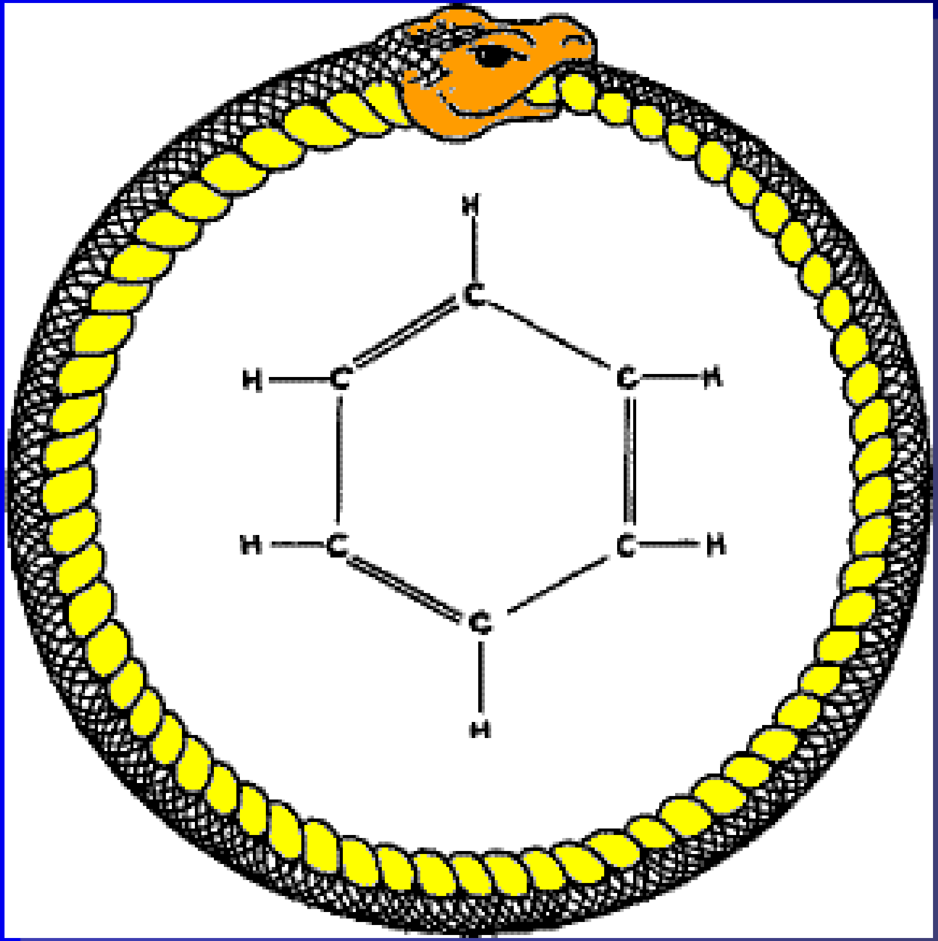
Lecture 9

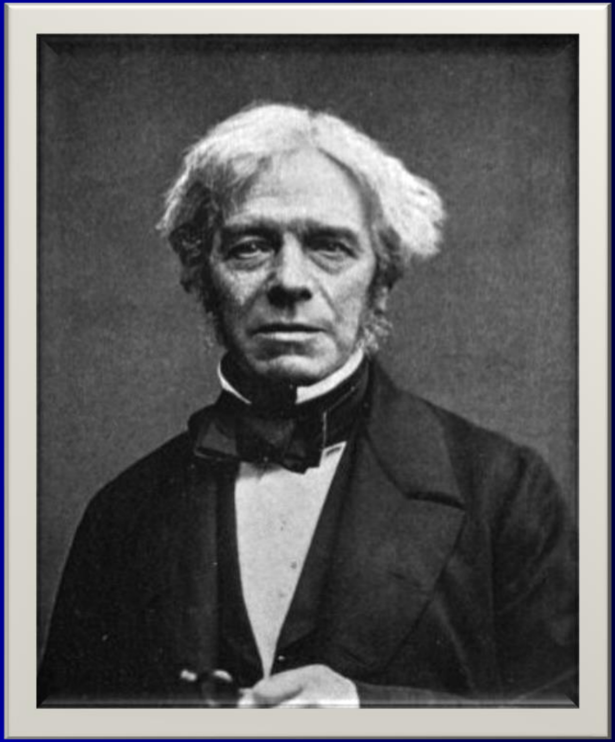
MOs and Benzene



February 19, 2019

Chemistry 328N

Some History



Michael Faraday 1791-1867

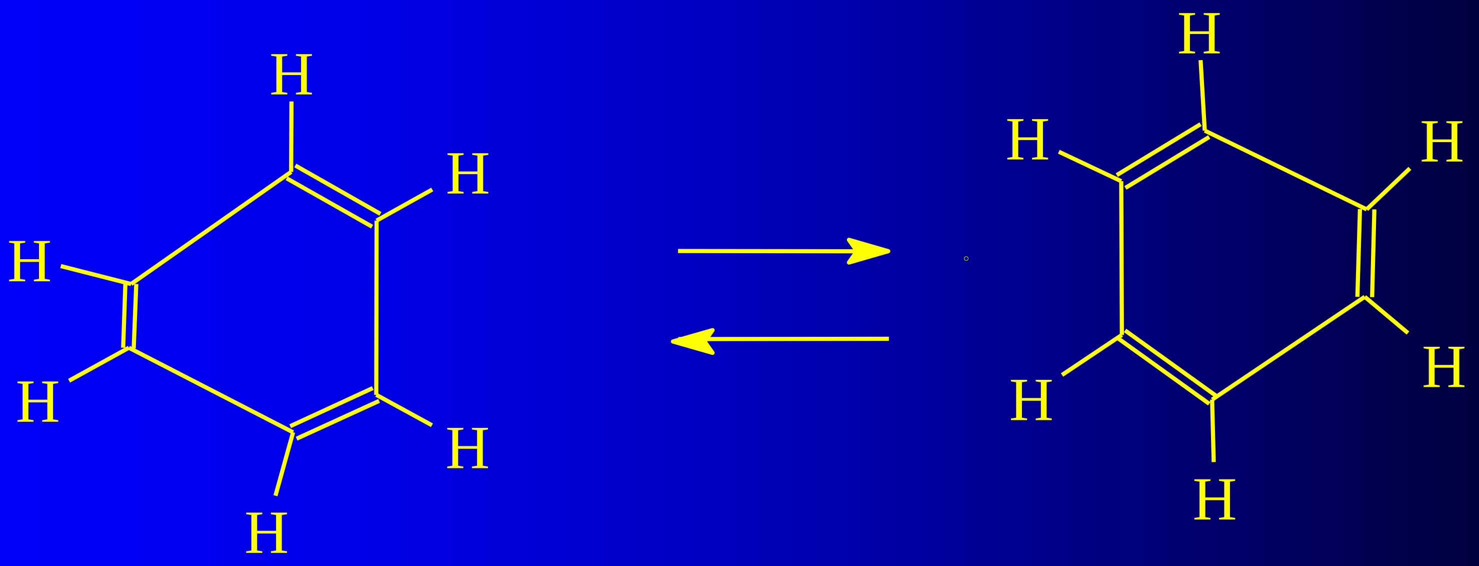
British physicist and chemist, best known for his discoveries of electromagnetic induction and of the laws of electrolysis. He also discovered benzene!

https://www.britannica.com/biography/Michael-Faraday

