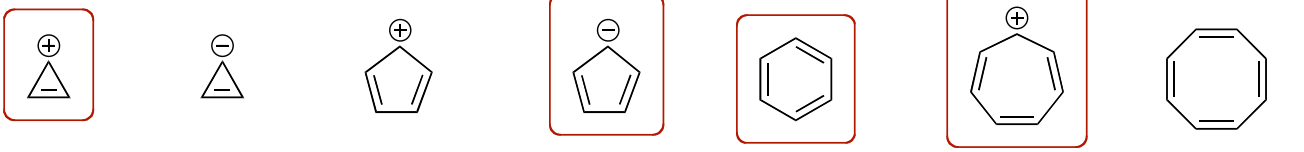
Chem 342 • Organic Chemistry II

Lecture Summary 09 - 04 Feb 2009

Chapter 15 - Benzene and Aromaticity

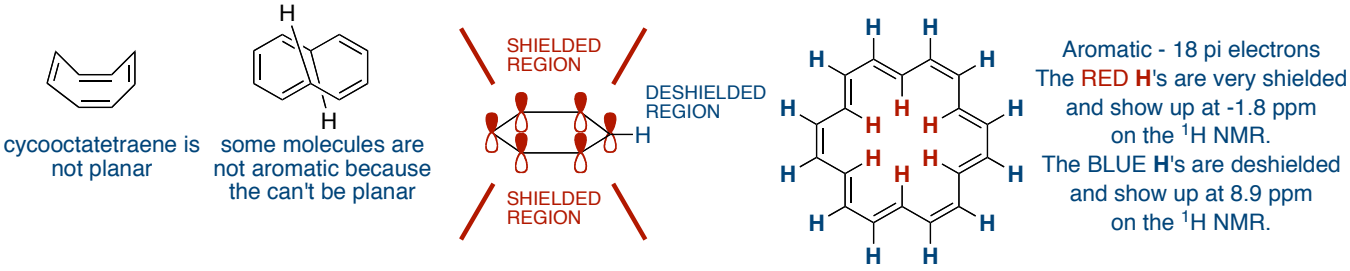
Aromatic Hydrocarbons

Below are some examples of fully conjugated systems which are aromatic or not aromatic. Note that carbocations or carbanions may be included in the conjugation. Thus, if the ring has the proper number of electrons, they can be aromatic.



AROMATIC 2 pi electrons | 4 pi electrons | 4 pi electrons | **AROMATIC** 6 pi electrons | **AROMATIC** 6 pi electrons | **AROMATIC** 6 pi electrons | 8 pi electrons

Some molecules, like cyclooctatetranene twist out of plane to avoid higher energy unpaired electrons. Other molecules that have the right number of electrons are not aromatic because the molecule cannot become planar and align all of the p-orbitals to be conjugated. Aromatic rings cause regions of extra shielding and deshielding that show sup on the proton NMR spectrum.



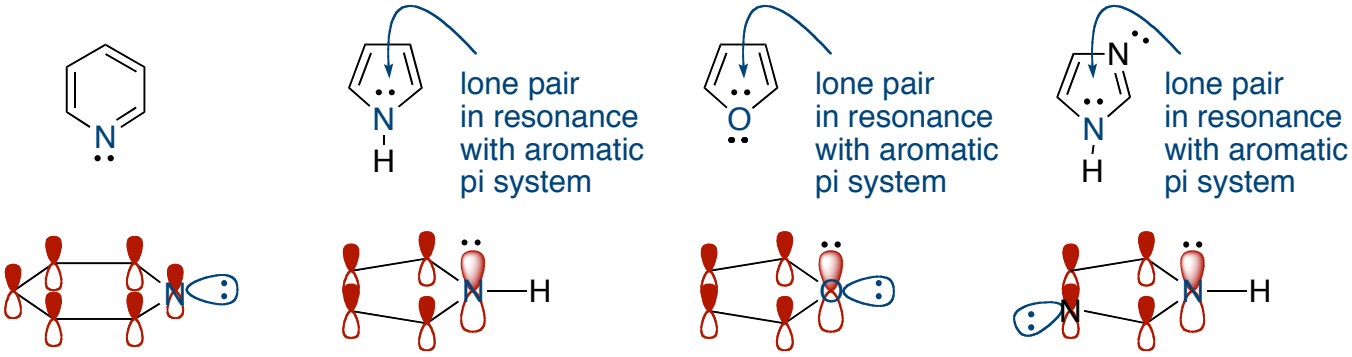
cycooctatetraene is not planar

some molecules are not aromatic because the can't be planar

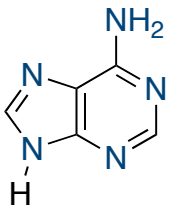
Aromatic - 18 pi electrons
The RED **H**'s are very shielded and show up at -1.8 ppm on the ^{1}H NMR.
The BLUE **H**'s are deshielded and show up at 8.9 ppm on the ^{1}H NMR.

Aromatic Heterocycles

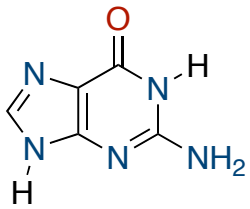
Heteroatoms can also be in aromatic rings. The lone pair on an oxygen may be part of the aromatic pi-electron system. If the heteroatom is drawn with a double bond to it, it's lone pair is orthogonal to the pi-system and is not part of the resonance. If the heteroatom has only single bonds drawn to it, the lone pair is in a p-orbital and part of the aromatic pi-electron system.



