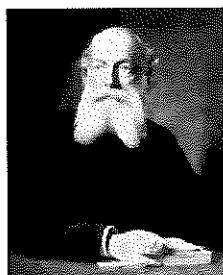
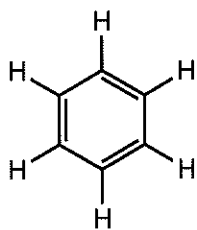


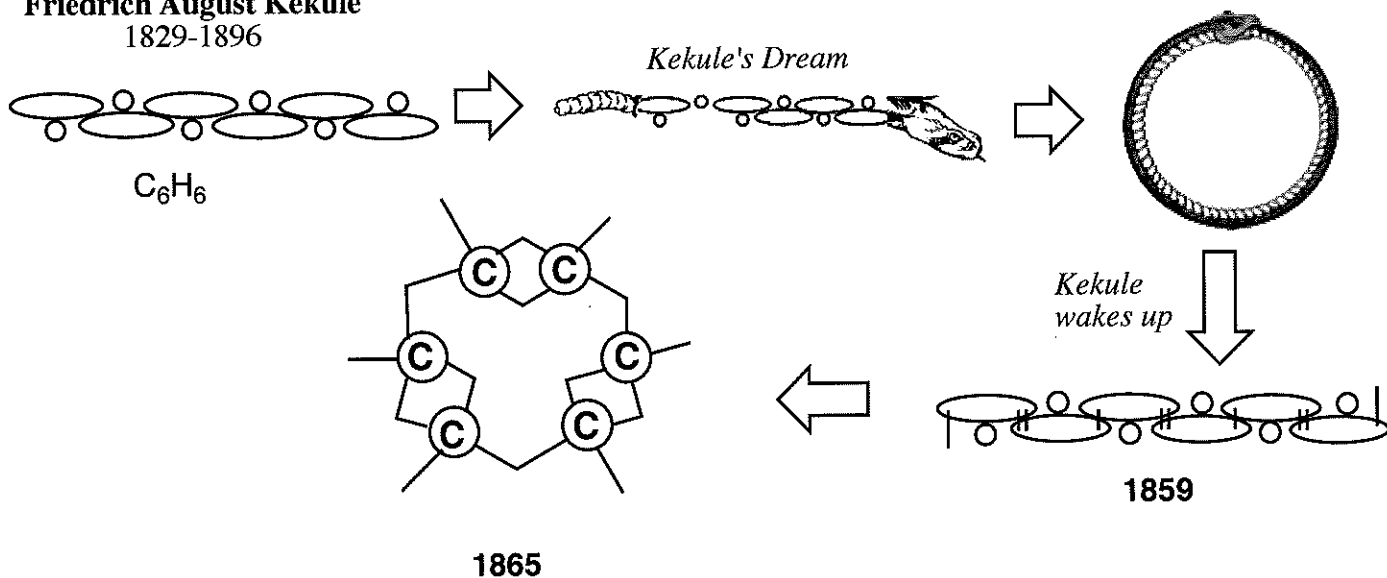
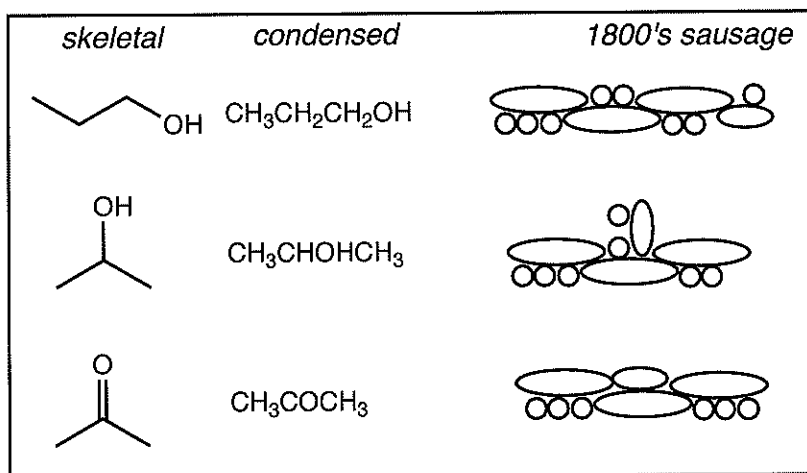
# Chapter 18: Aromatic Compounds

[Sections: 18.1, 18.3-18.5, 18.8]