The Old Lamp Lighter

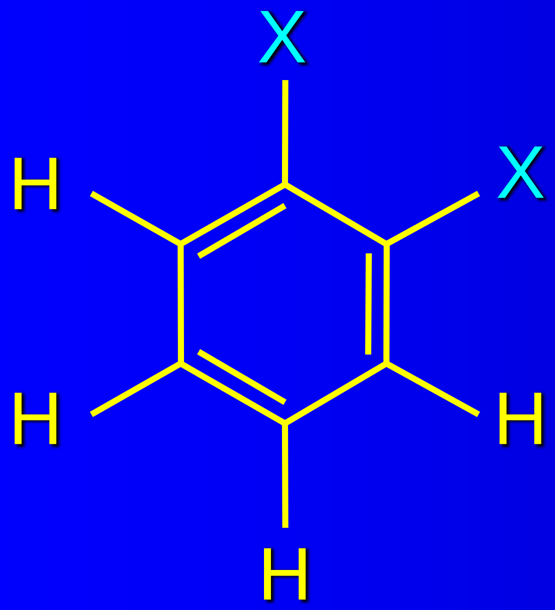
Benzene – per Kekulé

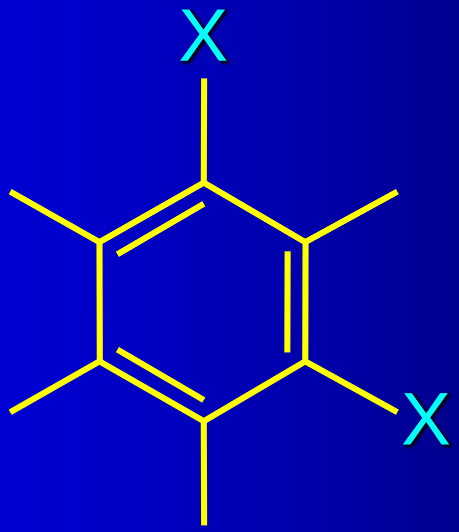
- August Kekulé proposed a structure for benzene in 1872

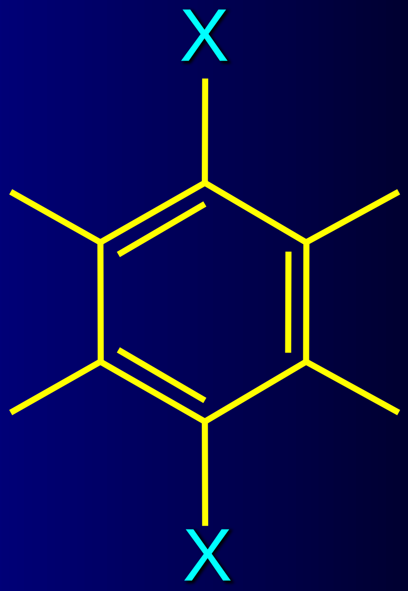


- This structure, however, did not really account for the unusual chemical reactivity of benzene

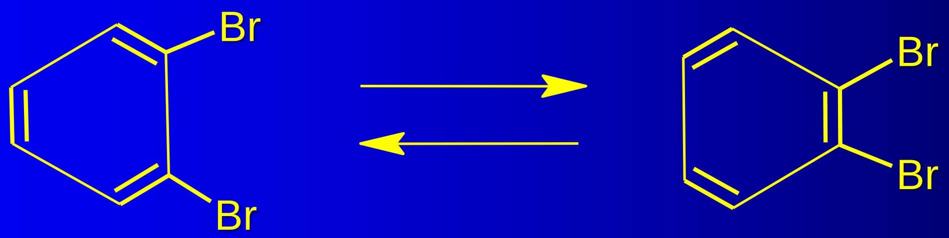
Kekule explains why there are only 3 isomers of dibromobenzene



