

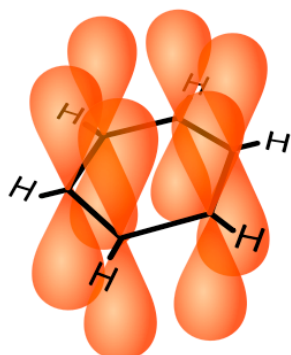
How to Determine Aromaticity: The Lone Pair Predicament

Still haven't unwrapped your thinkbook? Don't worry! Here's a brief overview of aromaticity:

DEFINITION

Aromaticity a special kind of stability a molecule possesses when it meets these three requirements:

- 1) There is a **Closed loop of p-orbitals** somewhere in the molecule
 - This means that the atoms in the ring must be sp^2 or sp (rarely) hybridized

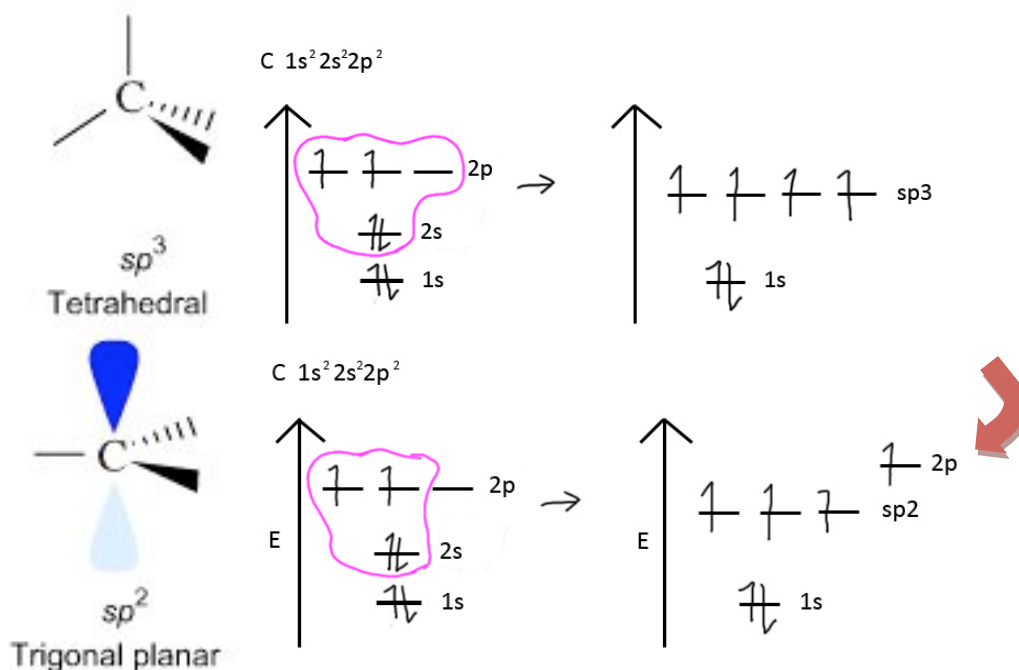


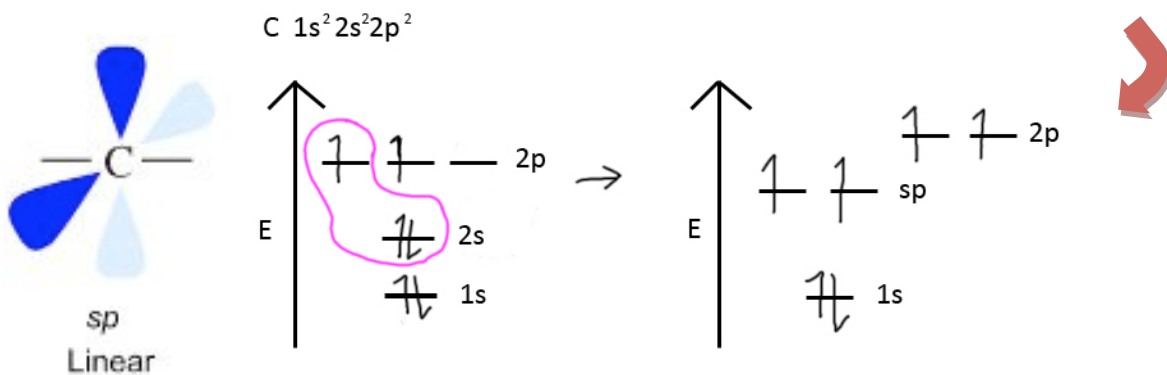
All the carbons in this **benzene** molecule are sp^2 hybridized.