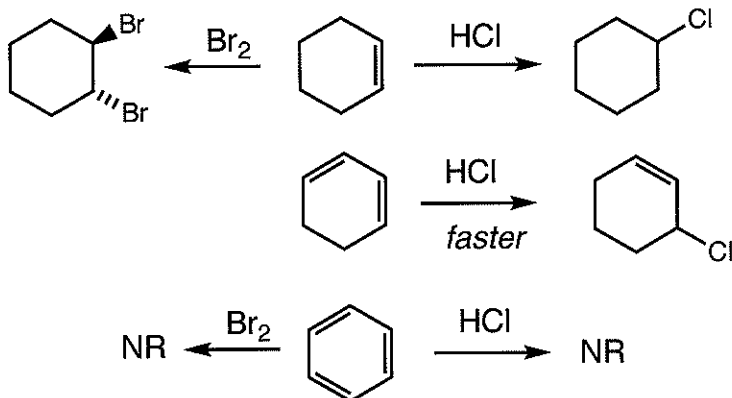
## The Structure of Benzene



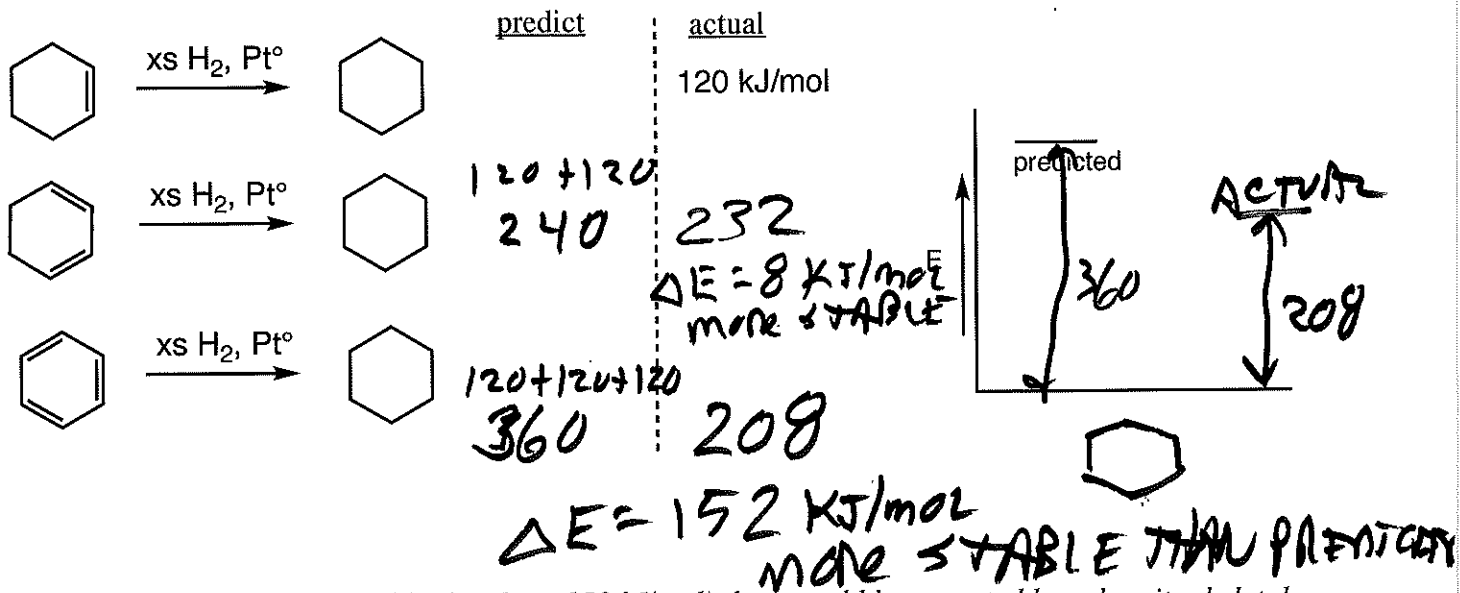
Friedrich August Kekule  
1829-1896



## Some Curious Things About Benzene

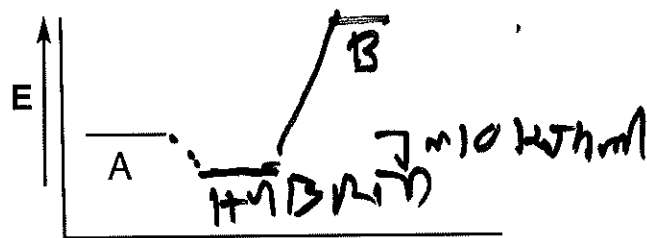
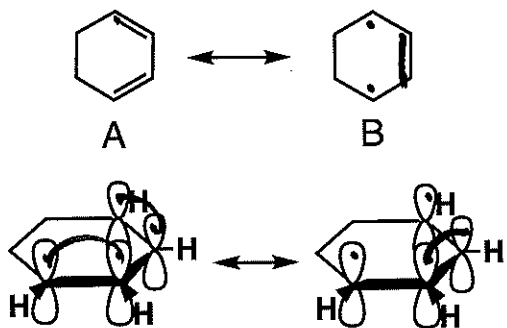


- the reactivity of benzene is **MUCH** less than what would be expected based on its skeletal structure alone
- it does **NOT** engage in the same type of reactions expected of alkenes



