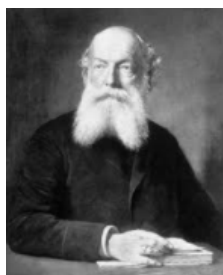
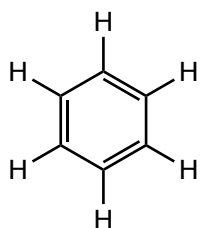


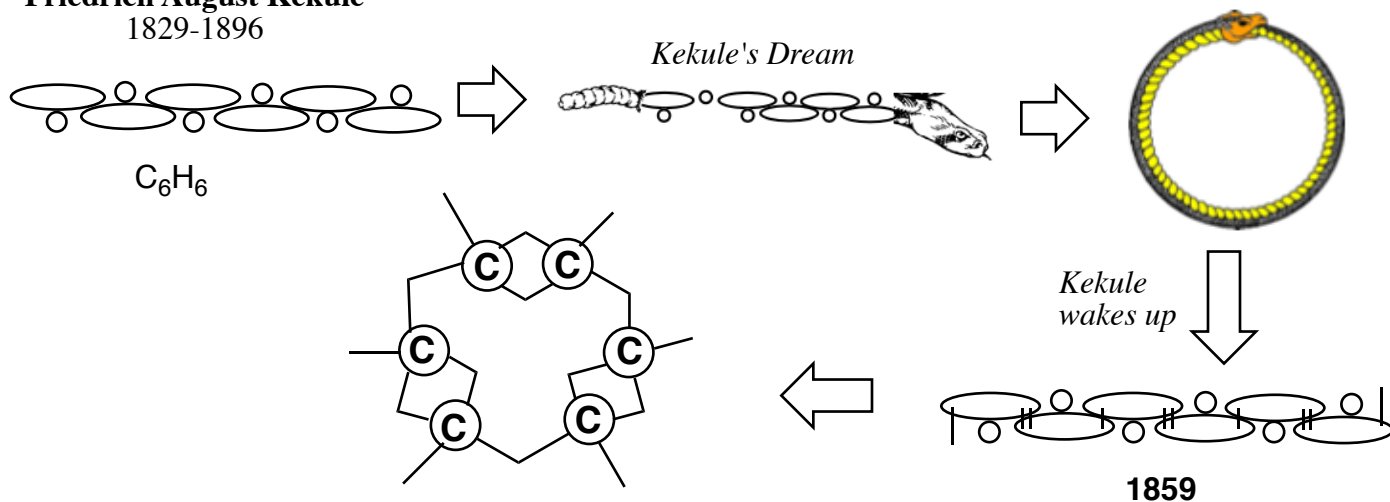
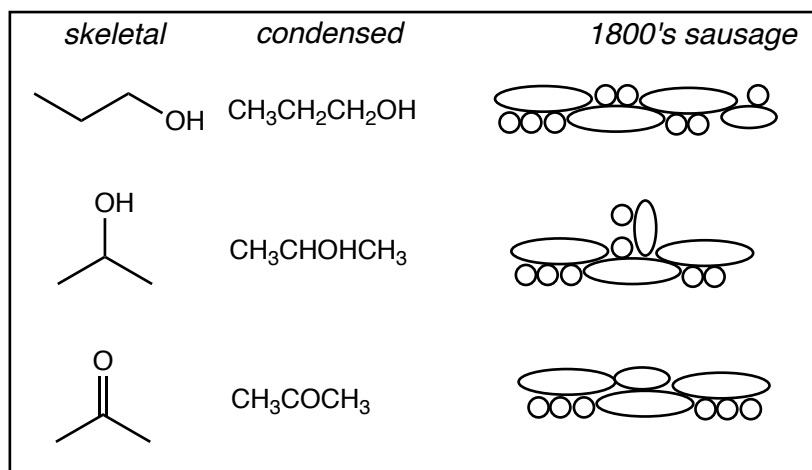
# Chapter 18: Aromatic Compounds

[Sections: 18.1, 18.3-18.5, 18.8]

