached to a benzene ring is called a benzyllic carbon. The simplest carbanion carrying its negative charge on a benzyllic carbon is called the benzyl carbanion.

A carbocation is a molecule with a carbon atom that bears a formal positive charge. The term is a contraction of carbon cation.
Answer: Strengthen your understanding of resonance by first verifying some formal charges: Carbon with three bonds and no lone pair bears a formal positive charge whereas boron with the same bonding is neutral.

Each resonance contributor pair differs by the position of a pi bond and an open octet. The electrons that used to form the pi bond now form a new pi bond between the “near” end of the old pi bond and the atom that used to have the open octet. The “far” end of the old pi bond lost an electron pair. The corresponding curved arrows for the allyl carbocation are shown here.

We do not draw a curved arrow that starts at the atom with the open octet, because it is not the source of an electron pair.

The comment leading into Think Ahead Question 5.5 suggested that the resonance pattern discussed in this section would be similar to the lone pair/pi bond switch pattern in the previous section. Do you see the similarity? In both cases a pi bond switched with an adjacent atom’s electron density (lone pair or open octet).

**Concept Focus Question 5.6**
Draw curved arrows that show the electron shifts for the benzyl carbocation and vinyl borane resonance contributors in the Think Ahead Question 5.5.

**Concept Focus Question 5.7**
The answer for Think Ahead Question 5.5 includes two resonance contributors for the benzyl carbocation, but in fact this cation has four important resonance contributors. Draw all four. See if you can do this without the curved arrows.

**Concept Focus Question 5.8**
Think Ahead Question 5.5 includes one important resonance contributor for \((\text{CH}_3)_2\text{C}=\text{CHCH}_2^+\). Draw one more important resonance contributor. Include the appropriate curved arrows.

Correct assignment of lone pairs and formal charge is absolutely necessary to master resonance. Practice these skills until you can assign them without hesitation!
**Concept Focus Question 5.9**
Draw two more important resonance contributors for these ions.

(a) \( \text{H}_3\text{C} \equiv \text{C} \equiv \text{C} \)

(b) \( \text{CH}_3\text{CH}_2\text{O} \equiv \text{CH}_2 \)

Can lone pairs be involved in resonance without an adjacent pi bond? We explore the idea in the next section, starting with a Think Ahead Question.

**Think Ahead Question 5.6**
Examine each pair of resonance contributors shown below. Write a one-sentence description of the single “electron accounting” change they have in common. Hint: It’s more than just the presence of a carbocation.

\[
\begin{align*}
\text{H}_3\text{C} \equiv \text{O} & \quad \equiv \quad \text{H}_3\text{C} \equiv \text{O} \\
\text{(CH}_3\text{)}_2\text{N} \equiv \text{C} \text{(CH}_3\text{)}_2 & \quad \equiv \quad \text{(CH}_3\text{)}_2\text{N} \equiv \text{C} \text{(CH}_3\text{)}_2 \\
\text{(CH}_3\text{)}_2\text{C} \equiv \text{O} & \quad \equiv \quad \text{(CH}_3\text{)}_2\text{C} \equiv \text{O}
\end{align*}
\]

**Answer:** In each case a lone pair is shared with an adjacent open octet atom to form a new pi bond. For example, in the first pair of resonance contributors, an oxygen lone pair is shared with the adjacent open octet carbon to form a new carbon-oxygen pi bond. Curved arrows clarify this shift.

\[
\begin{align*}
\text{H}_3\text{C} \equiv \text{O} & \quad \equiv \quad \text{H}_3\text{C} \equiv \text{O} \\
\text{H}_2\text{C} \equiv \text{O} & \quad \equiv \quad \text{H}_2\text{C} \equiv \text{O}
\end{align*}
\]

Conversely, a pi bond is sacrificed to give a lone pair and an open octet.

If you said that each resonance contributor pair also involves a carbocation or an open octet on carbon, you are also correct. Will see in the sample problems, however, that while these changes often occur with this lone pair/pi bond resonance pattern, it is not the only possibility.
Concept Focus Question 5.10

Draw one additional resonance contributor for each.