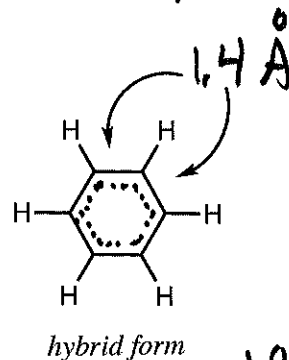
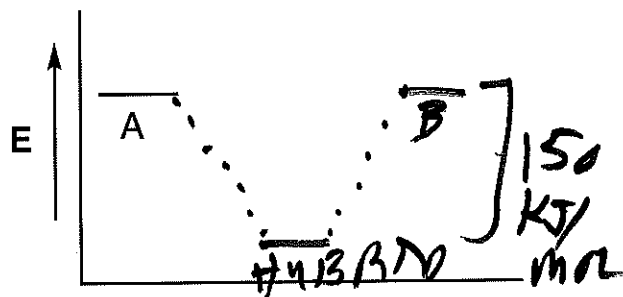
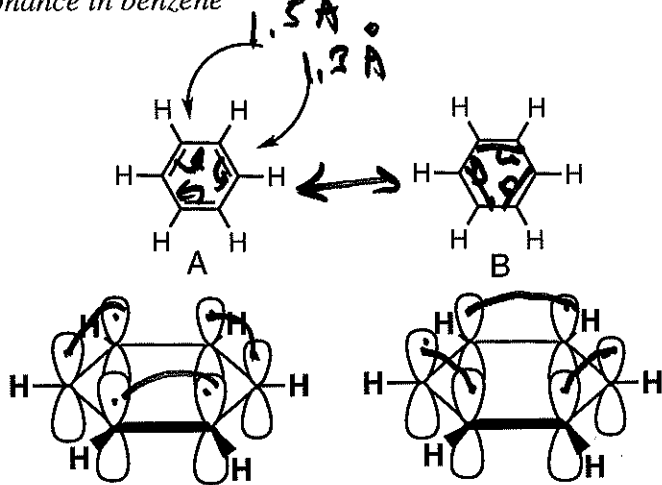
• benzene is MUCH more stable (by about 150 kJ/mol) than would be expected based on its skeletal structure alone!

flashback to dienes



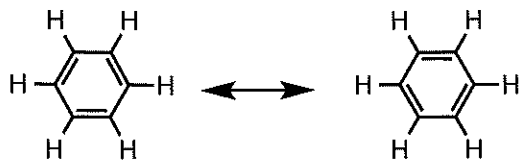
- small amount of stabilization by conjugation
- still behaves essentially like an alkene

resonance in benzene

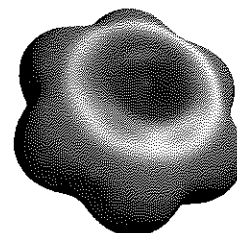
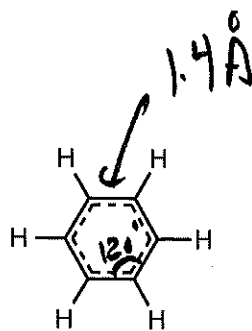


- individual resonance forms (kekule forms) suggest "alternating" bond lengths for the structure
- the hybrid form correctly predicts "non-alternating" bond lengths
- does NOT behave like an alkene!!

$\text{\AA} = \text{ANGSTROM} = 10^{-10} \text{ m}$



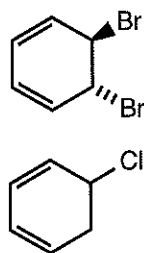
"KEKULE" FORMS



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

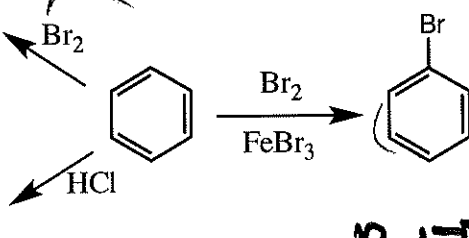
- the surprising stability of benzene comes from the strong stabilization of the hybrid form by the equal contribution of two excellent resonance forms of equivalent energy
- the two contributing resonance forms (kekule forms) allow the electrons in the benzene pi system to be completely delocalized 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<sup>2</sup> 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°) are equivalent

ADDITION



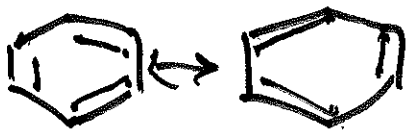
LOSE AROMATICITY!

SUBSTITUTION



RETAIN AROMATICITY

- 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  $sp^2$  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
	✓	NON-ALT	SUBSTITUTION
<p>← SATURATED <math>sp^3</math> CARBON INTERRUPTS RING + P-ORBITALS</p> <p> <math>\square \xrightarrow{Br_2} \square_{1,1}Br</math>  <math>\square \xrightarrow{H_2, Pt^0} \square + 130 \text{ kJ/mol}</math>  <math>\square \xrightarrow{H_2, Pt^0} \square</math> predict = <math>130 + 130 = 260</math>                      actual = 368  <math>\Delta E = 108 = \underline{\underline{LE}}</math> stable than predicted!                 </p>	X	ALT.	ADDITION
<p> <math>\square \xrightarrow{Br_2} \square_{1,1}Br</math>  <math>\square \xrightarrow{H_2, Pt^0} \square + 100 \text{ kJ/mol}</math>  <math>\square \xrightarrow{H_2, Pt^0} \square</math> predict = 400                      actual = 410  <math>\Delta E = 10 \text{ kJ/mol}</math> </p>	X	ALT.	ADDITION
<p> <math>\square \xrightarrow{H_2, Pt^0} \square + 120 \text{ kJ/mol}</math>  <math>\square \xrightarrow{H_2, Pt^0} \square</math> predict = 600                      actual = 510  <math>\Delta E = 90 = \text{more}</math> stable than predicted!                 </p>	✓	NON-ALT	SUBSTITUTION

ANTI-AROMATIC

NOT AROMATIC  
NOT ANTI-AROMATIC  
ART.