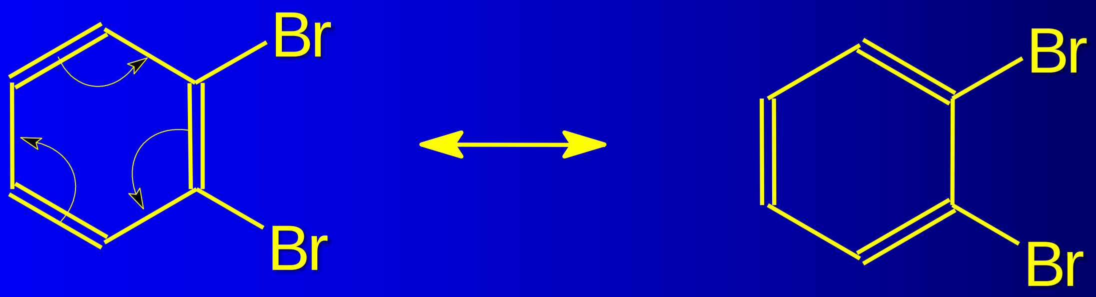




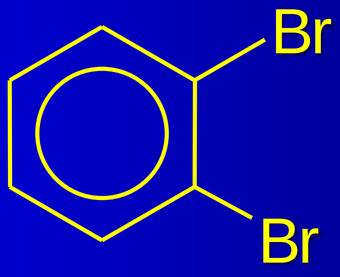
- Kekule’s proposal is an **<u>equilibrium</u>** between two structures



•Pauling’s <u>Resonance Theory</u> describes resonance structures generated by electron movement (only!) that are not real, they are constructs the weighted sum of which describes the real molecule, which is presented as the resonance hybrid

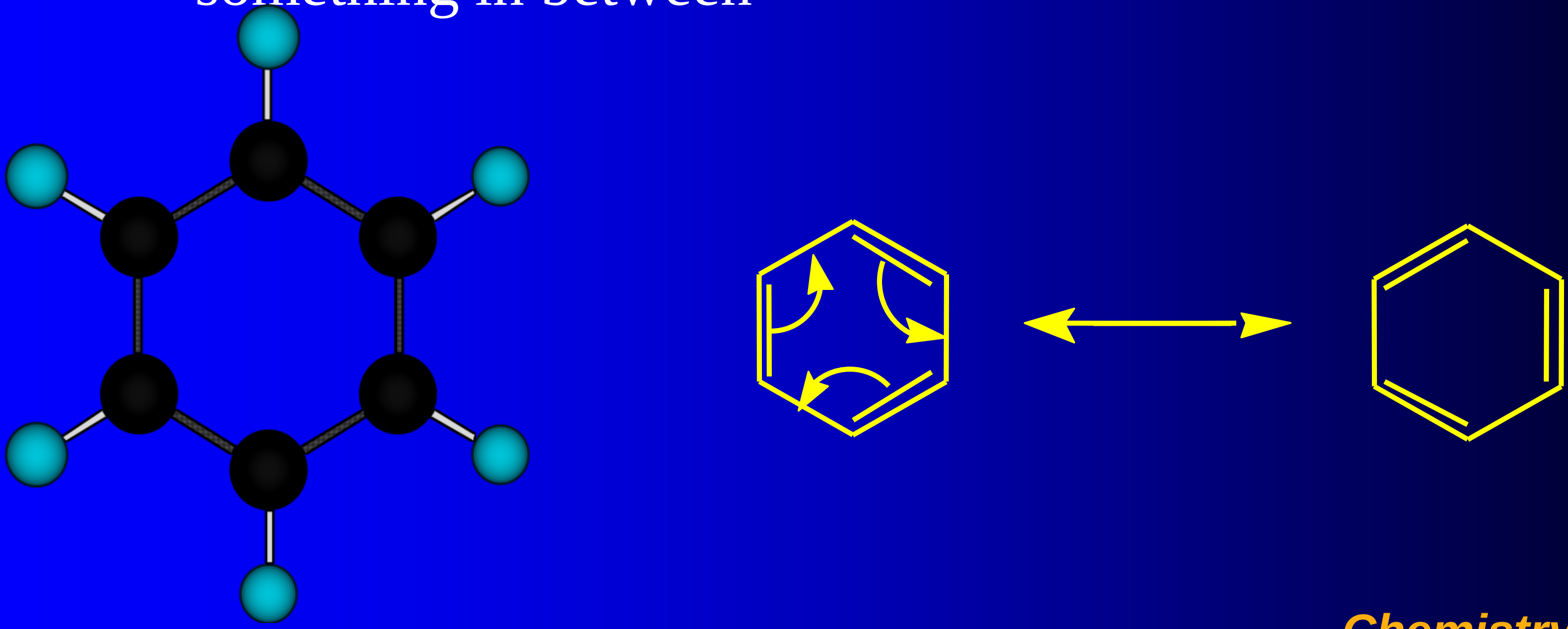


“Resonance hybrid”