(a) \[ \text{NH}_2 \]  
(b) \[ \text{O} \]  
(c) \[ \text{H}_2\text{C} \]  
(d) \[ \text{H}_2\text{C} \]  
(e) \[ \text{H}_2\text{C} \]  
(f) \[ \text{(CH}_3\text{)}_2\text{C} \]  

Here are some additional two-electron resonance contributor patterns that you may encounter.

Pi bonds alternate: In a cyclic molecule two or more pi bonds that are separated by a single bond can switch places. The two most important resonance contributors of benzene (shown below) illustrate this resonance pattern.

\[ \begin{array}{c}
\text{ benzene } \\
\text{ (above)} \\
\text{ (below)} \\
\end{array} \]

This is a very important resonance feature of aromatic molecules, and usually not encountered elsewhere.

When electrons are flowing in a circular pattern, the direction of flow – clockwise or counterclockwise – does not matter, because they both produce the same result. For example, resonance in benzene can be show with a counterclockwise flow (above) or a clockwise flow (below).

A molecule is said to be aromatic if it has extraordinary stability associated with its particular arrangement of pi bonds, \( p \) orbitals and the associated electrons. This concept is covered in Topic 10.

Concept Focus Question 5.11

Draw one additional important resonance contributor each molecule.

\[ \begin{array}{c}
\text{1,3-Cyclobutadiene} \\
\text{Pyridine} \\
\end{array} \]
Concept Focus Question 5.12
Provide the additional important resonance contributors as indicated.

Naphthalene
(2 more)

Anthracene
(3 more)

Phenanthrene
(4 more)

Here are a few more cases to round out our collection of two electron resonance patterns.

Sigma bond becomes a lone pair: The pair of electrons that is shared between two atoms in the form of a sigma bond moves to become a lone pair on one atom, leaving an open octet on the other atom.

Conversely a lone pair and open octet combine to make a new sigma bond. (Do you see the parallel with another resonance pattern that you explored earlier in this Topic?)

In general disruption of a sigma bond leads to insignificant resonance contributors, but in a few circumstances it will be quite useful to explain aspects of certain reactions.

Concept Focus Question 5.13
Draw all the sigma-bond-becomes-a-lone-pair resonance contributors for these ions. Ignore the disruption of carbon-carbon and carbon-hydrogen bonds.

(a)  (b)
Summary of General Two-Electron Resonance Patterns

Each illustration is generic (i.e., we do not specify if X is carbon, oxygen, etc.) so formal charges are ignored.

(a) Exchange of a lone pair and a pi bond:

(b) Exchange of an open octet and a pi bond:

(c) A lone pair is shared with an adjacent open octet atom to form a new pi bond. Conversely, a pi bond is sacrificed to give a lone pair and an open octet:

(d) Pi bonds alternate in cyclic (usually aromatic) molecule:

(e) Sigma bond becomes a lone pair and an open octet. Conversely a lone pair and open octet combine to make a new sigma bond:

5.5 Learning to Recognize One-Electron Resonance Patterns

In the previous section we learned to recognize resonance contributor patterns when electrons shift in pairs. We will also encounter examples when resonance occurs by the shift of single (unpaired) electrons,
although these unpaired electron resonance examples are less common than paired electron resonance cases.

**Think Ahead Question 5.7**
Examine each pair of radical resonance contributors shown below. Write a one-sentence description of the single “electron accounting” change they have in common.

**Answer:** In each case, the unpaired electron switches places with an adjacent pi bond. We can show this with curved arrows. Recall that we use a curved arrow with a single barb like this \( \rightarrow \) to indicate relocation of a single electron. Here are the curved arrows that show electron redistribution for the allyl radical resonance contributors.

Note that the pi bond electrons are forced to move individually, and in opposite directions, to avoid having a carbon with more than eight electrons.

**Concept Focus Question 5.14**
Using the allyl radical as a model, draw the curved arrows that show electron redistribution between the two resonance contributors of the propargyl radical.

**Concept Focus Question 5.15**
Using the single electron/pi bond exchange pattern you have developed, draw all the resonance contributors for the benzyl radical. Include curved arrows.