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

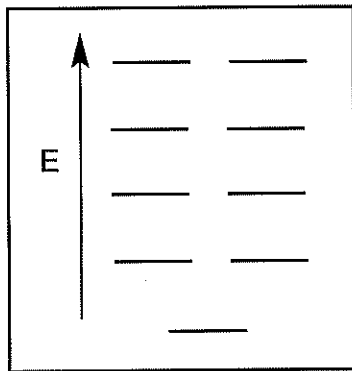
Flashback to atomic orbital electron configurations:

Fluorine AN = 9  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$   
 Neon AN = 10  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

**UNPAIRED e<sup>-</sup>!**

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

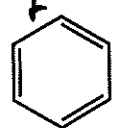
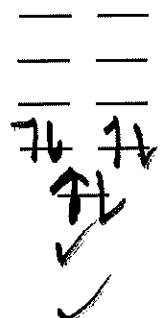
- all molecules have a set of molecular orbitals that are filled in the same manner as atomic orbitals
- for systems with pi bonds, the pi molecular orbitals can be viewed separately from the sigma molecular orbitals
- all planar cyclic polyenes have the same approximate distribution of pi molecular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


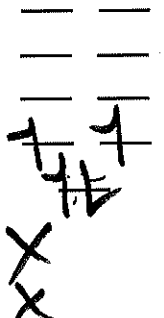


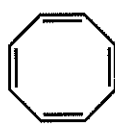
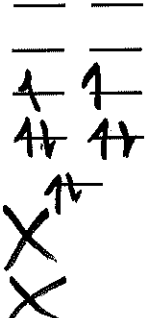
• When a proper number of electrons is contained in the pi system to completely fill all of the occupied molecular orbitals an aromatic system will result (if all other criteria for aromaticity are fulfilled).  
 • This occurs when there is an ODD number of electron pairs in the pi system = Huckel Rule (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

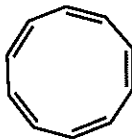
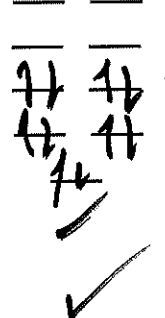


**Erich Huckel**  
1931-1980

6  $\pi e^-$    ✓

4  $\pi e^-$    X


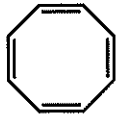
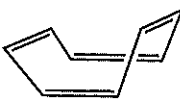
8  $\pi e^-$    X

10  $\pi e^-$    ✓

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

  →  ← NON-AROMATIC

CANNOT AVOID PLANARITY      BOAT      ANTI-AROMATIC!

### 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. DIAMAGNETIC RING CURRENT

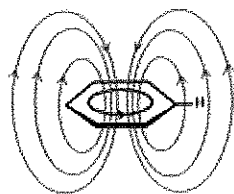
• there are not many cases of anti-aromatic compounds since such cyclic polyenes will adopt a non-planar conformation to avoid anti-aromaticity

### Properties of Anti-Aromatic Compounds

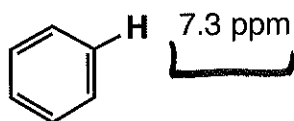
1. Cyclic array of uninterrupted  $SP^2$  hybridized atoms
2. Fully planar structure
3. Very low stability beyond what simple Lewis Dot structures would predict
4. Undergo typical alkene addition reactions (in order to LOSE anti-aromaticity)
5. Alternating carbon-carbon bond lengths
6. EVEN number of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

### 7. PARAMAGNETIC RING CURRENT

### NMR Effects

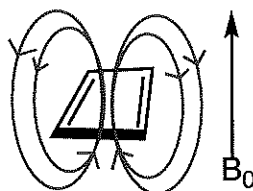


• circulation of the pi electrons in an aromatic system create a magnetic field that increases the effect of the external magnetic field and pushes resonance to higher PPM (i.e., deshields the protons)  
• this is a diamagnetic ring current effect

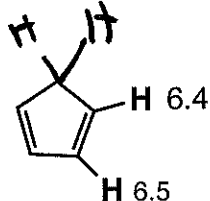


aromatic protons show up at higher PPM than typical alkene protons (deshielded)

6.5 - 8.5

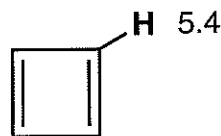


• circulation of the ~~ANTI-~~ pi electrons in an aromatic system create a magnetic field that decreases the effect of the external magnetic field and pushes resonance to lower PPM (i.e., shields the protons)  
• this is a paramagnetic ring current effect