## The Structure of Benzene

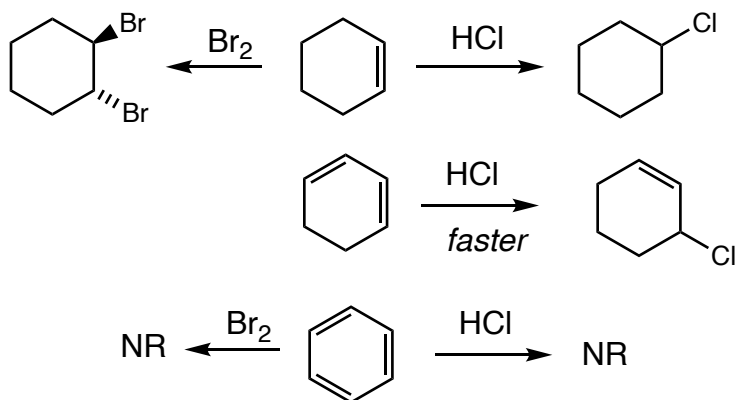


**Friedrich August Kekule**  
1829-1896

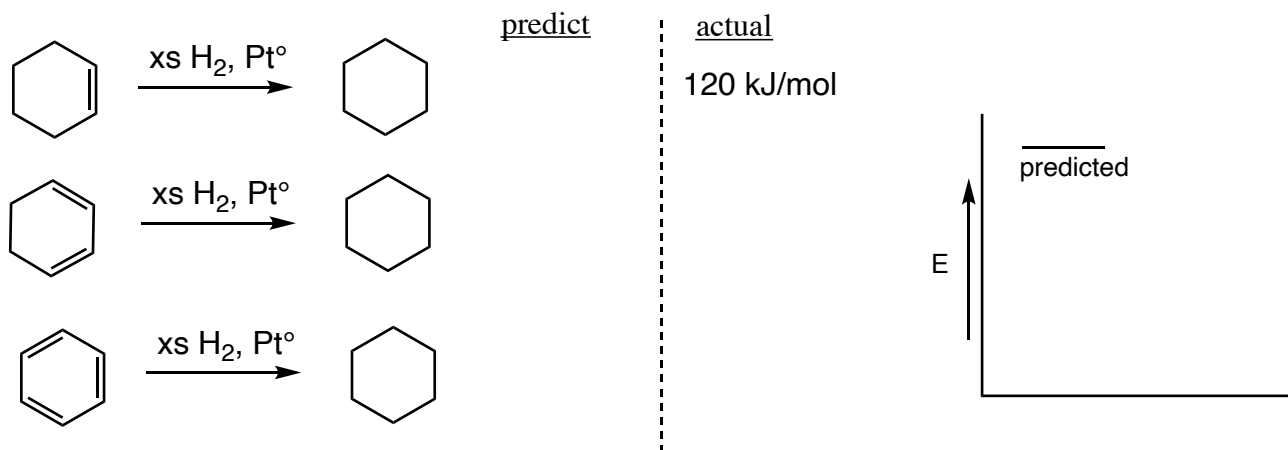


1865

## Some Curious Things About Benzene

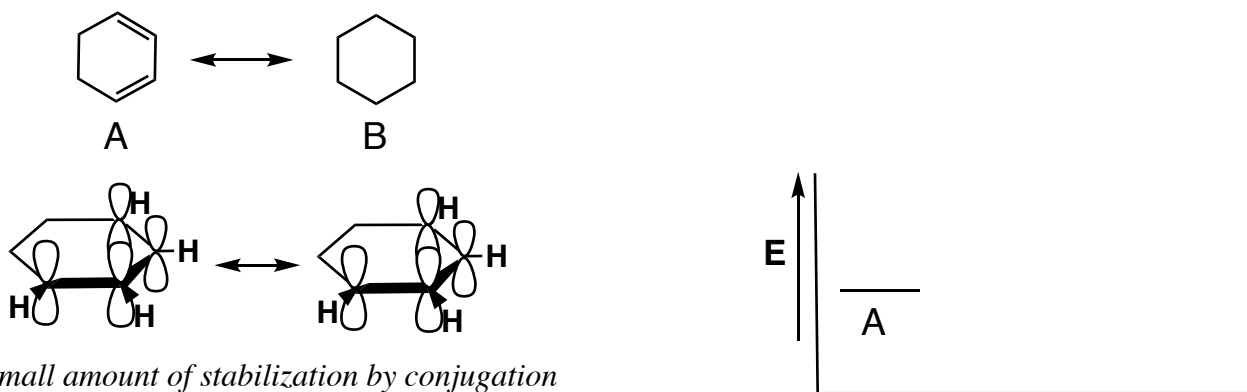


- the reactivity of benzene is **MUCH** less than what would be expected based on its skeletal structure alone
- it does **NOT** engage in the same type of reactions expected of alkenes