**Concept Focus Question 5.16**
Draw the resonance contributors for each of these radicals.
An atom that has an open octet because it is short a pair of electrons allows important two-electron resonance stabilization with an adjacent pi bond or lone pair. What about an atom that has seven valence electrons?

**Think Ahead Question 5.8**
An atom bearing a radical has an open octet, so it might be able to gain electron density (and greater stability) through resonance with an adjacent electron source, such as a pi bond. Can a lone pair also serve this role? Explore this point by drawing the resonance contributors for this radical.

**Answer:** The carbon atom has an open octet (six electrons shared in bonds and one unpaired electron), so we would like to complete its octet by borrowing electron density from neighboring atoms. We did this previously by borrowing from an adjacent pi bond. A lone pair is another tempting source of electrons, so let’s use the lone pair to form a C=O bond.

This is no good! The new resonance contributor has nine electrons on carbon, so it is not valid. (Remember that elements in the second row of the periodic table, such as carbon, oxygen and nitrogen are limited to eight electrons.) How about shifting just one of the lone pair electrons into the new pi bond, and use the unpaired electron on carbon for the other half?
Also no good, because carbon has eight electrons, but oxygen has nine.

Exploring other examples quickly shows that an unpaired radical electron cannot interact with an adjacent lone pair to give an additional resonance contributor. This is an important (and often forgotten!) difference between open octet and radical resonance contributors. (Radicals do interact with adjacent lone pairs, but not through resonance. We will explore this when we study radicals in more depth in Topic 31.)

**Concept Focus Question 5.17**
Draw the resonance contributors for these radicals.

(a) \( \text{CH}_3\text{O} \) 
(b) \( \text{N} \)

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**5.6 Relative Significance of Resonance Contributors**

Previously we saw that the actual “real world” structure of a molecule is often not adequately represented with just a single resonance contributor, but rather as the resonance hybrid. The hybrid is a blend of the individual contributors, but the contributors are often unequally represented in the hybrid. How can we determine which contributors are most important? This is useful to know when drawing resonance hybrids, or when use of a structure with delocalized electrons would be vague (as in a reaction mechanism), as well as in many other situations we will encounter throughout our studies of organic chemistry (and other chemistries as well).

We need a set of rules to determine the most important resonance contributor. These rules are based on the idea that if individual resonance contributors did indeed exist, the most thermodynamically stable structures would make more significant contributions to the resonance hybrid. Factors that enhance thermodynamic stability are maximization of covalent bonding and minimization of charge. Resonance increases stability by increasing the bonding between adjacent atoms and by distributing charge over a greater number of atoms.

**Preference Rule 1:** The most important contributor has the maximum number of atoms with full octets.
The carbon of structure A has an open octet. All the atoms of structure B have full octets. Therefore contributor B is more important than contributor A, despite the fact that the positive charge is on the more electronegative oxygen atom instead of the less electronegative carbon atom.

This preference gets priority over the other rules for determining the most important resonance contributor. Preference rules 2 – 5 all carry approximately weight.

Concept Focus Question 5.18
Draw the curved arrows that show the electron redistribution, and select the most important resonance contributor.

(a) \[(\text{CH}_3)_2\text{C} \rightarrow \text{O} \leftarrow (\text{CH}_3)_2\text{C} \rightarrow \text{O}\]

(b) \[\text{H}_2\text{C} \rightarrow \text{C} \leftarrow \text{H}_2\text{C} \rightarrow \text{C}\]

(c) \[\text{H}_2\text{C} \rightarrow \text{P(\text{CH}_3)_3} \leftarrow \text{H}_2\text{C} \rightarrow \text{P(\text{CH}_3)_3}\]

Preference Rule 2: If a resonance contributor must have formal charge, the most important contributor has these charge(s) on the atoms most willing to accommodate them. Negative charges are best accommodated on more electronegative atoms, whereas positive charges are best accommodated on the least electronegative atoms.

All atoms of resonance contributors C and D have a complete octet, so we turn to other preferences to determine the most important resonance contributor. The most electronegative atom best accommodates a negative charge. Because oxygen is more electronegative than carbon, contributor D is more important than contributor C. (If the ion shown above was a cation, then the resonance contributor with the positive charge on carbon would be more important than the contributor with the positive charge on oxygen.)
Preference Rule 3: **The most significant contributor has the maximum number of covalent bonds.** Contributor B (above) is more important than contributor A because B has the carbon-oxygen pi bond absent in A.

