Objectives

After completing this section, you should be able to

• use the concept of resonance to explain structural features of molecules and ions.
• understand the relationship between resonance and relative stability of molecules and ions.

Recognizing resonance

Resonance contributors involve the ‘imaginary movement’ of pi-bonded electrons or of lone-pair electrons that are adjacent to (i.e. conjugated to) pi bonds. You can never shift the location of electrons in sigma bonds – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule cannot change between two resonance contributors.

Because benzene will appear throughout this course, it is important to recognize the stability gained through the resonance delocalization of the six pi electrons throughout the six carbon atoms. Benzene also illustrates one way to recognize resonance - when it is possible to draw two or more equivalent Lewis structures. If we were to draw the structure of an aromatic molecule such as 1,2-dimethylbenzene, there are two ways that we could draw the double bonds:

\[ \text{CH}_3 \quad \text{CH}_3 \] \hspace{1cm} \[ \text{CH}_3 \quad \text{CH}_3 \]

Which way is correct? There are two simple answers to this question: ‘both’ and ‘neither one’. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, \textit{when considered together}, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.

When it is possible to draw more than one valid structure for a compound or ion, we have identified \textbf{resonance contributors}: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:
In order to make it easier to visualize the difference between two resonance contributors, small, curved arrows are often used. Each of these arrows depicts the 'movement' of two pi electrons. In the drawing of resonance contributors, however, this electron 'movement' occurs only in our minds, as we try to visualize delocalized pi bonds. Nevertheless, use of the curved arrow notation is an essential skill that you will need to develop in drawing resonance contributors.

The depiction of benzene using the two resonance contributors A and B in the figure above does not imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B.

**Caution!** It is very important to be clear that in drawing two (or more) resonance contributors, we are not drawing two different molecules: they are simply *different depictions of the exact same molecule*. Furthermore, the double-headed resonance arrow does NOT mean that a chemical reaction has taken place.

Benzene is often drawn as only one of the two possible resonance contributors (it is assumed that the reader understands that resonance hybridization is implied). However, sometimes benzene will be drawn with a circle inside the hexagon, either solid or dashed, as a way of drawing a resonance hybrid.

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**Resonance Delocalizes Charge to Increase Stability**

Resonance is most useful when it delocalizes charge to stabilize reactive intermediates and products. Recognizing, drawing, and evaluating the relative stability of resonance contributors is essential to understanding organic reaction mechanisms.
Rules for drawing and working with resonance contributors

Learning to draw and interpret resonance structures, there are a few basic guidelines to help avoid drawing nonsensical structures. All of these guidelines make perfect sense as long as we remember that resonance contributors are merely a human-invented convention for depicting the delocalization of pi electrons in conjugated systems.

• 1) There is ONLY ONE REAL STRUCTURE for each molecule or ion. This real structure (the resonance hybrid) takes its character from the average of all the individual resonance contributors.  
  ◦ When we see two different resonance contributors, we are not seeing a chemical reaction! We are seeing the exact same molecule or ion depicted in two different ways.

• 2) The resonance hybrid is more stable than any individual resonance contributor.

• 3) Resonance forms do not have to contribute equally to the resonance hybrid (explained further in section 4.6).

• 4) All resonance contributors must be correct Lewis structures.  
  ◦ Each atom should have a complete valence shell and be shown with correct formal charges.
  ◦ A carbocation (carbon with only 6 valence electrons) is the only allowed exception to the valence shell rules.

• 5) Only delocalizable electrons (pi bond or lone pair electrons) move between one resonance form and another.  
  ◦ Sigma bonds are never broken or made, because of this atoms must maintain their same position.
  ◦ All resonance contributors must have the same molecular formula and net charge.

Rules for estimating stability of resonance structures

1. The resonance form in which all atoms have complete valence shells is more stable.
2. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets.

3. The structure with the **least number of formal charges** is more stable.

4. The structure with the **least separation of formal charges** is more stable.

5. A structure with a **negative charge on the more electronegative atom** will be more stable.

6. **Positive charges on the least electronegative atom** (most electropositive) is more stable.

7. **Resonance forms that are equivalent have no difference in stability and contribute equally.** (eg. benzene)

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The above resonance structures show that the electrons are delocalized within the molecule and through this process the molecule gains extra stability. Ozone with both of its opposite formal charges creates a neutral molecule and through resonance it is a stable molecule. The extra electron that created the negative charge one terminal oxygen can be delocalized by resonance through the other terminal oxygen.

Benzene is an extremely stable molecule due to its geometry and molecular orbital interactions, but most importantly, due to its resonance structures. The delocalized electrons in the benzene ring make the molecule very stable and with its characteristics of a nucleophile, it will react with a strong electrophile only and after the first reactivity, the substituted benzene will depend on its resonance to direct the next position for the reaction to add a second substituent.

**Example 2.5.1: Multiple Resonance of other Molecules**

Molecules and ions with more than one resonance form

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Some structural resonance conformations are the major contributor or the dominant forms that the molecule exists. For example, if we look at the above rules for estimating the stability of a molecule, we see that for the third molecule the first and second forms are the major contributors for the overall stability of the molecule. The nitrogen is more...
electronegative than carbon so, it can handle the negative charge more than carbon. A carbon with a negative charge is the least favorable conformation for the molecule to exist, so the last resonance form contributes very little for the stability of the ion.

The Hybrid Resonance forms show the different Lewis structures with the electron been delocalized. This is very important for the reactivity of chloro-benzene because in the presence of an electrophile it will react and the formation of another bond will be directed and determine by resonance. The lone pair of electrons delocalized in the aromatic substituted ring is where it can potentially form a new bond with an electrophile, as it is shown there are three possible places that reactivity can take place, the first to react will take place at the para position with respect to the chloro substituent and then to either ortho position.

**Exercises**

**Questions**

**Q2.5.1**

Are all the bond lengths the same in the carbonate ion, \( \text{CO}_3^{2-} \)?

![Carbonate ion diagram]

**Solutions**

**S2.5.1** Yes, the bond lengths in carbonate ion are all the same. Carbonate ion exists as the resonance hybrid of the three resonance forms below.

![Carbonate ion resonance forms]

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