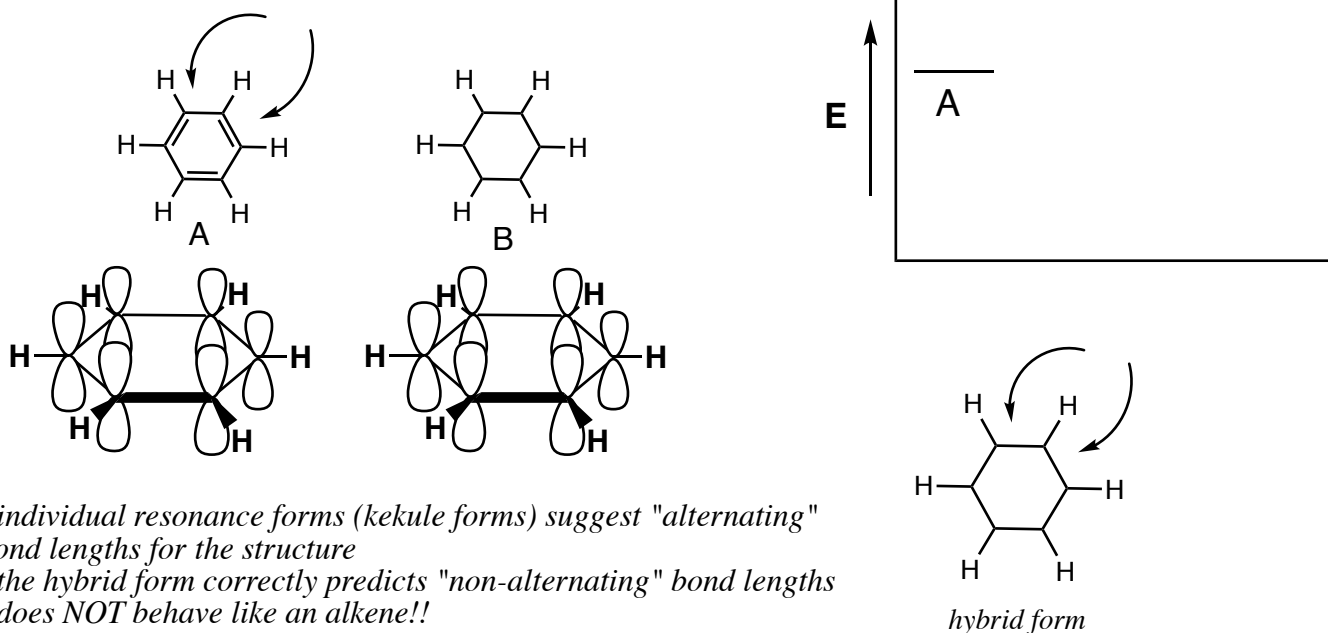
• benzene is *MUCH* more stable (by about 150 kJ/mol) than would be expected based on its skeletal structure alone!

flashback to dienes

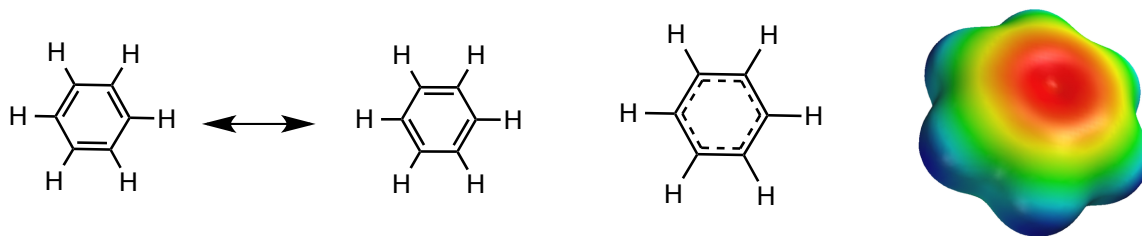


- small amount of stabilization by conjugation
- still behaves essentially like an alkene

resonance in benzene

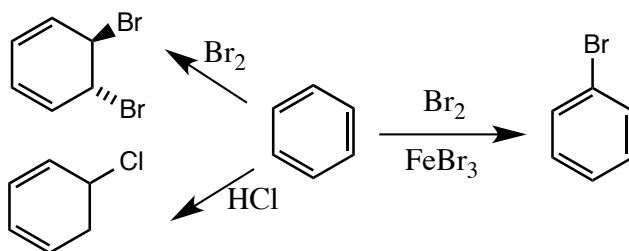


- individual resonance forms (kekule forms) suggest "alternating" bond lengths for the structure
- the hybrid form correctly predicts "non-alternating" bond lengths
- does *NOT* behave like an alkene!!



- hybrid form
- much more stable than either resonance form alone
- does not resemble either individual resonance form, but is a true mixture of both

- the surprising stability of benzene comes from the strong stabilization of the hybrid form by the equal contribution of two excellent resonance forms of equivalent energy
- the two contributing resonance forms (Kekulé forms) allow the electrons in the benzene pi system to be completely delocalized amongst 6 different carbon atoms!
- the special stabilization resulting from this electron delocalization due to resonance is called "aromaticity"
- all of the carbons of benzene are  $sp^2$  hybridized, thus the molecule is flat. In addition, the equal contribution of the two resonance forms means all of the bond lengths (1.4 Å) and bond angles ( $120^\circ$ ) are equivalent

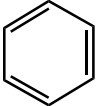
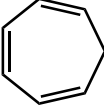







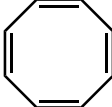






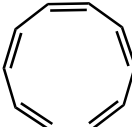






- thus, the lack of reactivity of benzene can be attributed to the reluctance of benzene to lose its aromatic stability if it were to react like a typical alkene via addition reactions!
- when forced, benzene WILL react with electrophiles, but the end result is a substitution reaction rather than addition because aromaticity is retained in substitution reactions

## Is Benzene the Only Aromatic Compound?

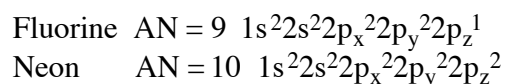
### Properties of Aromatic Compounds

1. Cyclic array of uninterrupted SP<sup>2</sup> hybridized atoms
2. Fully planar structure
3. High stability beyond what simple Lewis Dot structures would predict
4. Undergo substitution reactions (to retain aromaticity) rather than typical alkene addition reactions (in which case aromaticity would be lost)
5. All carbon-carbon bonds are of the same length (non-alternating bond lengths)
- 6.
- 7.