Preference Rule 4: **The most significant contributor has the least possible number of formal charges.**

Resonance contributor F is more significant than contributor E because F has no atoms with formal charges, whereas E has two atoms with formal charges. (Contributor F is also favored by Preference Rule 3 as well.)

Preference Rule 5: **The most significant contributor has the least number of unpaired electrons.**

For example, contributors G and H each have one unpaired electron, and thus are preferred over contributor I which has three unpaired electrons. Resonance contributors that include avoidable unpaired electrons are rarely of any consequence and thus should not be considered.

There is one common exception: molecular oxygen. Due to molecular orbital considerations, molecular oxygen is best described as having two unpaired electrons and an oxygen-oxygen single bond (contributor J) and not as lacking unpaired electrons with an oxygen-oxygen double bond (contributor K).
**Concept Focus Question 5.19**

Draw the curved arrows that show the electron redistribution, and select the most important resonance contributor.

(a) ![Diagram](image1)

(b) ![Diagram](image2)

(c) ![Diagram](image3)

(d) ![Diagram](image4)

(e) ![Diagram](image5)

(f) ![Diagram](image6)

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**5.7 In the Real World: Resonance Effects on Structure and Reactivity**

Many molecules are influenced by resonance. Throughout our study of organic chemistry – and beyond – we will see many examples of physical and chemical properties that are explained by the presence or absence of resonance. (Flip through the pages of this book. How many times do you see ➔?) As a simple and very relevant example of the role played by resonance, let us consider the amide functional group. This structural unit links the amine group of one amino acid with the carboxylic acid of another amino acid to form peptides and proteins. (A peptide or protein chain can include anywhere from a few to many hundreds of amino acids.)

*Review functional groups in section 1.xx if necessary.*
Rotating around the bond that connects the carbonyl and adjacent nitrogen atoms changes the structure of the amide. (Verify this by comparing models of the cis and trans amides. Are they identical?)

The biological function of a protein is very strongly controlled by its structure. Even small changes in structure may cause great changes in how a protein operates. Therefore it is critical that the protein’s structure is constant, and that it does not flop around at random. Resonance plays a very significant role in maintaining protein structure, as we shall discover in the following Think Ahead Question

**Think Ahead Question 5.9**
Draw the resonance hybrid for the trans-amide. What does the resonance hybrid suggest about the bond order of the C-O and C-N bonds in this molecule?

**Answer:** Applying the two - electron resonance pattern in which a lone pair switches places with an adjacent pi bond (two – electron resonance pattern xx), we get two resonance contributors for the amide. We can also sacrifice the pi bond to form a lone pair (two – electron resonance pattern xx). This contributor has atoms with avoidable formal charges, so it does not make a significant contribution to the resonance hybrid.

With the resonance contributors in hand, we can construct the resonance hybrid. We learned in section 5.3 that the resonance hybrid, and not any single resonance contributor, is the best representation of reality. Thus any consideration of a molecule’s structure should be based on the hybrid. In the amide case, one electron pair from the carbonyl pi bond switches to become an oxygen lone pair. The nitrogen lone pair also switches to become part of a carbon – nitrogen

![Amino acid link together to form Protein](image)
double bond. In the resonance hybrid drawing, these delocalized electron pairs are shown as dashed lines.

Does the resonance hybrid structure suggest anything about the structure of the amide that the localized structures do not? The resonance hybrid suggests that the C-N bond has some pi character, meaning it is more than just a normal single bond but not quite a full double bond. As you may have already learned (sections 3.xx and 8.xx) this partial pi bond inhibits rotation around the C-N bond, thus helping the amide (and the protein as a whole) to maintain a fixed shape. Resonance also forces the amide group and the attached atoms to lie in a plane because the nitrogen atom must use \( sp^2 \) hybridization (section 3.xx). The local planarity at each amide plus the barrier to rotation has a strong influence on maintaining a well-defined (almost rigid) structure for the entire protein molecule. If proteins were “floppy” without fixed structures their enzyme specificity would probably be greatly reduced.