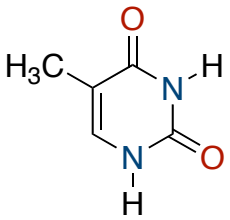
Take a look at the DNA bases. Which are aromatic? What lone pairs are conjugated with the pi-systems? Can you draw resonance forms that are aromatic?



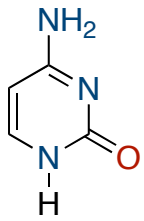
Adenine



Guanine



Thymine

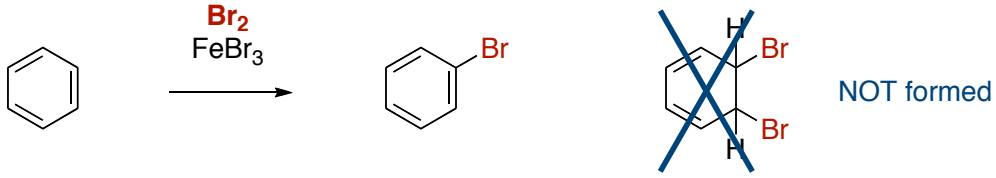


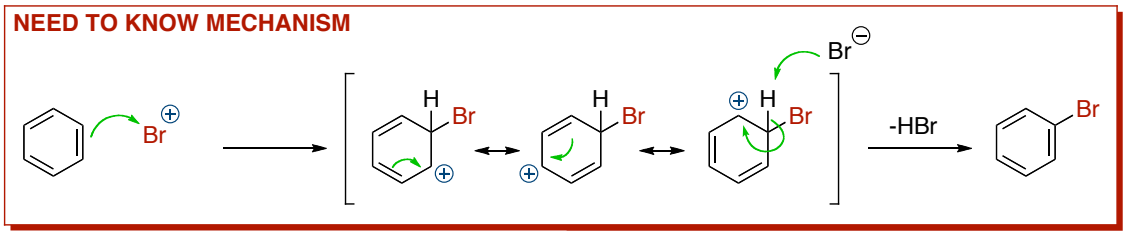
Cytosine

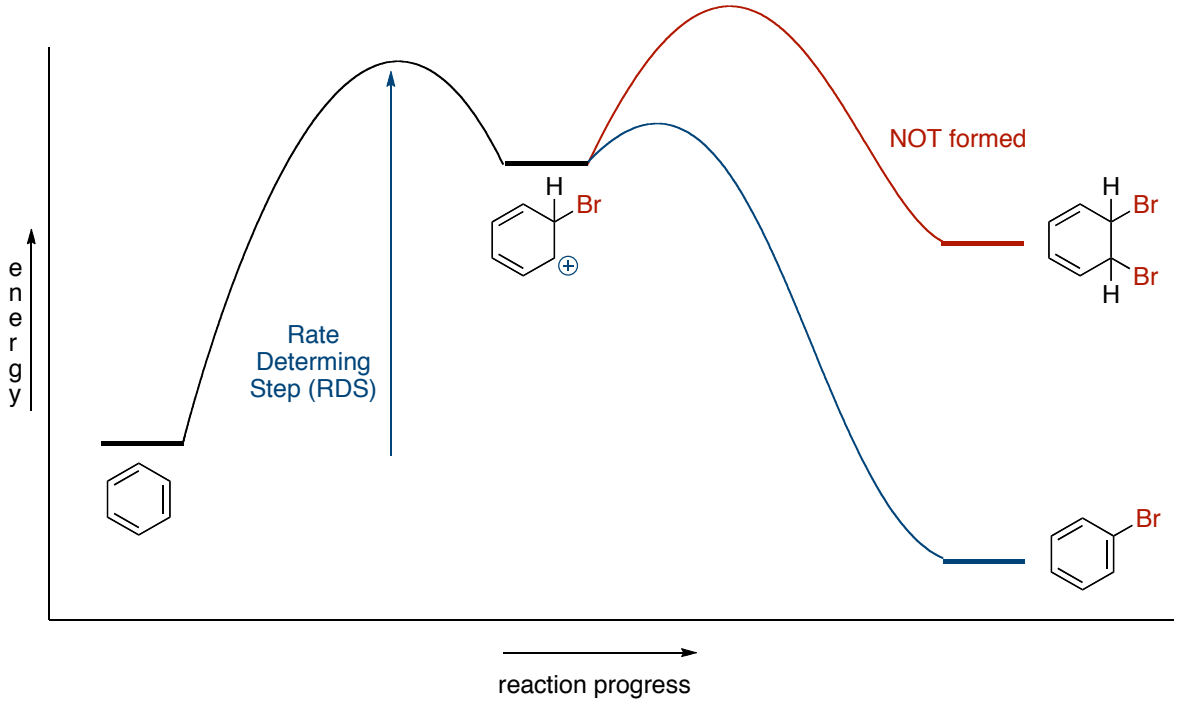
Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

A stepwise mechanism

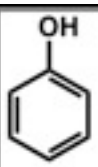
Aromatic rings do not react with electrophiles like typical double bonds. Although the first step is very similar, the second step is very different. An electrophile will add to form an intermediate carbocation (of which you can draw a number of resonance structures). Instead of a nucleophile adding to the carbocation, the intermediate will deprotonate to regenerate the stable aromatic ring. This is a much lower energy pathway than the addition product.







Daily Quiz

Q: Which of the following molecules is NOT aromatic?		
	☐ 1:	
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