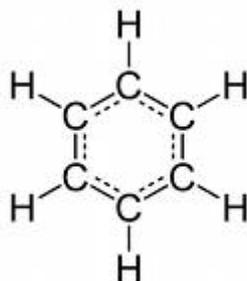


Chemistry Tutorial: Aromaticity

Based on a Chemistry 14C Honors Project

*Six carbons once formed in a ring,
with sp^2 hybridization.
The strain was relieved,
and all six achieved
electron delocalization*



*'The stability, itself is dramatic,'
said a puzzled o-chemist fanatic.
'All these factors at work
just add a new perk.'
And thus was proclaimed aromatic.*

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Section 1: Vocabulary

(a) Define each term

(b) Explain how it relates to aromaticity

- Aromaticity
- Conjugation
- Cyclic delocalization
- Resonance
- Pi bonds
- Partial Pi bonds
- Ring Strain

Section 1: Vocabulary – Solutions

Aromaticity

- a) *Extra stability possessed by a molecule that meets specific criteria: pi bonds all must lie within a cyclic structure, loop of p orbitals, p orbitals must be planar and overlap, must follow Hückel's Rule.*
- b) *n/a*

Conjugation

- a) *The special stability provided by three or more adjacent, parallel, overlapping p orbitals.*
- b) *Aromatic molecules, by default, have conjugation. As it takes a minimum of three, adjacent, overlapping p orbitals for planarity, aromaticity requires a minimum of this for conjugation. Aromaticity is like conjugation, but extra stable.*

Cyclic delocalization

- a) *Electron delocalization, or distribution of electron density, occurs as a result of overlapping p orbitals in a planar, cyclic structure.*
- b) *A closed loop of overlapping p orbitals must be present for aromaticity to occur; therefore, cyclic delocalization occurs in aromatic molecules and is a contributor to the molecule's extra stability.*

Resonance

- a) *A situation in which a molecule can be represented by two or more valid Lewis structures.*
- b) *By looking at resonance structures such as a benzene ring, we can determine where p orbitals and partial pi bonds occur. Partial pi bonds and planar p orbitals can contribute to aromaticity, so resonance also contributes to the stability of aromatic molecules.*

Pi bonds

- a) *Pi bonds are formed by the overlap of p orbitals between two adjacent atoms.*
- b) *In order for a molecule to have aromaticity, it must first have pi bonds so that overlapping p orbitals and electron delocalization are present.*

Partial Pi bonds

- a) *Partial pi bonds are formed as a result of close pi bonds lying in the same plane.*
- b) *Through resonance, aromatic molecules achieve conjugation and a ring of overlapping p orbitals through partial pi bonds within a structure.*

Ring Strain

- a) *Ring strain occurs as a combination of torsional and angle strain and from deviation from the ideal or preferred bond angles.*
- b) *Because aromatic molecules include a closed ring of p orbitals, ring strain occurs; however, the benefits of aromaticity generally outweigh the ring strain in terms of molecular stability.*

Check the Illustrated Glossary of Organic Chemistry (available at the course web site) for more definitions.

Section 2: Determining Aromaticity

Overview:

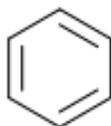
Aromaticity is special stability provided to a molecule upon possessing four specific qualities mentioned below. To determine if a molecule is aromatic, investigate its structure for the qualifiers. If all are present within the molecule, then it is aromatic.

Criteria for Aromaticity:

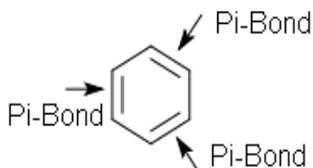
- Pi bonds must lie within cyclic structure
- Each atom in the cycle must have p orbital, forming p orbital loop
- All p orbitals in the loop must overlap (planarity)
- Hückel's Rule: orbital arrangement must result in a lowering of energy. $4n + 2$ pi electrons (n is an integer: 0, 1, 2, 3, etc...) in the loop

Example Problem:

Determine if the following molecule is aromatic.



- Step 1: Do pi bonds lie within a cyclic structure?



- Three pi bonds are present, each lying within the cyclic structure of benzene

Yes

- Step 2: Does each atom in the cycle have a p orbital, forming a p orbital loop?



- Each atom has a p orbital, forming a loop

Yes

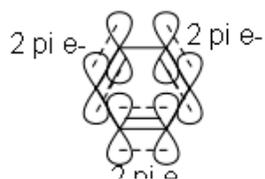
- Step 3: Do all p orbitals overlap and lie within the same plane?



- By rotating the molecule, we see that all orbitals lie within the same plane

Yes

- Step 4: Does the molecule follow Hückel's Rule?