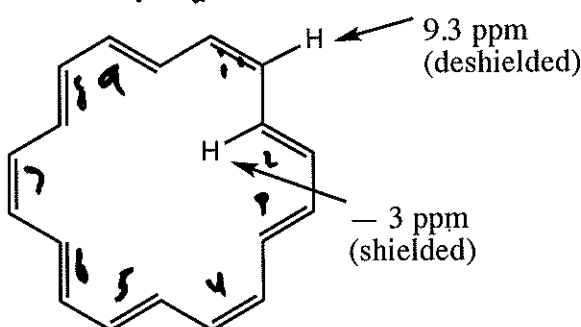


non-aromatic cyclic compounds have typical alkene proton chemical shifts

4.5 - 6.5



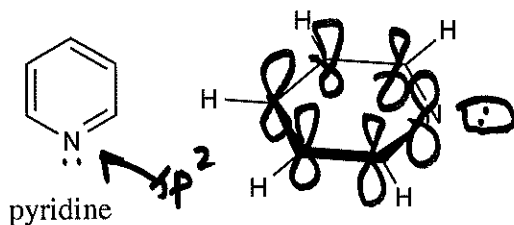
anti-aromatic protons show up at lower PPM than typical alkene protons (shielded)



18  $\pi e^-$   
 $4n+2$   
 $n=4$

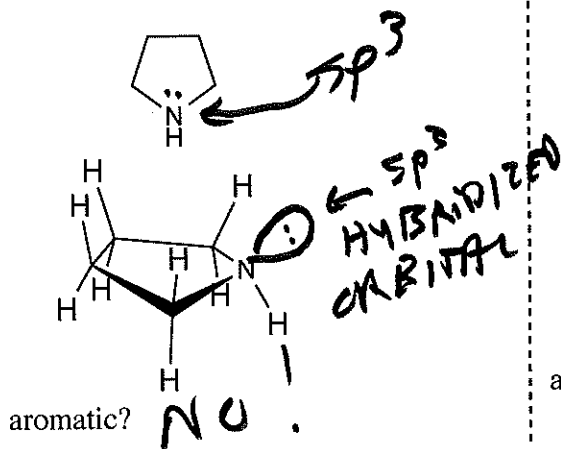
## Aromatic Heterocycles

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

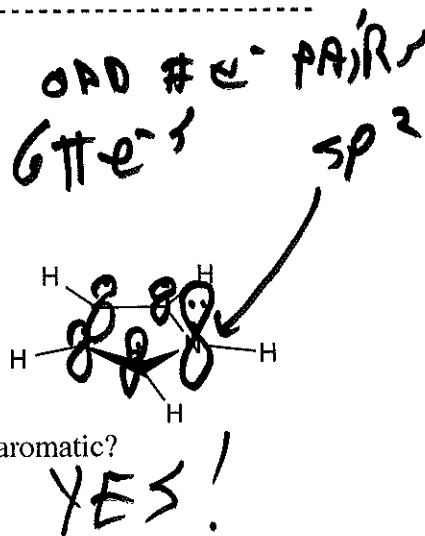
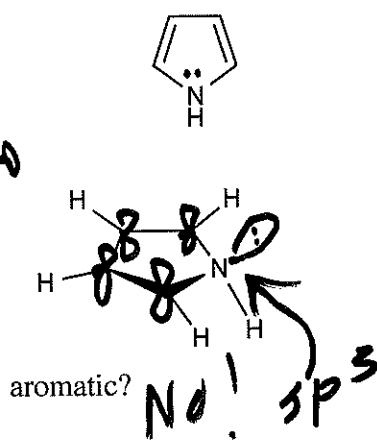


- pyridine is essentially a benzene ring in which one of the carbons has been replaced by a nitrogen atom
- the pi system of pyridine is equivalent to that of benzene and contains a Huckel number (6) of pi electrons
- the lone pair on the nitrogen is orthogonal to the pi system and cannot contribute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

typical cyclic amine

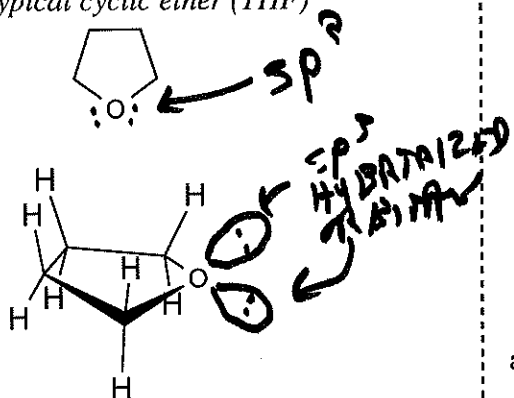


pyrrole

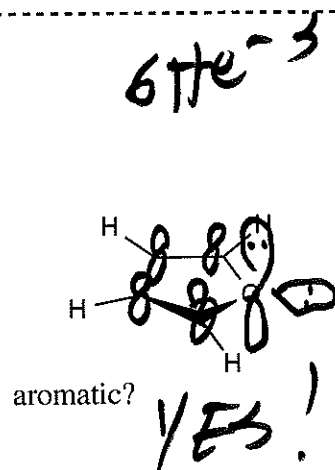
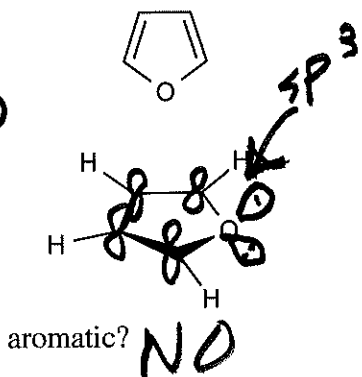