Image 1

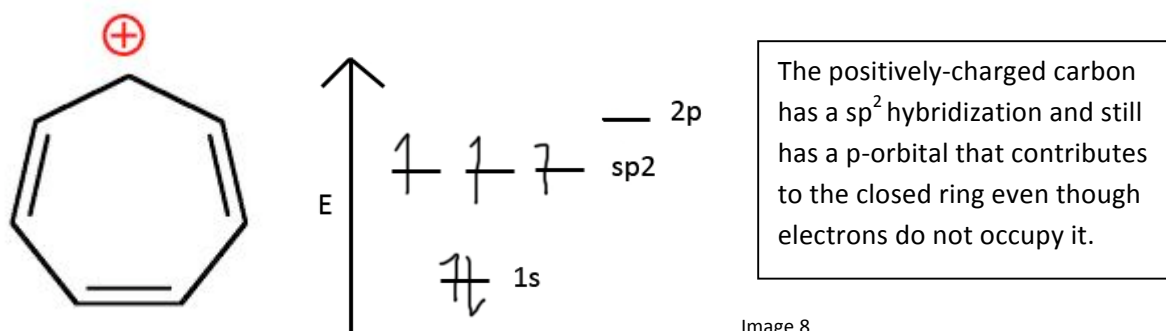
6 p-orbitals

- *Remember:* sp^3 hybridized atoms do not contribute any p-orbitals.
Images 2, 3, 4 and 5 clockwise from top left



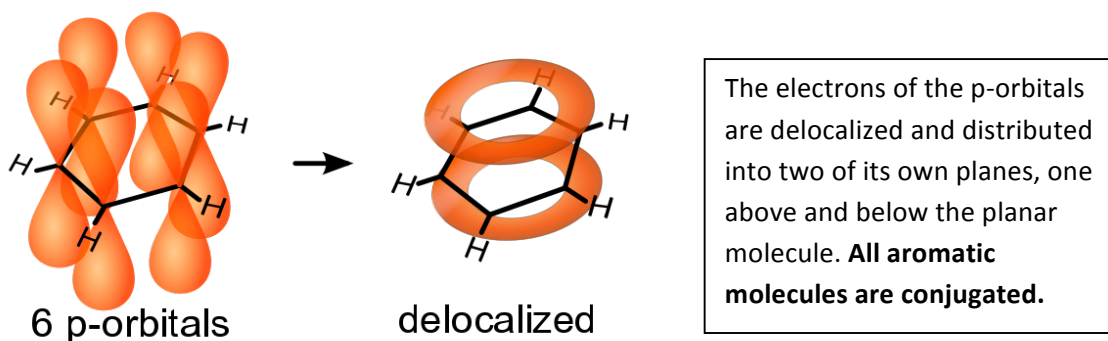


- The p-orbitals do not necessarily have to be filled with electrons



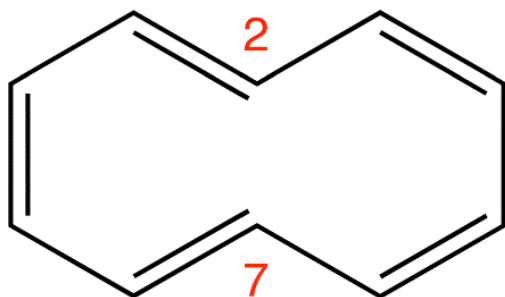
2) These p-orbitals must **overlap**. In other words, the molecule must be **planar**

Image 9



- Note: If molecule has a large substituent(s), torsional strain can force it out of planarity
 - This case happens when torsional strain > aromatic stability
 - How can I tell? *Below are a few cases you should remember*
 - Note: A wrong answer with the right assumption (assuming that torsional strain will overcome the aromatic stability) will earn credit if correct reasoning is shown

- Ex) Annulene



- Why isn't this aromatic? *Hint*: don't forget to draw in the hydrogens!

Image 10

Hydrogen atoms that are not drawn on carbons 2 and 7 try to occupy the same space. This leads to torsional strain that outweighs the stability the molecule would gain from aromaticity.

The molecule assumes a non-planar conformation and is not aromatic.

- Ex) Benzene can hold up to 5-tert butyl groups until torsional strain > aromatic stability

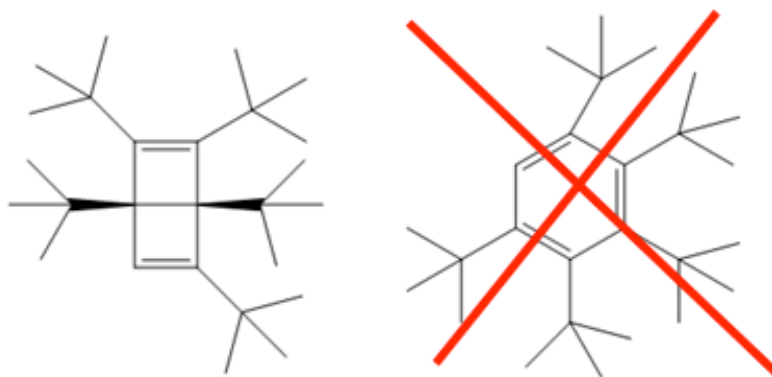


Image 11

3) Huckel's rule: **$4n+2$ pi electrons**; n is *any* integer (0, 1, 2...)