	other information	aromatic?	bond lengths? alt? non-alt?	type of reaction? substitution/ addition
				
				
	 $\xrightarrow{\text{Br}_2}$   $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  + 130 kJ/mol  $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  predict = actual = $\Delta E =$ = stable than predicted!			
	 $\xrightarrow{\text{Br}_2}$   $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  + 100 kJ/mol  $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  predict = actual = $\Delta E =$			
	 $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  + 120 kJ/mol  $\xrightarrow{\text{H}_2, \text{Pt}^\circ}$  predict = actual = $\Delta E =$ = stable than predicted!			

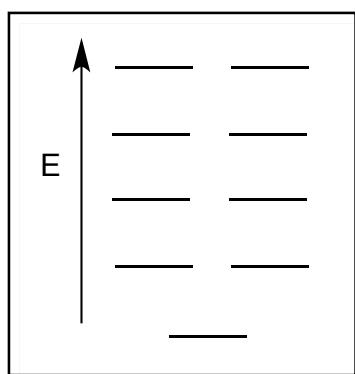
## What Determines Whether a Planar Cyclic Polyene is Aromatic or Not?

Flashback to atomic orbital electron configurations:



- closed shell configurations lead to stable species
- unfilled (or open shell) configurations lead to unstable species

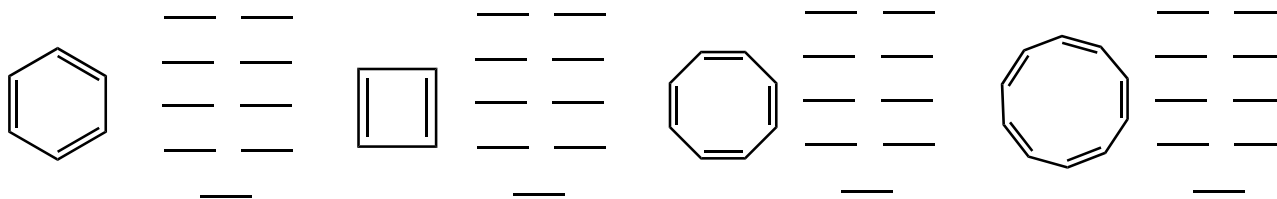
- all molecules have a set of molecular orbitals that are filled in the same manner as atomic orbitals
- for systems with pi bonds, the pi molecular orbitals can be viewed separately from the sigma molecular orbitals
- all planar cyclic polyenes have the same approximate distribution of pi molecular orbitals



- When a proper number of electrons is contained in the pi system to completely fill all of the occupied molecular orbitals an aromatic system will result (if all other criteria for aromaticity are fulfilled).
- This occurs when there is an ODD number of electron pairs in the pi system = Huckel Rule (also fits the equation  $4n+2$ ). This is a general equation such that if a cyclic pi system contains a number of electrons that satisfies this equation, it will have the proper number of pi electrons to completely fill all of the occupied molecular orbitals for a planar cyclic aromatic molecule

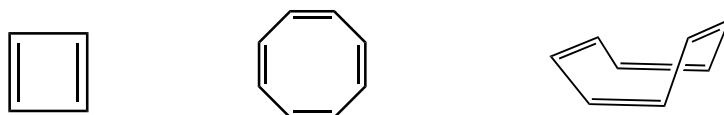


**Erich Huckel**  
1931-1980



**Huckel satisfied?**  
**Aromatic?**

- When an improper number of electrons is contained in the pi system such that singly-occupied molecular orbitals are created, the system will be especially unstable! such systems are termed anti-aromatic
- This occurs when there is an EVEN number of electron pairs in the pi system = Huckel Rule (also fits the equation  $4n$ ). This is a general equation such that if a cyclic pi system contains a number of electrons that satisfies this equation, it will have the improper number of pi electrons to completely fill all of the occupied molecular orbitals and an antiaromatic molecule may result



### Properties of Aromatic Compounds

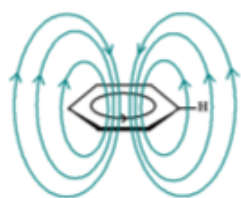
1. Cyclic array of uninterrupted  $sp^2$  hybridized atoms
2. Fully planar structure
3. Very high stability beyond what simple Lewis Dot structures would predict
4. Undergo substitution reactions (in order to retain aromaticity) rather than typical alkene addition reactions (in which case aromaticity would be lost)
5. All carbon-carbon bonds are of the same length
6. ODD number of electron pairs in pi system ( $4n+2$  pi electrons)
- 7.