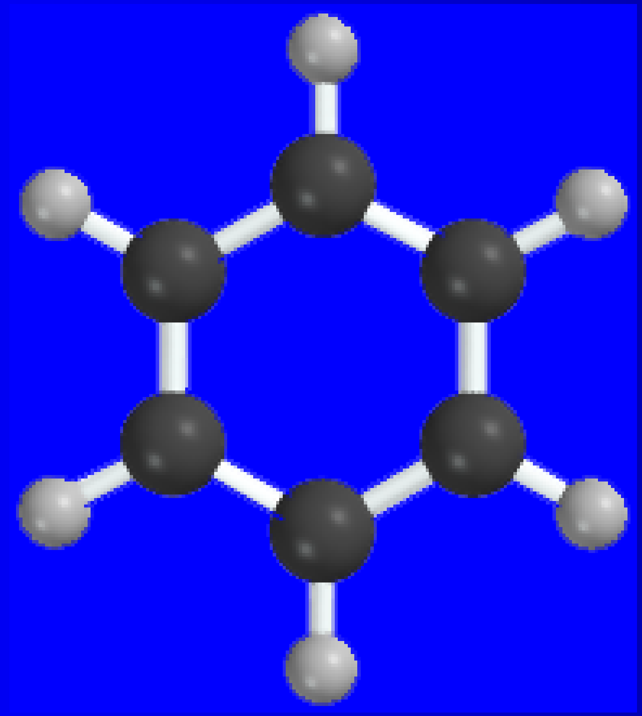


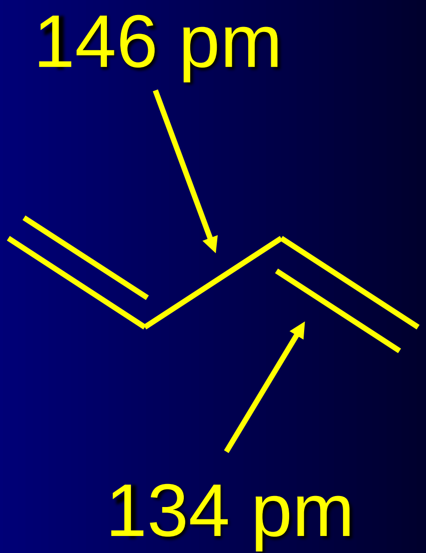
Benzene - Resonance

- We can represent benzene as the hybrid of two equivalent Kekulé structures
  - each makes an equal contribution to the hybrid, and thus the C-C bonds are neither double nor single, but something in between



All C—C bond distances = 140 pm (1.4 Å)





140 pm is the average between the C - C single bond length and the C=C double bond length in 1,3-butadiene.

Unusual Stability of Benzene

Benzene is the best and most familiar example of a substance that possesses "special stability" or "aromaticity"

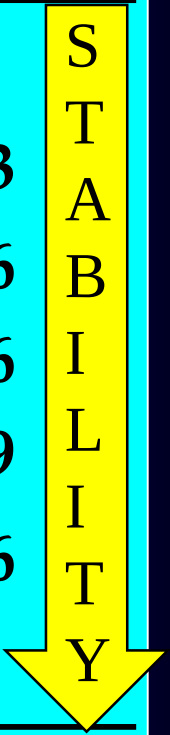
Aromatic molecules have stability that is substantially greater for a molecule than would be expected on the basis of any of the Lewis structures written for it

