Quick Review of Resonance, Aromaticity and Conjugation!

If you are beginning to review for final’s week, and are worried about cramming in the entire quarter’s information here is a quick review over aromaticity and conjugation. Have fun and enjoy!

Some key words to keep in mind as you review include:

- Conjugation
- Conjugated System
- Electron Delocalization
- Resonance
- Aromaticity
- P Orbital Overlap
- Electron Density
- Lewis Structures
- Resonance Hybrids

Also recall that there are THREE ways to obtain a higher stability
1. Resonance
2. Conjugation
3. Aromaticity

Let’s start with resonance:

**Resonance:** A condition in which a molecule cannot be adequately represent by a single Lewis structure. Two or more structures are needed. (Illustrated Glossary)

*Remember: Prof. Hardinger’s example of his “dragon-unicorn” hybrid.*

The idea behind resonance, is that a molecule that allows electron delocalization, by having either pi electrons, a pi bond or open p orbitals, cannot be represented by a single structure.

**WHY?** The constant activity that occurs among the electron densities in a molecule cannot just be attributed to ONE single structure.

**Example:** Carbon Monoxide

\[\text{\textbullet} \quad \widehat{\text{C}} \equiv \text{O}^+ \quad \leftrightarrow \quad \text{C} \equiv \text{O}^- \quad \leftrightarrow \quad \text{C}^+ \equiv \text{O}^- \]

**Figure 1: Resonance Contributors of Carbon Monoxide**

**Figure 1** shows that the actual structure of Carbon Monoxide cannot be drawn by just ONE structure.

- The first structure is not accurate because Oxygen, who is the second most electronegative element, will NOT want to share that many bonds with Carbon.
- The second structure is also not accurate since the Carbon has an open octet which is not likely to occur. Carbon is “unhappy” with an open octet.
- The third structure is also not accurate since although Oxygen does have the most electrons which fits its electronegative nature, Carbon has an open octet making it highly unstable.
There are 4 common electron pair shift patterns:

1. Lone Pair & Pi bond Switch

2. Pi Bond and Open Valence Shell Switch

3. Lone Pair & Open Valence Shell Switch with Bond

4. Pi Bonds Switch in Ring

The Next Step after Finding the Contributors is to draw a Resonance Hybrid...

**Resonance Hybrid:** A weighted average or blend of resonance contributors; the MOST accurate representation of the electronic structure of a molecule.

**Drawing the Resonance Hybrid**

1. Draw Contributors
2. Draw the features that are the same for all contributors
3. Add features that are not the same for all contributors (this is when partial pi bonds and charges are drawn)

Now, let’s look at conjugation... (Next page)
Conjugation: A special stability resulting from three or more adjacent, parallel, or overlapping p orbitals. (Illustrated Glossary)

Figure 7: P Orbital Overlap

Figure 7 shows a simple p orbital overlap between two molecules. Notice that the sp2 orbitals cause a sigma bond, while the p orbital overlap causes a pi bond.

Conjugated System: A conjugated system has a region of overlapping p-orbitals, bridging the interjacent single bonds. They allow a delocalization of pi electrons across all the adjacent aligned p-orbitals.

Delocalization: is the process of removing electron density from an atom or group due to resonance, inductive effects, or other phenomena. (Hardinger’s Illustrated Glossary)

Remember: Some consequences of p orbital overlap
- Atoms with p orbitals must be planar
- Partial pi bond(s)
- Barrier to Rotation

3 Consequences of Conjugation
1. More extensive conjugation=greater stability
2. Partial pi bond character
3. Highly conjugated molecules may be colored
Relation of Conjugation & Color (Energy of photons absorbed)

- Electron is excited to higher energy molecular orbital

![Diagram of electron energy levels](Image)

- ↑ number of conjugated p orbitals ↓ DE
- When DE low enough, photons of visible light absorbed
- Unabsorbed portion of visible light spectrum perceived as c

Now let’s look at Aromaticity:

**Aromaticity:** A special stability caused by a closed loop of adjacent, parallel, overlapping p orbitals which contains $4N+2=\pi$ electrons (This number being a whole integer $n=0,1,2,3$)

[*Aromaticity is the highest level of stability that a molecule could acquire]*

**How to determine whether a molecule is aromatic?**

1. Is there a closed loop of p orbitals?
2. Is the molecule planar?
3. Does it follow Hückel's rule of $4N+2=\pi$ electrons (where $n$= whole integer)

**Example:**
Is this molecule aromatic?

1. Closed loop of p orbitals? Yes, benzene has a closed loop of p orbitals caused by the adjacent pi bonds in a ring

![Benzene molecule](Image)

2. Is the molecule planar?
(Looking for planarity can be tricky so the best thing to do is ask yourself “Does this molecule have a reason not to be planar?”)

In this case, the molecule is planar due to the conjugation cause by the p orbital overlap inside the ring.

3. Does the molecule follow Hückel's rule?

\[ 4N + 2 = \pi \text{ electrons} \]

In this case, there are 6 \( \pi \) electrons (two for each \( \pi \) bond) so ... 

\[ 4N + 2 = 6 \]
\[ 4N = 4 \]
\[ N = 1 \]

So yes benzene follows Hückel’s rule

Since, ALL three criteria for benzene were met then benzene IS aromatic.