- a typical nitrogen atom with a lone pair of electrons will adopt  $SP^3$  hybridization (tetrahedral shape)
- pyrrole could NOT be aromatic if the nitrogen atom were  $SP^3$  hybridized
- additionally, pyrrole has two  $C=C$  bonds which contribute only 4 pi electrons
- by adopting  $SP^2$  hybridization at the nitrogen atom, pyrrole attains a cyclic array of  $SP^2$  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



- a typical oxygen atom with two lone pairs of electrons will adopt  $SP^3$  hybridization
- furan could NOT be aromatic if the oxygen atom were  $SP^3$  hybridized
- additionally, furan has two  $C=C$  bonds which contribute only 4 pi electrons
- by adopting  $SP^2$  hybridization at the oxygen atom, furan attains a cyclic array of  $SP^2$  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

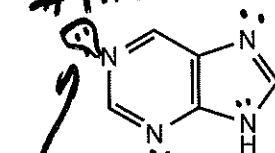
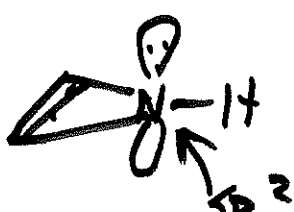
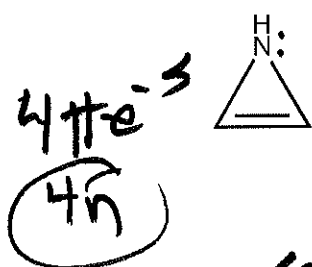
## How can I tell if a heteroatom will donate its lone pair to a pi system?



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

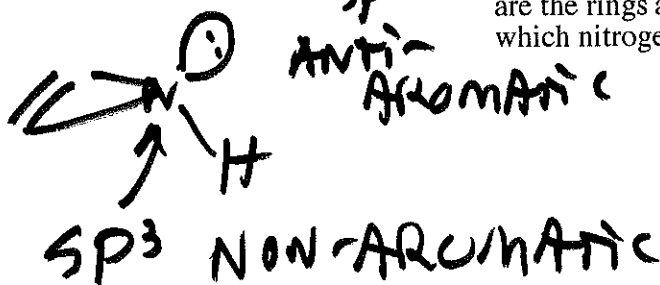
2 PAIRS  $sp^2$  = EVEN # PAIRS



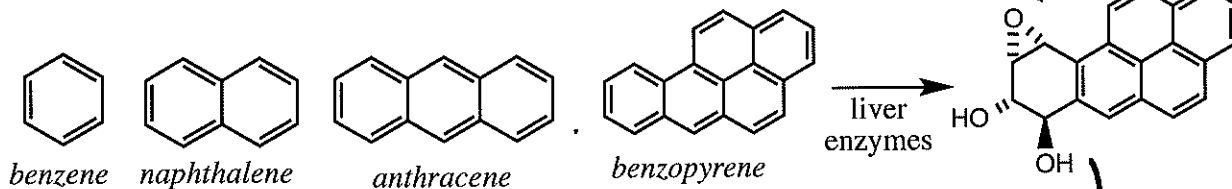
purine  
critical component  
of nucleic acids

CANNOT BE PART of  $\pi$ -SYSTEM

are the rings aromatic?  
which nitrogens contribute lone pairs?



## Fused Benzenes



EPOXIDE

DNA  
CANCER





## 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  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

$Li^+$  AN = 3, # electrons = 2  $1s^2$

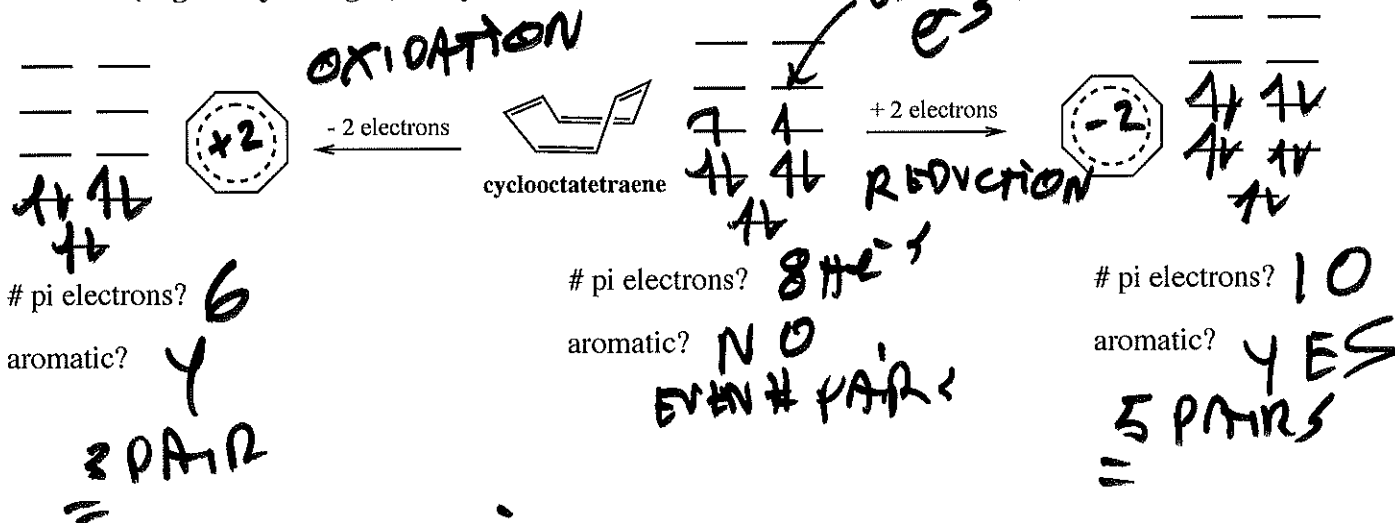
Fluoride,  $F^-$  AN = 9, # electrons = 10  $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