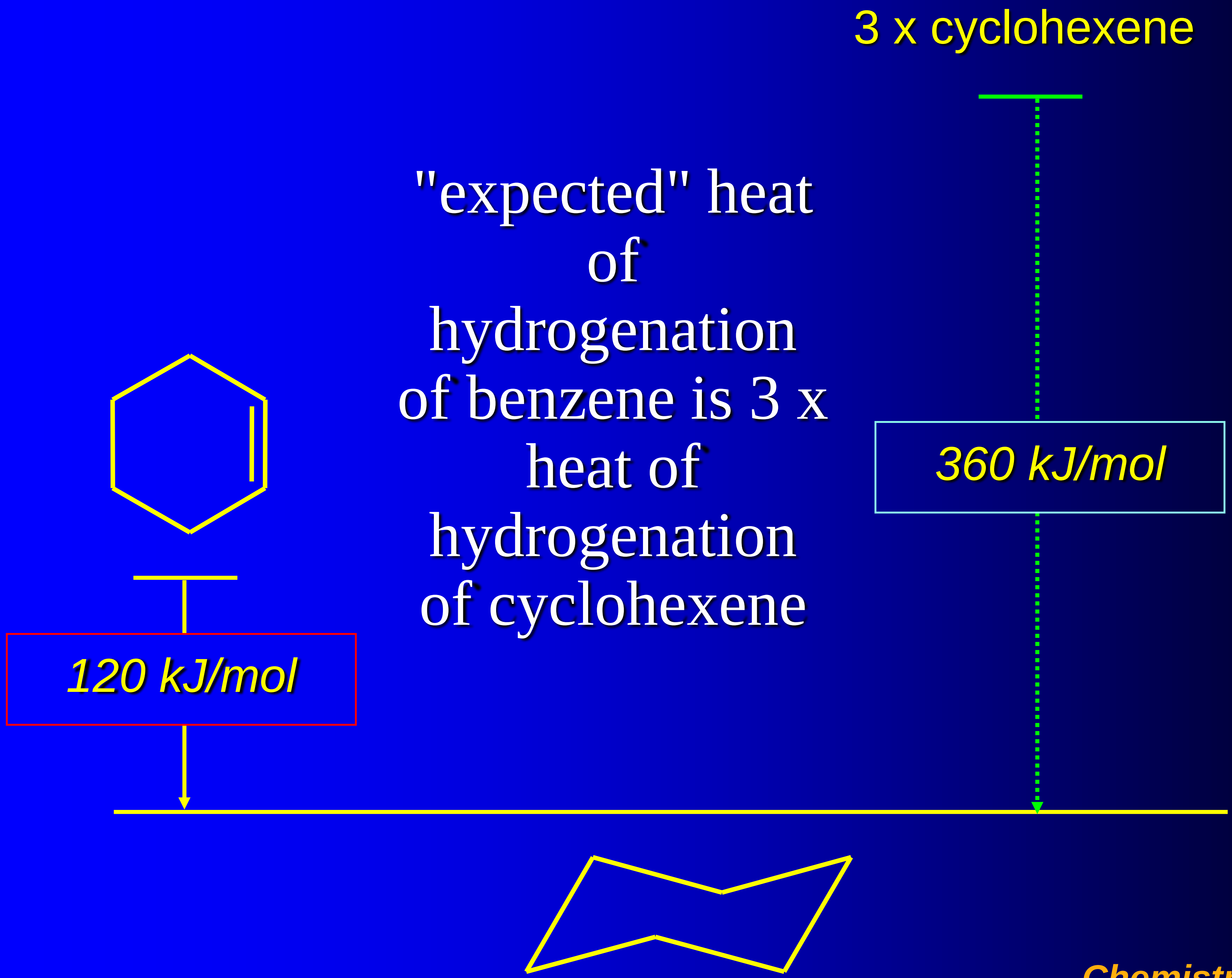
Benzene - Resonance

- Resonance energy: the difference in energy between a resonance hybrid and the most stable of its hypothetical contributing structures in which electrons are localized on particular atoms and in particular bonds
- One way to estimate the resonance energy of benzene is to compare the heats of hydrogenation of benzene and cyclohexene.
- This theory provides an explanation for the reactivity of benzene

ΔH° of Hydrogenation

Name	Structural Formula	ΔH° (kcal/mol)
1-butene	$CH_3CH_2CH{=}CH_2$	-30.3
cis-2-butene	$CH_3CH{=}CHCH_3$	-28.6
trans-2-butene	$CH_3CH{=}CHCH_3$	-27.6
2-methyl-2-butene	$(CH_3)_2C{=}CHCH_3$	-26.9
2,3-dimethyl-2-butene	$(CH_3)_2C{=}C(CH_3)_2$	-26.6