- *Tricky rule*: take *resonance structures* into account
- Pi electrons = pi bond(s) within the closed loop (1 pi bond = 2 electrons) + lone pairs participating in resonance structures' pi bonds
 - Which lone pairs count? Well that's the *Lone Pair Predicament*!

THE LONE PAIR PREDICAMENT

Remember before when we said that **sp^3 hybridized atoms could not participate in aromaticity**? Well that's true, but it's not as easy as a rule as it sounds.

Sometimes, an atom can *look* like it is sp^3 hybridized, but it is actually be sp^2 hybridized.

How can this happen? Has your life come crashing down at the very thought of sp^2 atoms appearing to be sp^3 ? Us too. Hopefully, this explanation will help you get to sleep tonight:

An atom that looks like it is sp^3 can be classified as sp^2 only when it would benefit the molecule for this to be so. What exactly does that mean? Well consider this circumstance:

Say you're dragging yourself through the Chemistry 14C midterm and you come across the aromaticity problem. It kindly asks you to determine if molecule X is aromatic. There are no formal charges. It looks something like this:

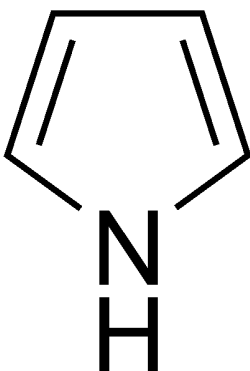


Image 12

You're a smart fella so you remember that sp^2 hybridized (contains p-orbitals) atoms in a closed ring can produce an aromatic molecule (assuming it follows Huckel's rule).

- ✓ 4 carbon atoms are sp^2 hybridized
- ✗ Nitrogen atom is sp^3 hybridized because it has *three sigma bonds and one lone pair*.
- **Done. Not aromatic.** It doesn't follow Huckel's Rule (4 pi electrons) AND not all atoms in the ring have p-orbitals.

WRONG!!!!

The resonance structures of this molecule are:

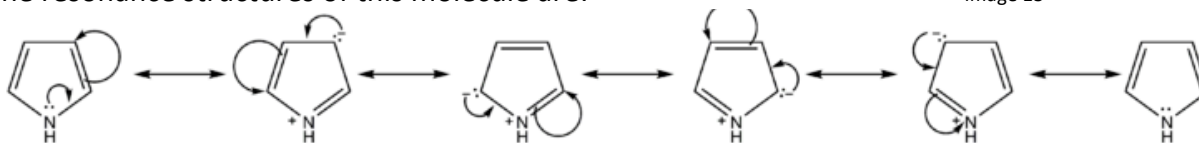


Image 13

Combined resonance structure:

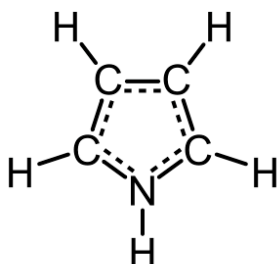


Image 14

One of the lone pairs of the nitrogen atom contribute to these resonance structures, creating partial pi bonds and causing the nitrogen to have a partial p-orbital.

Therefore the lone pair contributes to the aromaticity. The structure follows Huckel's Rule (6 electrons = $4(1) + 2$) AND all atoms in the ring have p-orbitals. The p-orbitals overlap making the molecule planar. The molecule *is aromatic*.

See! You, my friend just fell victim to lone pair play – a cheap trick used by these con artists that will cost you points on exams and admission into medical school. *How do you know if a seemingly sp^3 hybridized atom is actually sp^2 hybridized?* Here's how we fix this:

ASK YOURSELF THESE QUESTIONS, IN ORDER:

1. Does this atom possess lone electrons that contribute to resonance structures?
2. Does this *seemingly sp^3* atom ruin the aromaticity?
*Remember, atoms really want to be aromatic. It decreases their energy and makes them more stable, so don't be fooled by sp^3 camouflage.
3. Would the atom that is ruining the aromaticity actually complete a closed loop of overlapping p orbitals if it had a p orbital?

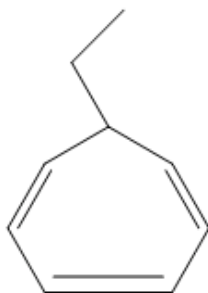
If all above is true, feel free to assign the molecule an sp^2 hybridization.

→ *Note:* When this happens, these lone pairs can count as pi electrons.