• there are not many cases of anti-aromatic compounds since such cyclic polyenes will adopt a non-planar conformation to avoid anti-aromaticity

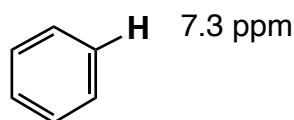
### Properties of Anti-Aromatic Compounds

1. Cyclic array of uninterrupted  $sp^2$  hybridized atoms
2. Fully planar structure
3. Very low stability beyond what simple Lewis Dot structures would predict
4. Undergo typical alkene addition reactions (in order to LOSE anti-aromaticity)
5. Alternating carbon-carbon bond lengths
6. EVEN number of electron pairs in pi system ( $4n$  pi electrons)
- 7.

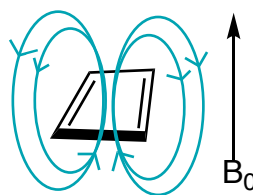
### NMR Effects



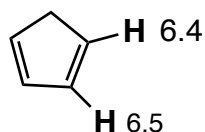
- circulation of the pi electrons in an aromatic system create a magnetic field that increases the effect of the external magnetic field and pushes resonance to higher PPM (i.e., deshields the protons)
- this is a diamagnetic ring current effect



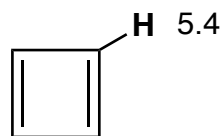
aromatic protons show up at higher PPM than typical alkene protons (deshielded)



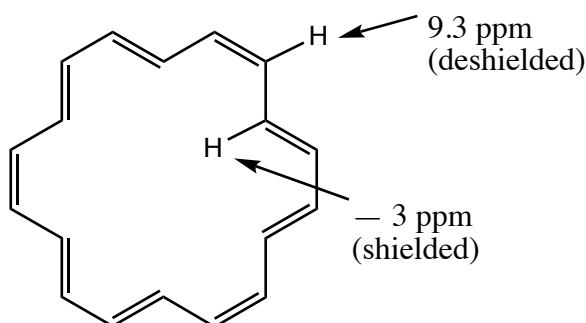
- circulation of the pi electrons in an aromatic system create a magnetic field that decreases the effect of the external magnetic field and pushes resonance to lower PPM (i.e., shields the protons)
- this is a paramagnetic ring current effect



non-aromatic cyclic compounds have typical alkene proton chemical shifts

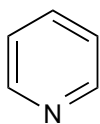


anti-aromatic protons show up at lower PPM than typical alkene protons (shielded)

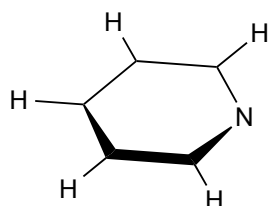


## Aromatic Heterocycles

*heterocycles are cyclic compounds that contain O, N or some other non-C atom*

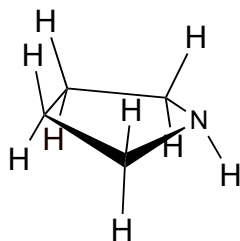
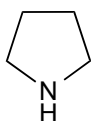


pyridine



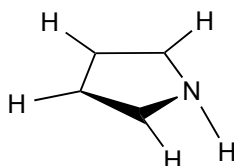
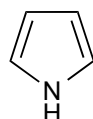
- *pyridine is essentially a benzene ring in which one of the carbons has been replaced by a nitrogen atom*
- *the pi system of pyridine is equivalent to that of benzene and contains a Huckel number (6) of pi electrons*
- *the lone pair on the nitrogen is orthogonal to the pi system and cannot contribute to the pi electron count*

*typical cyclic amine*

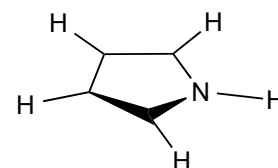


aromatic?

*pyrrole*



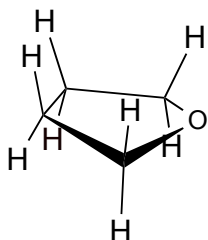
aromatic?



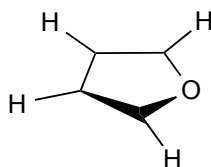
aromatic?

- *a typical nitrogen atom with a lone pair of electrons will adopt SP3 hybridization (tetrahedral shape)*
- *pyrrole could NOT be aromatic if the nitrogen atom were SP3 hybridized*
- *additionally, pyrrole has two C=C bonds which contribute only 4 pi electrons*
- *by adopting SP2 hybridization at the nitrogen atom, pyrrole attains a cyclic array of SP2 hybridized the orbitals and also adds the two electrons from its lone pair to the pi system to give a Huckel number (6) of pi electrons and becomes aromatic!*

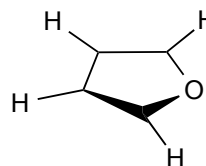
*typical cyclic ether (THF)*



*furan*



aromatic?



aromatic?