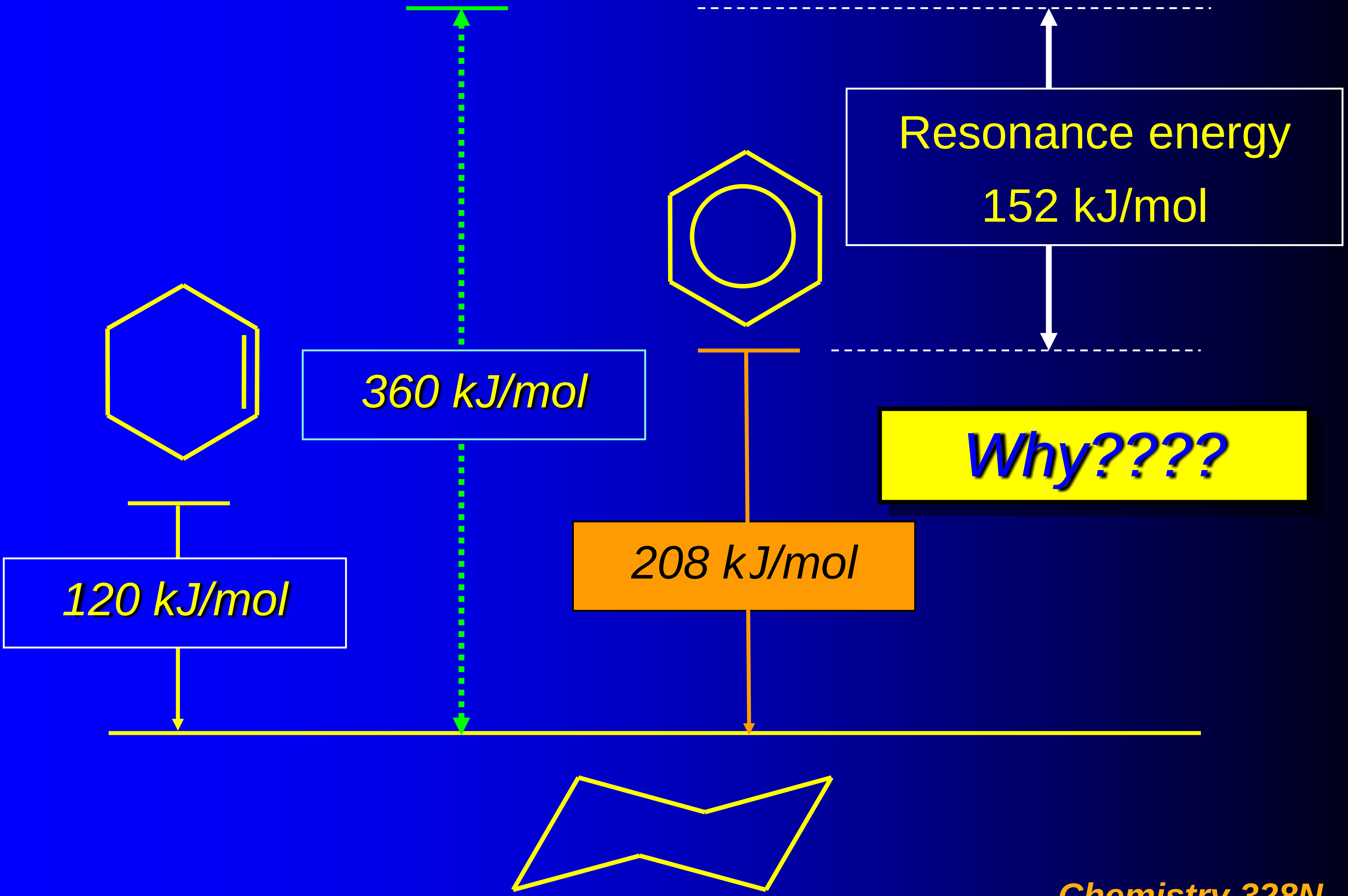


3 x cyclohexene

"expected" heat of hydrogenation of benzene is 3 x heat of hydrogenation of cyclohexene

360 kJ/mol

120 kJ/mol



3 x cyclohexene

Resonance energy

152 kJ/mol

360 kJ/mol

120 kJ/mol

208 kJ/mol

Why????

The answer comes from MO Theory

1. But … s
   conf

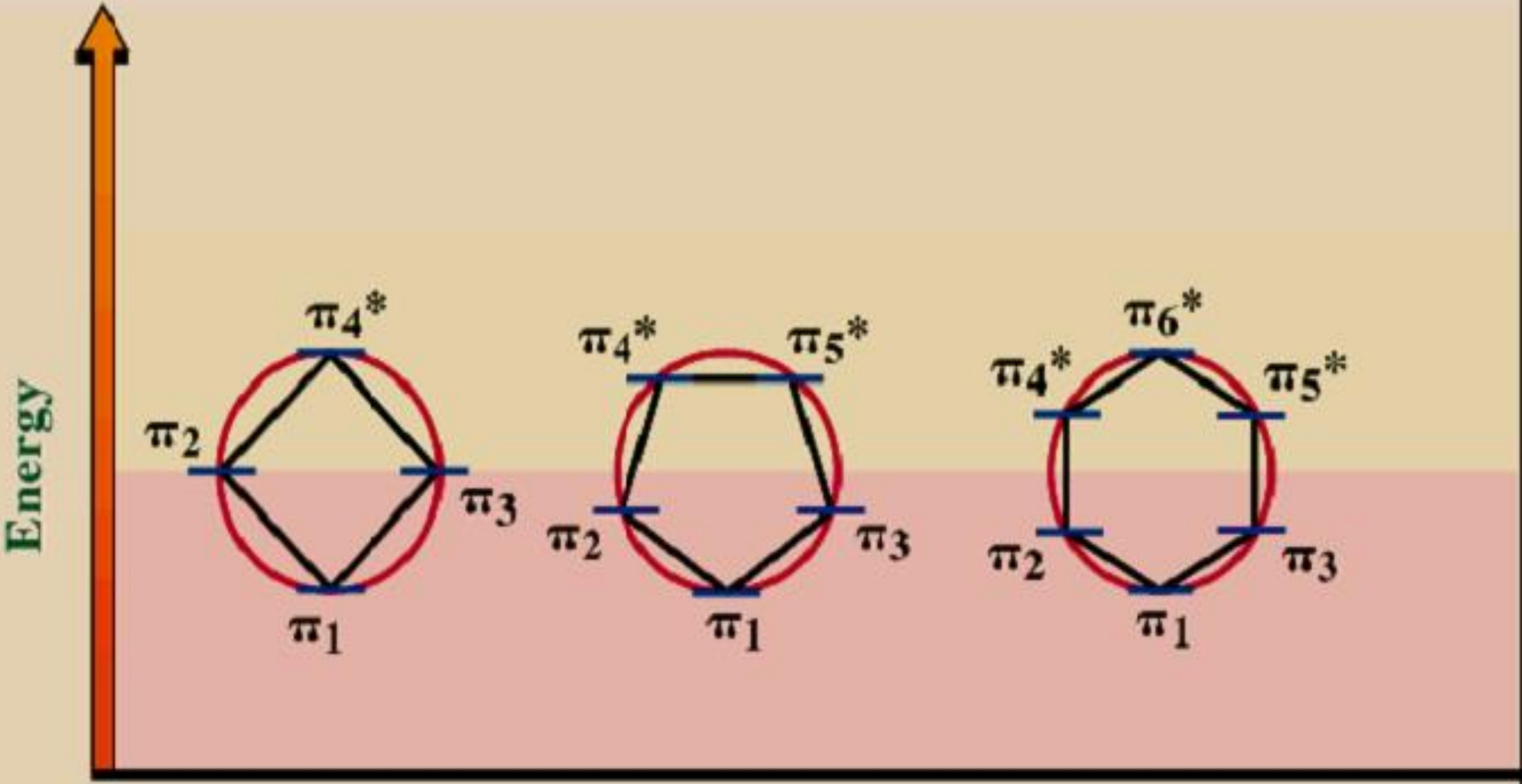
2. How … ow many
   MO

3. How … ative
   energie

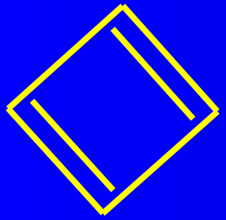
For Cyclic Structures
Frost Circles…a Great Trick