PRACTICE PROBLEMS

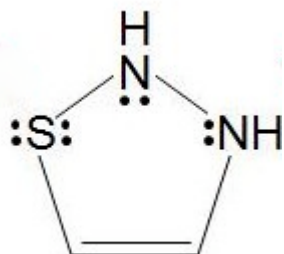
Are you still confused? We understand if you are. This topic is pretty confusing and goes against so many topics we covered in 14A and 14B. Fear not! Here are some SUPER FUN examples to get you pumped for hybridizing even the most complex molecules:

Image 15



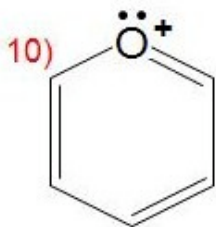
This molecule is **not aromatic** because the carbon at the top of the closed-ring (where the ethyl group is attached) has no p orbital. It is sp^3 hybridized. Don't be fooled, even though the molecule has the correct number of pi electrons to follow Huckel's rule!

Image 16



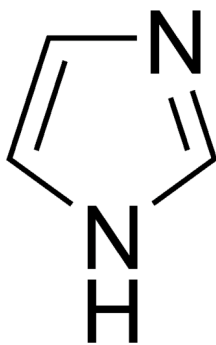
This molecule is **not aromatic** because it disobeys Huckel's rule. The nitrogens contribute its' lone pairs to the resonance structures (therefore are sp^2 hybridized). This is also the case with Sulfur, but Sulfur can only contribute one of its lone pairs. Because it only uses one lone pair, the total number of pi electrons is 8, which does not fit with $4n+2$ ($n=1.5$ – not an integer). *Remember: an atom will never use both lone pairs to contribute to aromaticity!*

Image 17



This molecule is **aromatic**. The oxygen's electrons do not contribute to resonance structure, and therefore do not lie in the p-orbital. Nevertheless, oxygen is still sp^2 hybridized AND it follows Huckel's Rule with 6 pi electrons, so it all works out!

Image 18



This molecule is **aromatic**. The nitrogen on the top does not contribute its lone pairs in resonance structures (therefore do not count as pi electrons). This is shown in the resonance contributors below. The nitrogen on the bottom contributes its lone pairs in resonance structures, therefore they do count as pi electrons. The total pi electron count = 6 (follows Huckel's Rule).

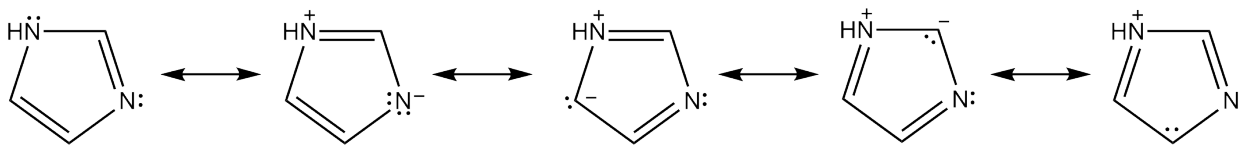
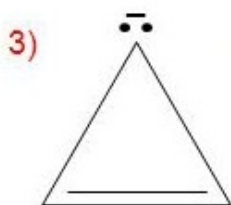


Image 19

Image 20



This molecule is **not aromatic**. The lone pair cannot make a pi bond with the other carbons because it will create a pentacarbon (unstable). Therefore, that carbon is sp^3 molecules and do not have a p-orbital. Also, the total number of pi electrons = 4 ($n=1.5$ – not an integer).

Cited Works

Images 1 and 9: Wikipedia. Wikimedia Foundation. Web. 27 Apr. 2012.
<http://en.wikipedia.org/wiki/File:Benzene_Orbitals.svg>.

Images 2, 5, 6: http://www.meta-synthesis.com/webbook/45_vsepr/VSEPR.html

Images 3, 4, 7:
http://chemwiki.ucdavis.edu/Theoretical_Chemistry/Chemical_Bonding/Valence_Bond_Theory/Hybridization

Image 8: <http://www.nku.edu/~russellk/tutorial/reson/C7H7+.GIF>

Image 10: <http://science.uvu.edu/ochem/wp-content/images/A/aromatic12.png>

Image 11: Created on ChemDraw

Image 12: http://en.wikipedia.org/wiki/File:Pyrrrole_structure.png

Image 13: http://en.wikipedia.org/wiki/File:Pyrrrole_Resonance.png

Image 14: <http://en.wikipedia.org/wiki/File:Pyrrrole-2D-full.svg>

Image 15: Created on ChemDraw

Images 16, 17, 20: http://chemwiki.ucdavis.edu/Organic_Chemistry/Aromatics/Hückel's_Rule

Image 18: http://upload.wikimedia.org/wikipedia/commons/3/31/Imidazole_structure.png

Image 19: <http://en.wikipedia.org/wiki/File:Resonance-imidazole.png>