6 total pi electrons
 $4n + 2 = 6$ $n = 1$

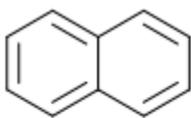
Yes

- Conclusion: Benzene is an aromatic molecule*

Practice Problems:

Determine whether or not the following molecules are aromatic.

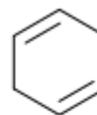
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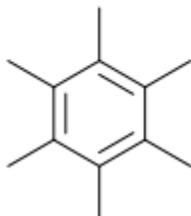
2



3



4



5



6



Practice Problems: Solutions

- Yes; meets all criteria*
- No; does not include loop of overlapping p orbitals*
- No; does not contain loop of overlapping p orbitals*
- Yes; meets all criteria*
- No; does not follow Hückel's Rule*
- Yes; meets all criteria*

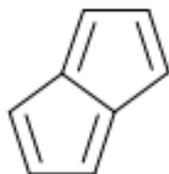
Section 3: Conjugation and Aromaticity

Overview:

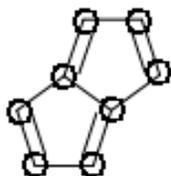
Conjugation requires at least three overlapping p orbitals in the same plane so that electrons can be delocalized for better stability. Aromaticity cannot exist without conjugation because aromatic molecules require planarity and overlapping p orbitals. However, conjugation can exist in a molecule without being aromatic.

Example Problem:

Determine if the molecule below has conjugation, aromaticity, both, or neither.

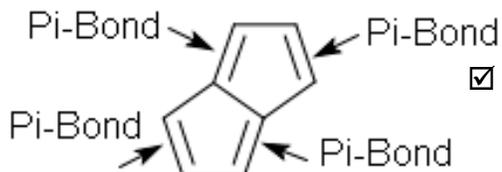


- Step 1: Does the molecule have conjugation?

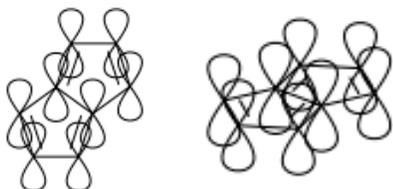


- Yes, the atoms are all planar with more than three overlapping p orbitals

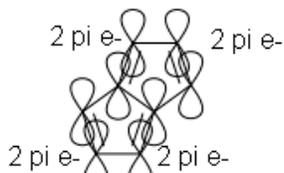
- Step 2: Is the molecule aromatic?



- Pi bonds are present within a cyclic structure



- Each atom has a p orbital, forming a loop
- p orbitals overlap and lie in the same plane



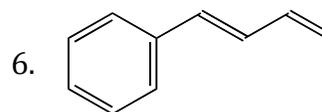
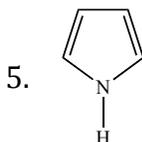
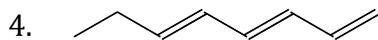
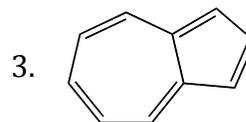
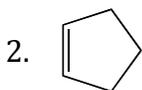
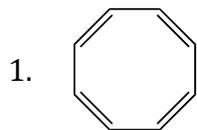
- Violates Hückel's Rule ($4n+2 = 8$; $n = 6/4$)

- Not aromatic

- *Conclusion: The molecule has conjugation, but is not aromatic.*

Practice Problems: - Conjugation and Aromaticity:

Determine if the molecules below have conjugation, aromaticity, both, or neither.



Practice Problems - Solutions

1. *Not conjugated (the molecule has a tub shape and the C=C are perpendicular); Not aromatic – violates Hückel's rule*

2. *Not conjugated – does not contain at least three atoms with planar p orbitals; Not aromatic – does not contain closed loop of planar, overlapping p orbitals*

3. *Conjugated; Aromatic – meets all criteria*

4. *Conjugated, Not aromatic – does not contain closed loop of planar, overlapping p orbitals*

5. *Conjugated; Aromatic – meets all criteria*

6. *Conjugated; Aromatic – meets all criteria*

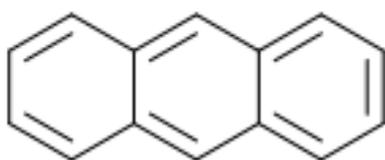
Section 4: Resonance and Aromaticity

Overview:

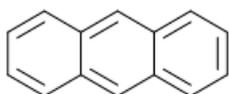
Resonance exists as a result of electron delocalization in a molecule. Different patterns emerge as a result of structure and atom arrangement within a molecule. Resonance provides an extra stability due to electron delocalization, and consequently; aromatic rings have resonance structures due to cycling double bonds. Aromatic molecules must have resonance; however, not all molecules with resonant structures are aromatic.