- Inscribe a polygon of the same number of sides as the ring to be examined such that <u>one of the vertices is at the bottom of the ring</u>
- The relative energies of the MOs in the ring are given by where the vertices touch the circle
- The MOs
  - below the horizontal line through the center of the ring are bonding MOs
  - on the horizontal line are nonbonding MOs
  - above the horizontal line are antibonding MOs

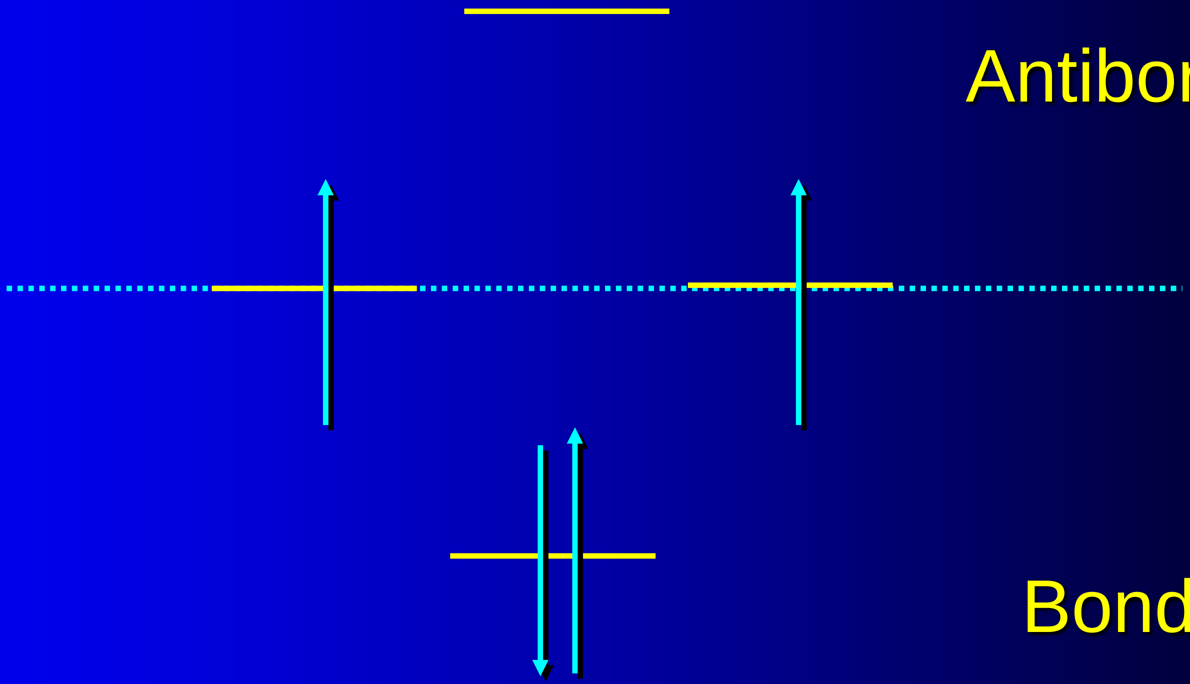
Frost circles for cyclic, fully conjugated 4-,5- and 6-membered rings



π-MOs of Cyclobutadiene (square planar)



Cyclo-
butadiene



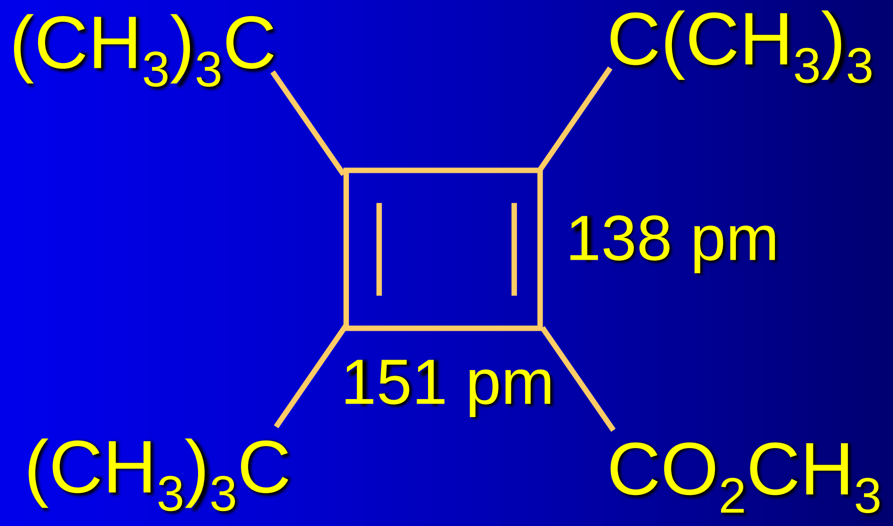
Antibonding

Bonding

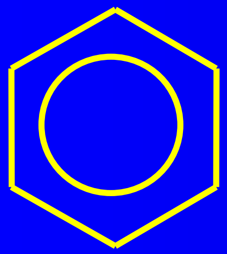
4 π electrons; bonding orbital is filled; other 2 π electrons singly occupy two nonbonding orbitals

Structure of Cyclobutadiene

structure of a stabilized derivative is characterized by alternating short bonds and long bonds