- *a typical oxygen atom with two lone pairs of electrons will adopt SP3 hybridization*
- *furan could NOT be aromatic if the oxygen atom were SP3 hybridized*
- *additionally, furan has two C=C bonds which contribute only 4 pi electrons*
- *by adopting SP2 hybridization at the oxygen atom, furan attains a cyclic array of SP2 hybridized the orbitals and also adds the two electrons from one of its lone pair to the pi system to give a Huckel number (6) of pi electrons and becomes aromatic!*

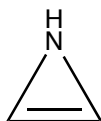
## Summary for aromatic heterocycles

- aromaticity is not restricted to all-carbon molecules
- as long as all of the requirements for aromaticity are fulfilled (uninterrupted cyclic array of  $sp^2$  hybridized atoms, planar structure,  $4n+2$  pi electrons) any molecule may exhibit aromaticity
- atoms with lone pairs may only contribute ONE of the lone pairs into the pi system to satisfy the  $4n+2$  rule

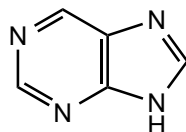
## How can I tell if a heteroatom will donate its lone pair to a pi system?



some guy



- a heteroatom will only adopt  $sp^2$  hybridization and donate a lone pair if it makes the system aromatic
- if the heteroatom is already part of a double bond, it cannot donate any lone pairs (the lone pairs will be orthogonal to the pi system)
- if an atom has two lone pairs, it can only contribute ONE pair into the pi system

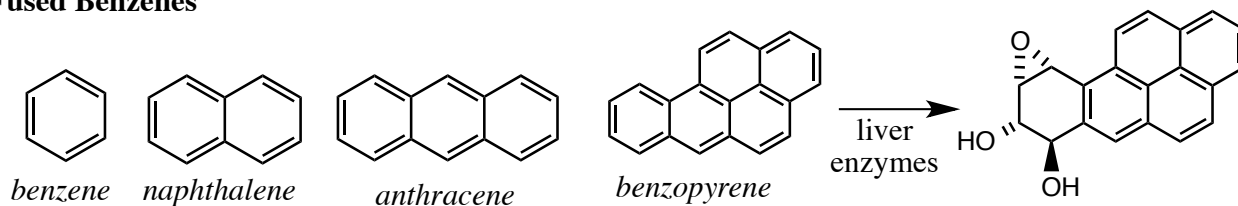


**purine**  
critical component  
of nucleic acids

are the rings aromatic?  
which nitrogens contribute lone pairs?

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## Fused Benzenes





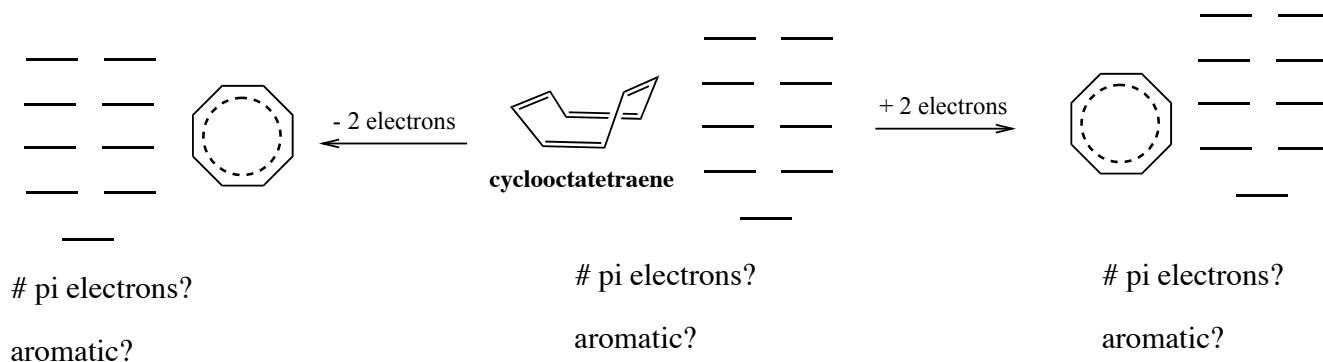
## Charged Aromatic Compounds

Flashback to atomic orbital electron configurations:

Lithium Li AN = 3, # electrons = 3  $1s^2 2s^1$       Fluorine, F AN = 9, # electrons = 9  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$   
 Li<sup>+</sup> AN = 3, # electrons = 2  $1s^2$                   Fluoride, F<sup>-</sup> AN = 9, # electrons = 10  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

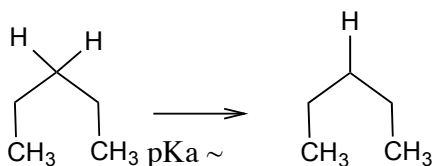
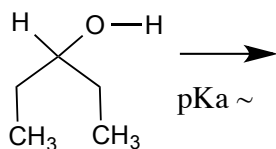
- unstable open-shell atoms could be made stable by adding (to form anions) or subtracting (to form cations) electrons to provide ions with complete outer shells
- aromatic anions and cations can also be formed if the  $4n+2$  Huckel number of pi electrons results
- anti-aromatic anions and cations can be formed if the  $4n$  number of pi electrons results

