

## Aromaticity and Reactions of Benzene Learning Objectives

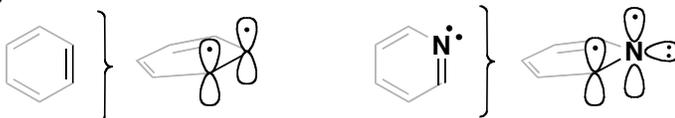
As we study this chapter, you should...

- 1) **Understand that aromaticity makes molecules (and intermediates) stable.** Aromaticity can cause many phenomena to occur (for example, it can influence the hybridization of an atom or it can cause a normally nonacidic proton to become very acidic).
- 2) **Understand that anti-aromaticity makes molecules (and intermediates) unstable.** Anti-aromaticity can cause many phenomena to occur (for example, it can influence the hybridization of an atom or it can cause a molecule to twist out of conjugation <as in cyclooctatetraene>).
- 3) **Know that Benzene, being aromatic, does not undergo the majority of the reactions that alkenes undergo.** In this text, we will only encounter a few reactions that occur on the benzene ring. The C=C bonds in benzene *do not* undergo the same reactions as the C=C bonds in alkenes.
- 4) **Know the criteria for aromaticity and how to determine them:**
  - a) the compound must be cyclic
  - b) the compound must be planar
  - c) the compound must be fully conjugated
  - d) the  $\pi$  system of the ring must have  $4n+2$   $\pi$  electrons (e.g. 2, 6, 10, 14, etc.)
  - e) if criteria a-c are valid, but the compound possesses  $4n$   $\pi$  electrons (e.g. 0, 4, 8, 12, etc.), it is considered **antiaromatic** (and will be especially unstable)

**Here are some guidelines for deciding whether orbitals or electrons are part of the  $\pi$  system:**

any double bond will have 2  $\pi$  electrons, one from each atom

e.g.

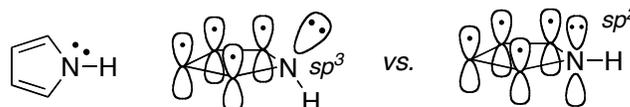


this nitrogen has a lone pair of electrons, but they are not part of the  $\pi$  system because the electron is double bonded to a carbon and already uses 1 electron from its valence set for this.

an atom will assume an unusual hybridization if it allows a p orbital to become part of an aromatic system

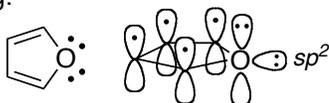
e.g.

Normally (and according to VSEPR theory), a nitrogen with 3 single bonds and a lone pair of electrons is  $sp^3$  hybridized. However, a lone pair of electrons in an  $sp^3$  hybrid orbital cannot participate as well in conjugation because it is angled away from the  $\pi$  system. Therefore, the nitrogen assumes  $sp^2$  hybridization instead so that the molecule can now be aromatic.

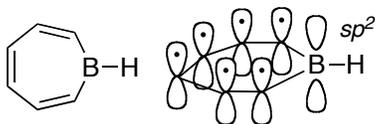


a p orbital can have a minimum of 0 electrons and a maximum of 2 electrons

e.g.



The oxygen atom assumes  $sp^2$  hybridization so that one lone pair of electrons can be in the p orbital and become part of the  $\pi$  system, making the molecule aromatic. The other lone pair can't reside in the same orbital, so it has to be in another orbital (the  $sp^2$  hybridized orbital).



The empty p orbital of boron can participate in the  $\pi$  system, allowing the molecule to satisfy all the criteria needed for aromaticity.

- 5) **Understand that although the double bonds in a benzene ring are not particularly reactive, the benzylic position of a benzene compound will undergo a variety of reactions.** This is because of the conjugation/resonance possibilities that occur to stabilize a charge or radical that is formed at the benzylic position.
- 6) **Understand that benzene, being aromatic, *does not* undergo the majority of the reactions that alkenes undergo.** In this chapter, we will only encounter 5 reactions of benzene. All 5 are classified as electrophilic aromatic substitution (EAS) reactions. These reactions have 3 main steps...
  - i) Formation of the electrophile
  - ii) Reaction of the benzene ring with the electrophile
  - iii) Rearomatization
- 7) **Be able to provide a mechanism for any EAS reaction.**
- 8) **Know how to name benzene compounds.**