**CATION**

**ANION**

- 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

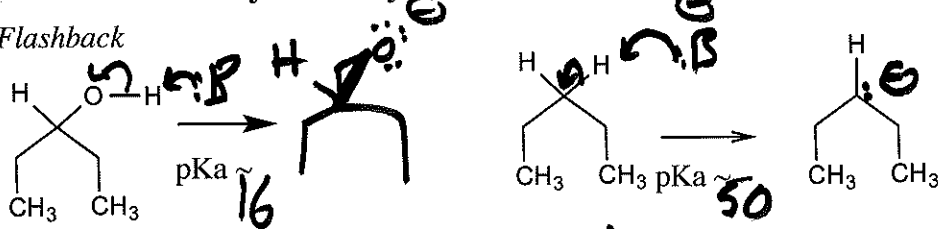
### Anionic (negatively charged) Pi Systems



## ALKOXIDES

### Effect of aromaticity on acidity

Flashback



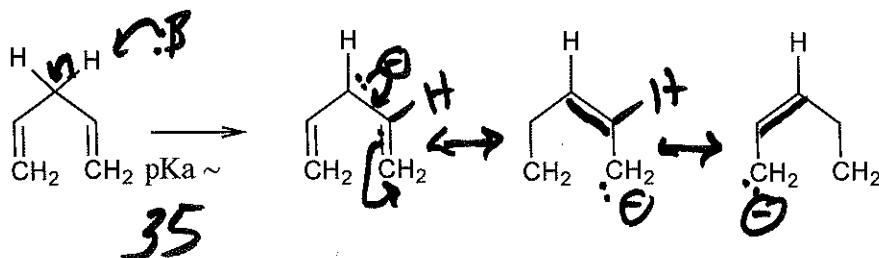
$\Delta pK_a = 50 - 16 = 34$

$10^{34}$  X MORE ACIDIC

- 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

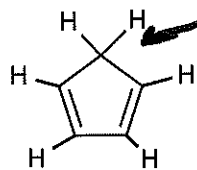




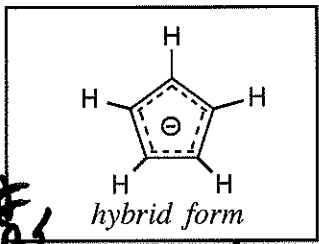
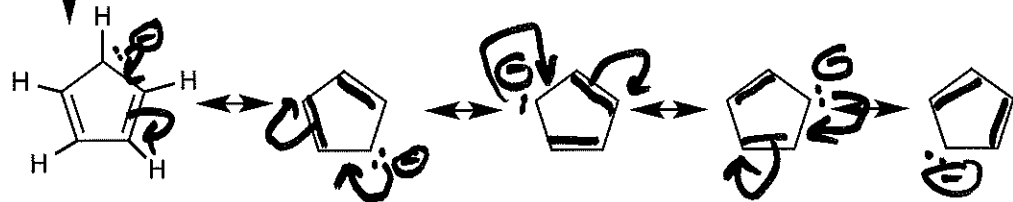
35

$\Delta pK_a = 35 - 10 = 25$   
 $10^{25}$  X MORE ACIDIC

acidity of cyclopentadiene



aromatic? NO  
 pKa ~ 10

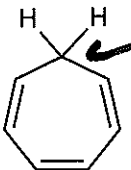


- cyclopentadiene is unusually acidic for a C-H bond!
- remember: acidic compounds have stabilized conjugate bases!
- its acidity can be traced to the strong stabilization of the resulting negative charge because the resulting pi system has an aromatic number of pi electrons (6 pi electrons)!
- thus, 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