### Anionic (negatively charged) Pi Systems



### Effect of aromaticity on acidity

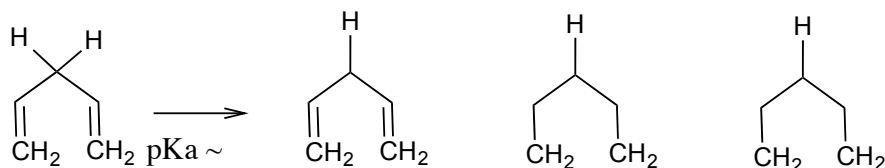
Flashback



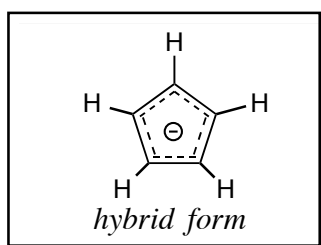
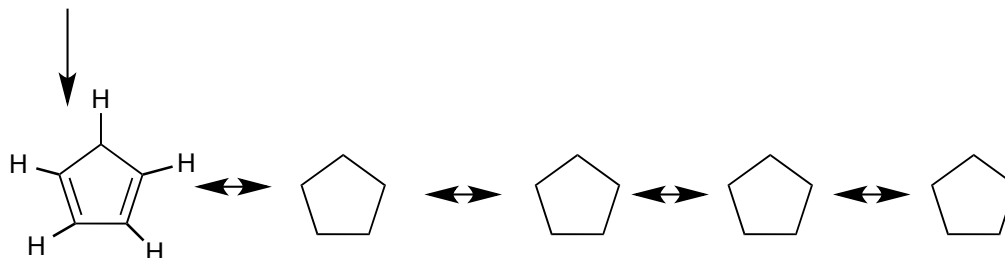
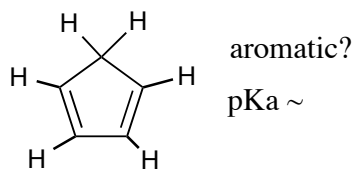
- stabilization of the conjugate base of a molecule by electronegativity or resonance strongly enhances acidity

• O-H bond is more acidic than C-H because O is more electronegative than C and can therefore stabilize the negative charge better

- resonance can increase acidity by stabilizing the negative charge via delocalization



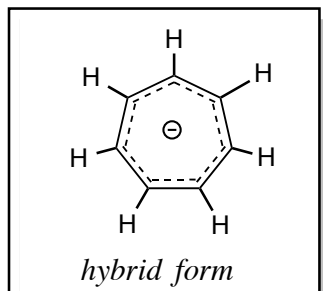
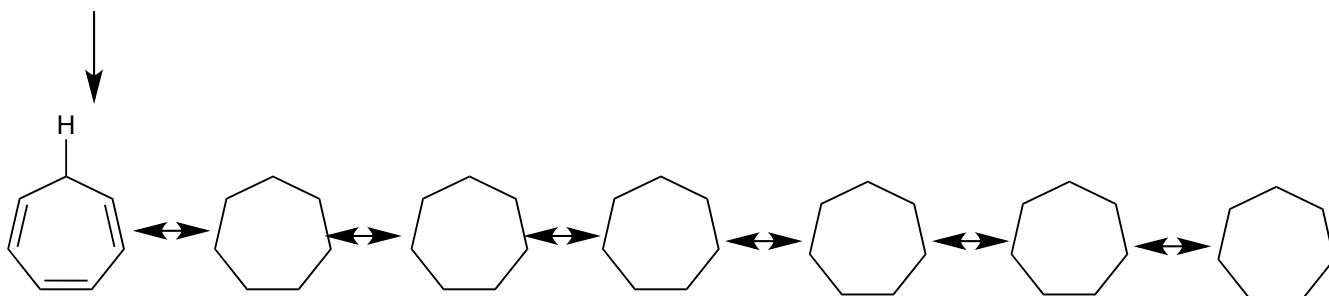
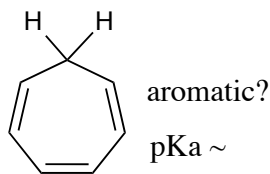
acidity of cyclopentadiene



# pi electrons?  
aromatic?

- cyclopentadiene is unusually acidic for a C-H bond!
- remember: acidic compounds have stabilized conjugate bases!
- its acidity can be traced to the strong stabilization of the resulting negative charge because the resulting pi system has an aromatic number of pi electrons (6 pi electrons)!
- thus, deprotonation of cyclopentadiene changes the molecule from something that is NOT aromatic to a molecule that IS aromatic!
- because the anion is so stable, it is easily formed via deprotonation and the C-H bond is observed to be unusually acidic