Resonance also influences the chemical stability of the amide. When the cell seeks to dispose of a protein because it is no longer needed or because it is harmful, the protein is “chopped up” into smaller proteins (and eventually individual amino acids) by enzyme-catalyzed hydrolysis (“water splitting”).

This amide hydrolysis process involves steps in which resonance must be sacrificed. (Amide hydrolysis and its enzyme catalysis are covered in Topic 35). Because resonance is a stabilizing feature, its loss costs energy and slows the reaction rate. This is critical for proteins because a cell contains quite a bit of water. If hydrolysis were too easy then proteins would be degraded too quickly for a cell to carry out its normal functions. The enzyme changes the details of the reaction in a way that counterbalances the loss of resonance.
Summary

5.1 Why Should I Study This?
Resonance is worthy of study because its influence is ubiquitous. Many aspects organic structure and chemical reactivity are controlled by resonance.

5.2 What is Resonance?
Resonance is a situation in which a molecule can be represented by two or more valid Lewis structures that differ only in the position of electrons. (The nuclei remain stationary.) These different structures are called resonance contributors. We use a double-headed arrow (↔) to indicate that Lewis structures are resonance contributors and not equilibrium structures.

5.3 The Resonance Hybrid
A. What is a Resonance Hybrid?
The resonance hybrid is the weighted average of all the resonance contributors. The hybrid is a more accurate representation of a molecule’s true structure than any single resonance contributor.

B. Drawing the Resonance Hybrid
The resonance hybrid is drawn by a two-step procedure. First we draw the portions of the structure that are identical for all the resonance contributors. Then we add the features that vary, such as dashed lines for electron pairs that are delocalized, and partial charges.
5.4 Learning to Recognize Two-Electron Resonance Patterns

Resonance contributors tend to fall into certain patterns. Learning to use these patterns will ease your studies of organic chemistry. Here are the patterns for resonance contributors that differ by shifts of one or more electron pairs.

(a) Exchange of a lone pair and a pi bond:

(b) Exchange of an open octet and a pi bond:

(c) A lone pair is shared with an adjacent open octet atom to form a new pi bond. Conversely, a pi bond is sacrificed to give a lone pair and an open octet:

(d) Pi bonds alternate in cyclic (usually aromatic) molecule:

(e) Sigma bond becomes a lone pair and an open octet. Conversely a lone pair and open octet combine to make a new sigma bond:

5.5 Learning to Recognize One-Electron Resonance Patterns

Here are the patterns for resonance contributors that differ by shifts of one or more single electrons.

(a) An unpaired electron can switch places with an adjacent pi bond.
(b) An unpaired electron cannot interact with an adjacent lone pair to give a new resonance contributor, because this requires one atom to have nine valence electrons.

5.6 Relative Significance of Resonance Contributors
Resonance contributors do not make equal contributions to the resonance hybrid. The most significant contributors have the greatest number of atoms with complete octets. Less important preference rules:
- If a resonance contributor must have formal charge, the most important contributor has these charge(s) on the atoms most willing to accommodate them.
- The most significant contributor has the maximum number of covalent bonds.
- The most significant contributor has the least possible number of formal charges.
- The most significant contributor has the least number of unpaired electrons.

5.7 In the Real World: Resonance Effects on Structure and Reactivity
Proteins are chains of amino acids joined by amides, functional groups with resonance interaction of the carbonyl pi bond and the nitrogen lone pair. The resonance hybrid reveals a C-N bond with some pi character, which causes a barrier to rotation and forces the amide to be planar. This has an effect on the structure of the whole protein molecule. The resonance also helps the protein’s amides resist hydrolysis in the absence of an enzyme.

New Terms
- Resonance (page 1)
- Resonance contributors (page 1)
- Double-headed arrow (page 1)
- Enolate (page 6)
- Carbanion (page 6)
- Allylic carbon (page 6)
- Allyl carbanion (page 6)
- Curved arrows (page 7)
- Benzylic carbon (page 8)
- Benzyl carbanion (page 8)
- Carbocation (page 8)
- Aromatic (page 11)
- Free radical (page 14)
- Radical (page 14)