Example Problem:

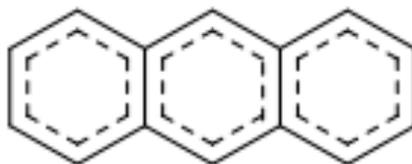
Determine if the molecule below has resonance, aromaticity, both, or neither.



- Step 1: Does the molecule have resonance?

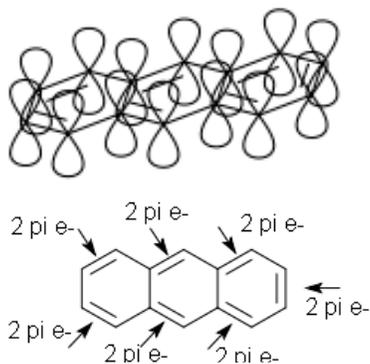


- The pi bonds in the molecule can switch places, a property seen in alkene rings, resulting in a resonance hybrid:



Has Resonance

- Step 2: Is the molecule aromatic?

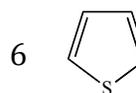
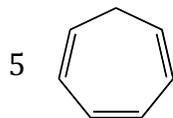
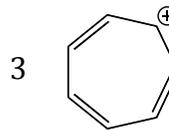
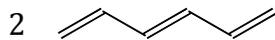
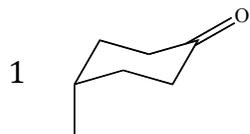


- Yes, the atoms are all planar with more than three overlapping p orbitals
- Pi bonds are present within a cyclic structure
- Each atom has a p orbital, forming a loop
- The p orbitals overlap and lie in same plane
- Satisfies Hückel's Rule ($4n+2 = 14$; $n = 3$)
- Aromatic

- *Conclusion: The molecule has resonance, and is aromatic.*

Practice Problems: Resonance and Aromaticity

Determine if the molecules below have resonance, aromaticity, both, or neither.



Practice Problems: Solutions

1. *No resonance; No aromaticity.*

2. *Resonance; No aromaticity*

3. *Resonance; Aromaticity*

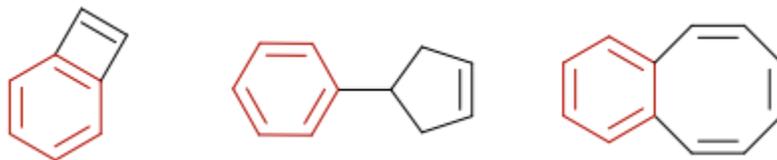
4. *No resonance; No Aromaticity*

5. *Resonance; No Aromaticity*

6. *Resonance; Aromaticity*

Section 5: Frequently Asked questions

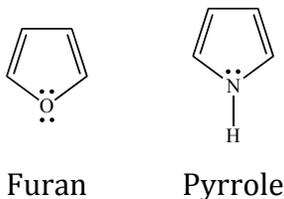
- **Are conjugation and aromaticity the same thing?**
 - Not quite. Conjugation occurs in aromatic molecules, but aromaticity is a higher level of stability with more requirements to be met. Conjugation can be viewed as simply a piece of aromaticity.
- **Why would a molecule prefer to be aromatic?**
 - Equilibrium favors stability. Aromatic molecules have a special “extra” stability caused by the nature of their structure, and are harder to break apart.
- **How can I tell if a molecule with Nitrogen is aromatic?**
 - It depends on the molecule. If nitrogen is part of a ring, check its hybridization and electrons. If it is sp^2 hybridized or if it can become sp^2 hybridized as a result of the overall structure and electron delocalization of the molecule, the molecule is aromatic.
- **What do lone pairs have to do with aromaticity?**
 - Lone pairs can lead to resonance hybrids or reside in pi bonds that contribute to the aromaticity of a molecule.
- **Can purely linear molecules have aromaticity?**
 - No. A requirement for aromaticity is a closed loop or ring or p orbitals. Since linear molecules cannot achieve this, they are unable to be classified as aromatic.
- **If a molecule contains an aromatic ring, such as a benzene ring, attached to a non-aromatic ring, how does that affect the overall aromaticity of the molecule?**
 - Overall, a molecule can fail to meet the qualifications for aromaticity as a whole, but still contain aromatic parts. If a molecule contains a benzene ring, we can say that the molecule has an aromatic ring, but we cannot say that the molecule is aromatic.