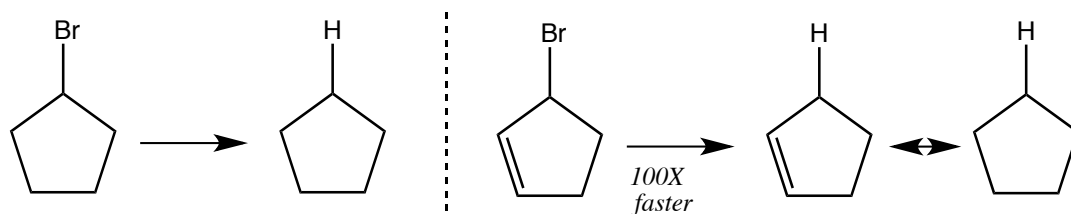
acidity of cycloheptatriene



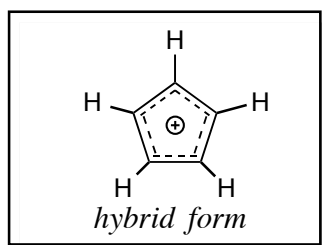
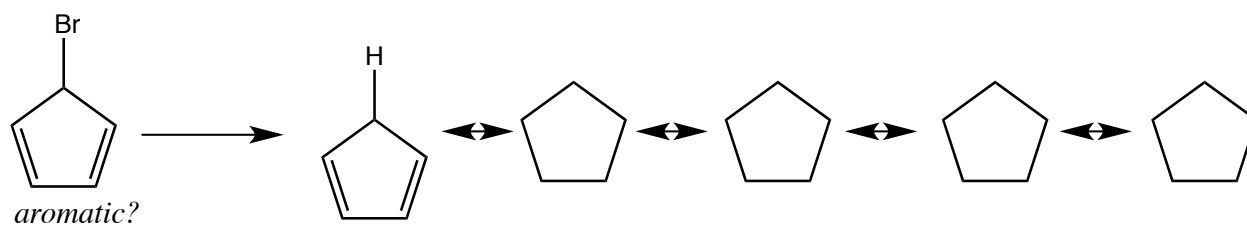
# pi electrons?  
aromatic?

- resonance considerations alone suggest it should be very easy to deprotonate cycloheptatriene since the negative charge is highly delocalized,
- unlike cyclopentadiene, however, cycloheptatriene is NOT unusually acidic
- addition of two electrons to the pi system yields 8 pi electrons, which is NOT a Huckel number
- thus, deprotonation of cycloheptatriene (a non-aromatic molecule) does NOT provide aromatic stabilization and it is therefore does not exhibit an acidic C-H bond

## Cationic (positively charged) Pi Systems

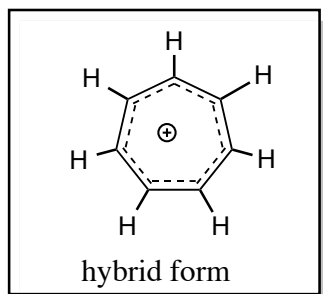
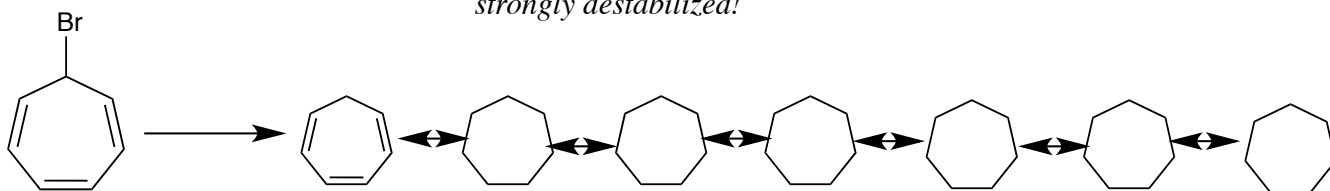


- resonance stabilization of the allylic carbocation results in faster reaction since the allylic carbocation is easier to form than the localized 2° carbocation



# pi electrons?  
aromatic?

- usually carbocations stabilized by resonance forms are very stable and easily formed
- thus, resonance alone suggests it should be very easy to lose the Br leaving group since the resulting carbocation is stabilized via delocalization of the positive charge.
- however, loss of the Br and formation of the carbocation creates an anti-aromatic pi system!
- thus, the Br refuses to act as a leaving group to avoid going from a molecule that is NOT aromatic to a molecule that is ANTI-AROMATIC and therefore strongly destabilized!



# pi electrons?  
aromatic?

- the cycloheptatrienyl carbocation (tropylium cation) is exceptionally stable (and therefore easily formed) because it contains a Huckel number (6) of pi electrons, making it an aromatic compound!
- thus, the Br leaving group is easily lost to form this strongly stabilized aromatic carbocation

## Chapter 18 *Essential Concepts*

1. Know the history of the development of the structure of benzene, development of the theory of aromaticity, and how orbital theory and resonance explain the stability of aromatic molecules.
2. Know all 7 characteristics of aromatic and anti-aromatic compounds (including heat of hydrogenation data) and how each characteristic can be used to confirm or dispel whether a compound is aromatic (or anti-aromatic).
3. Understand how Huckel theory conveniently explains the stability of aromatic molecules and instability of anti-aromatic molecules.
4. Understand how lone pairs on heteroatoms contribute (or not) to the aromaticity or anti-aromaticity of molecules.
5. Understand how charge (negative or positive) can contribute (or not) to the aromaticity or anti-aromaticity of molecules, and how this can impact reactivity of molecules.
6. Given the structure or properties of ANY molecule (and sufficient information), you should be able to designate it as non-aromatic, aromatic or anti-aromatic.