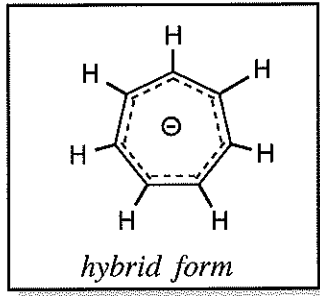
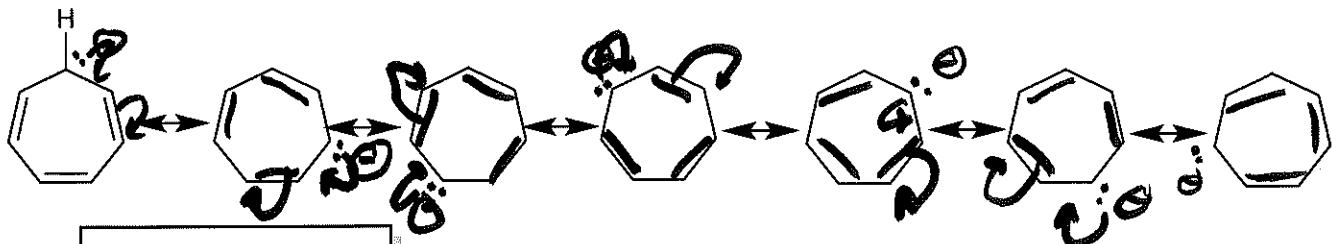
0 PAIR

# pi electrons? 6  
 aromatic? YES

acidity of cycloheptatriene



aromatic? NO  
 pKa ~ 40

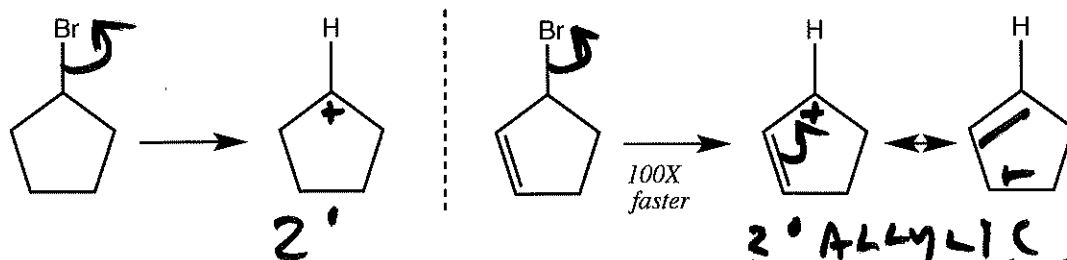


- resonance considerations alone suggest it should be very easy to deprotonate cycloheptatriene since the negative charge is highly delocalized,
- unlike cyclopentadiene, however, cycloheptatriene is NOT unusually acidic
- addition of two electrons to the pi system yields 8 pi electrons, which is NOT 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

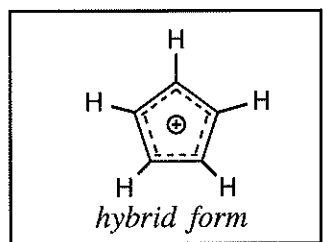
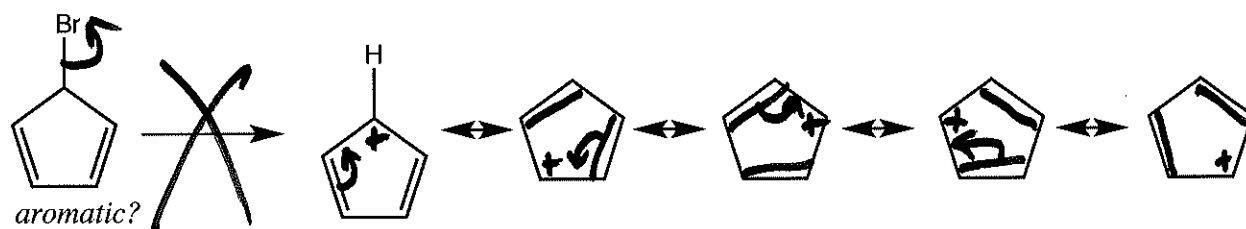
# pi electrons? 8  
 aromatic? NO

EV EV # PAIR

## Cationic (positively charged) Pi Systems



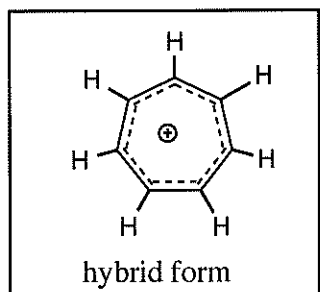
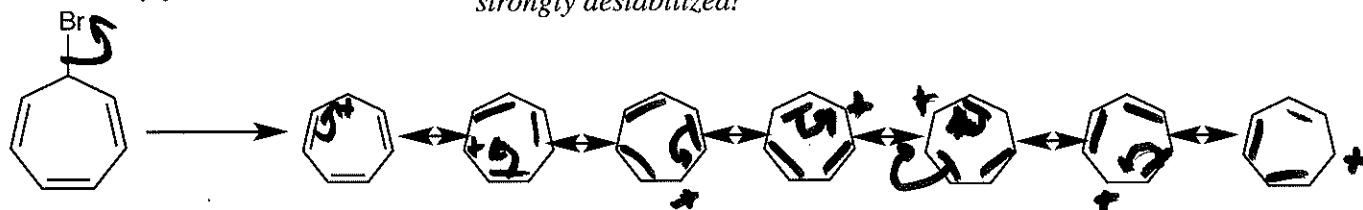
• resonance stabilization of the allylic carbocation results in faster reaction since the allylic carbocation is easier to form than the localized 2° carbocation



# pi electrons? 4  
aromatic?

**ANTI-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? 6  
aromatic?

**YES!**  
**6 pi e- = 0 DD # PAIR**

- 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