- Example: Within the above molecules, there are aromatic parts, outlined in red. However, the molecules as a whole are not aromatic.
- **What does the n of Hückel's Rule represent, and what does it mean if it is an integer or not an integer?**
 - The “ n ” of Hückel's Rule is simply an indicator of aromaticity. It does not “stand for” a certain word, but is instead used as a calculator. If “ n ” is a whole number integer, the molecule can be aromatic, and if “ n ” is a fraction or non-integer, the molecule is not aromatic.
- **How can I tell if a molecule has planarity?**
 - The best way is to build a model. Remember that to have a planar loop of p orbitals, the molecule must have at least three ‘points’ of interest, atoms or p orbitals, in order to form a plane. After you have determined this, check to see if the atoms have p orbitals, and that they are adjacent.
- **Does an aromatic molecule need to have conjugation and resonance?**
 - Aromatic molecules must have conjugation, and generally, because they contain a series of p orbitals and pi bonds, resonance occurs. An aromatic molecule always has conjugation and resonance, but not all molecules that have conjugation and/or resonance are also aromatic.
- **How do I count the pi electrons to plug into the equation of Hückel's Rule?**
 - Hückel's Rule ($4n + 2 = \# \text{ pi electrons}$) applies only to the pi electrons present in the closed loop of p orbitals. Find the p orbitals present in molecule and determine the number of electrons in each. Sometimes, this is very apparent, as double bonds imply two pi electrons. Be careful, though, as oxygen and nitrogen atoms can sometimes have an ‘empty’ p orbital, or electrons can be forced into a p orbital to achieve conjugation and aromaticity.

Section 6: Common Errors

Aromaticity of Furan and Pyrrole



Furan and pyrrole are both aromatic molecules. At first sight, these molecules seem to be non-planar without a closed loop of p orbitals; however, because of the benefits of achieving aromaticity, the structure is such that two lone pair electrons are delocalized, shown below:



By looking at the resonance hybrid, we can see the delocalization of one lone pair of electrons on the oxygen.



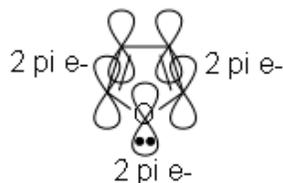
The other electron pair is located somewhere in the p orbital of oxygen, which is now sp^2 hybridized.



Rotated



The electrons are delocalized throughout the planar ring, creating a cloud of pi electrons.



In a final determinant of aromaticity, by counting the pi electrons, we see that furan follows Hückel's rule.

Counting Pi electrons

- **What is a pi electron?**
 - A pi electron is an electron involved in a pi bond.
- **What is a pi bond?**
 - A pi bond is an overlap of two adjacent *p* orbitals between two atoms.
- **Double Bonds:**
 - Consist of 1 sigma bond and 1 pi bond.
 - A pi bond contains 2 pi electrons.
 - Therefore, when counting pi electrons, you know that for each double bond, there are two pi electrons present.
- **Be Careful: Furan/Pyrrrole:**
 - Sometimes, resonance will cause sp^3 atoms to become sp^2 hybridized. Electron delocalization and aromaticity is achieved by delocalizing one lone pair, which will count as two pi electrons in the system for the purpose of Hückel's equation.

Section 7: Other Readings and Extra Sources to Consult

Aromaticity in Chemistry 14C Books:

Chemistry 14C Thinkbook

Chemistry 14C Lecture Supplement

Organic Chemistry as a Second Language (Klein)

Organic Chemistry: Structure and Function (Vollhardt and Schore) and Study Guide

Online Websites

"Aromatic Compounds and Aromaticity." Dr Andy Cammidge's Homepage. University of East Anglia. 24 Nov. 2008 <<http://www.uea.ac.uk/~c286/aromaticnotes.htm>>.

This website gives great insights about the basics of aromaticity, general concepts, and related vocabulary. It also gives in-depth views of aromatic compounds and the quantum mechanics behind their electron delocalization.

"Aromaticity and Hückel's Rule." O=CHem. University of Southern Maine. 24 Nov. 2008 <http://web1.uct.usm.maine.edu/~newton/Chy251_253/Lectures/Aromaticity/AromaticityFS.html>

This website talks about Hückel's rule. It specifically elaborates about the electron placement in aromatic rings and compounds, relating it back to molecular orbitals, bonding, and how hybridization works.

Wikipedia. "Aromaticity." Aromaticity. 14 Nov. 2008. Wikipedia: The Free Encyclopedia. 24 Nov. 2008 <<http://en.wikipedia.org/wiki/aromaticity>>.

Although this site does not go in depth like the others, it provides useful information about the general topic of aromaticity, the qualifications, and molecular structure.

Wikipedia. "Furan." Furan. 14 Nov. 2008. Wikipedia: The Free Encyclopedia. 24 Nov. 2008 <<http://en.wikipedia.org/wiki/furan>>.

This page specifically talks about why furan achieves aromaticity. It provides a useful diagram of the resonance structures and electron delocalization leading to stability.