**Important things to remember:**

• When counting \( \pi \) electrons, **only** count the ones that contribute to aromaticity

Example:

Pyridine:

When counting the \( \pi \) electrons needed for Hückel’s rule, you count 6 \( \pi \) electrons.

Why 6 & not 8?

Although Nitrogen has a lone pair, this lone pair **DOES NOT** participate in the overall aromaticity of this molecule.

Notice that the lone pair attached to Nitrogen is not part of the p orbital overlap inside of the ring therefore does not participate in aromaticity

• Also when considering whether there is a closed loop of p orbital, an open valence shell **DOES** count.

**Example:**

Is cyclopropene aromatic?

1. Closed loop of p orbitals?

Yes, the + charge on the top carbon demonstrates a **lack** of electrons, however it means that there is an unoccupied p orbital. This means that it still contributes to the closed loop rule.

2. Is it planar? This molecule has a lot of steric strain however the
overall aromatic character of the molecule overrides this.
3. Does it follow Hückel’s rule?
   Yes, \(4N+2=2\) (notice that because of the lack of electrons on the +Carbon, you only count the pi bond electrons)
   \[
   \begin{align*}
   4N+2 &= 2 \\
   4N &= 0 \\
   N &= 0
   \end{align*}
   \]

   Therefore, cyclopropene IS aromatic.

   -----------------------------------------------------------

   We have now looked at the three methods to gain greater molecular stability:
   **Resonance, Conjugation, & Aromaticity.**
   (Next page)
Resonance

Draw ALL the resonance structures of the following (show electron-pushing arrows):

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

Conjugation Problems
Aromaticity Problems:

PROBLEMS ON AROMATICITY

1. Determine the number of π electrons for each compound below, then indicate whether they are aromatic, antiaromatic, or neither. Assume the molecules are neutral and planar unless otherwise indicated.

Number of π electrons: ____  Number of π electrons: ____  Number of π electrons: ____  Number of π electrons: ____

Aromatic, Antiaromatic, or Neither?  Aromatic, Antiaromatic, or Neither?  Aromatic, Antiaromatic, or Neither?  Aromatic, Antiaromatic, or Neither?
Resonance Answers:

Draw ALL the resonance structures of the following (show electron-pushing arrows):

- \( \text{H}_2\text{C} - \text{C} = \text{O} \)
- \( \text{H}_2\text{C} - \text{C} = \text{N} \)
- \( \text{H}_2\text{C} = \text{C} = \text{O} \)
- \( \text{H}_2\text{C} = \text{C} = \text{N} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{O} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{N} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{O} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{N} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{O} \)
- \( \text{H}_2\text{C} = \text{C} = \text{C} = \text{N} \)
Conjugation Answers

All are conjugated!

Aromaticity Answers

PROBLEMS ON AROMATICITY  ©2004 OCHeM.com

1. Determine the number of $\pi$ electrons for each compound below, then indicate whether they are aromatic, antiaromatic, or neither. Assume the molecules are neutral and planar unless otherwise indicated.

- Number of $\pi$ electrons: 6
  - Aromatic, Antiaromatic, or Neither?

- Number of $\pi$ electrons: 6
  - Aromatic, Antiaromatic, or Neither?

- Number of $\pi$ electrons: 6
  - Aromatic, Antiaromatic, or Neither?

- Number of $\pi$ electrons: 10
  - Aromatic, Antiaromatic, or Neither?

Cite list
NOTE: Dr. Hardinger’s Lecture Supplement was my main source of information used throughout this tutorial. Make sure to go back and look over his stuff!!!


Image 2: http://t3.gstatic.com/images?q=tbn:ANd9GcSnEnFJeqJSxlB-Hh1T27bRUPXtmfAmWdlC8ebfjllu_Yuq9aj-dw

Image 3: Lecture Supplement (21)

Image 4: Lecture Supplement (22)

Image 5: Lecture Supplement (22)

Image 6: Lecture Supplement (23)

Image 7: http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Images/piorb.gif

Image 8: http://t3.gstatic.com/images?q=tbn:ANd9GcQgh40AP89ZmBx0g79OlhonrrGkWTT-jH3cORX2TYldg4IFkI-p

Image 9: Lecture Supplement (42)

Image 10: Lecture Supplement (43)

Image 11: http://t3.gstatic.com/images?q=tbn:ANd9GcRqoCmr3HQWAsASlroaNXXn_uSrgnTnBfPLwfy4uySy7lo4s3yz

Image 12: http://t1.gstatic.com/images?q=tbn:ANd9GcTn-XHLHO7-9Uh34CWDHdHyMJoDpwURqiSQ6g0uLN8BGJ2A48j5pEA


Image 14: http://swift.cmbi.ru.nl/teach/theory/IMAGE/pyridine.gif

Image 15: http://bbruner.org/obc/arom_fig/c2_cat.gif

Practice Problems:
Resonance Problems:  http://chem.stthomas.edu/pages/ippoliti/resonance1.gif
Resonance Answers: http://chem.stthomas.edu/pages/ippoliti/resonance1ans.gif
Conjugation Problems: http://masterorganicchemistry.com/2011/03/08/are-these-alkenes-conjugated/

Aromaticity Problems: http://ochem.jsd.claremont.edu/practice/Aromaticity_Probs.htm
Aromaticity Answers: http://ochem.jsd.claremont.edu/practice/Aromaticity_Probs_a.htm