π-MOs of Benzene

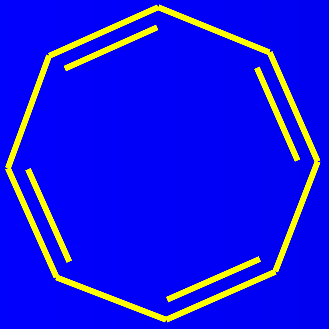


Benzene

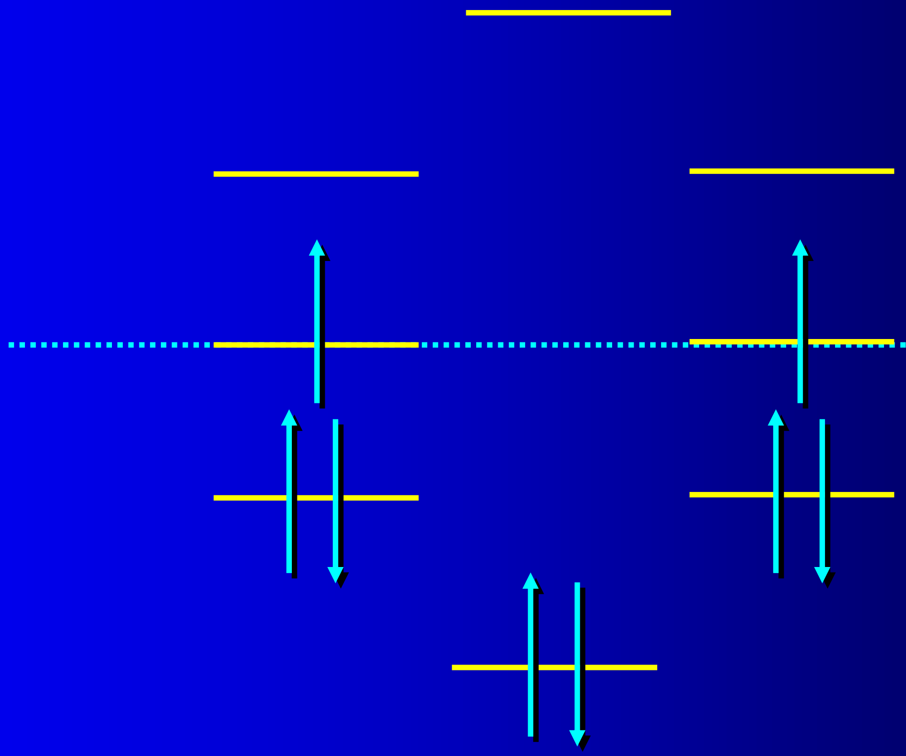
6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

π-MOs of Cyclooctatetraene (square planar)



Cyclo-
octatetraene



Antibonding

Non Bonding

Bonding

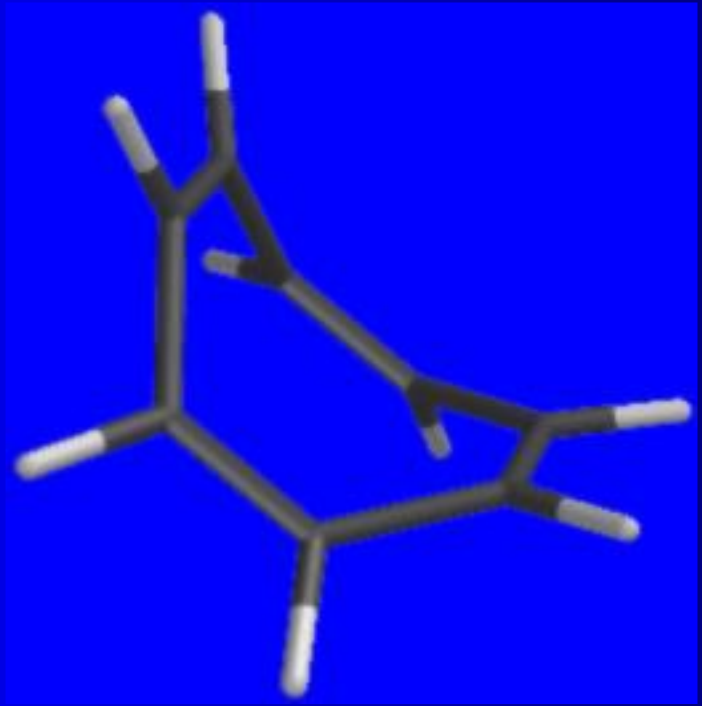
8 π electrons

3 bonding orbitals are filled; 2 nonbonding orbitals are each half-filled

Structure of Cyclooctatetraene

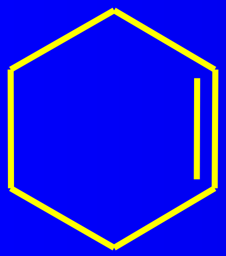
cyclooctatetraene is not planar

has alternating long (146 pm)
and short (133 pm) bonds

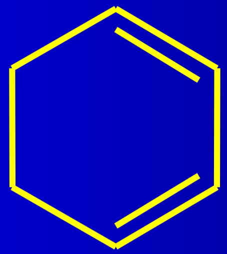


Heats of Hydrogenation

to give cyclohexane (kJ/mol)



120



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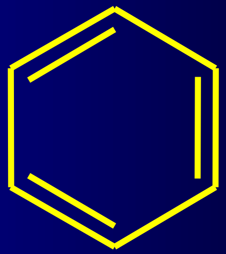
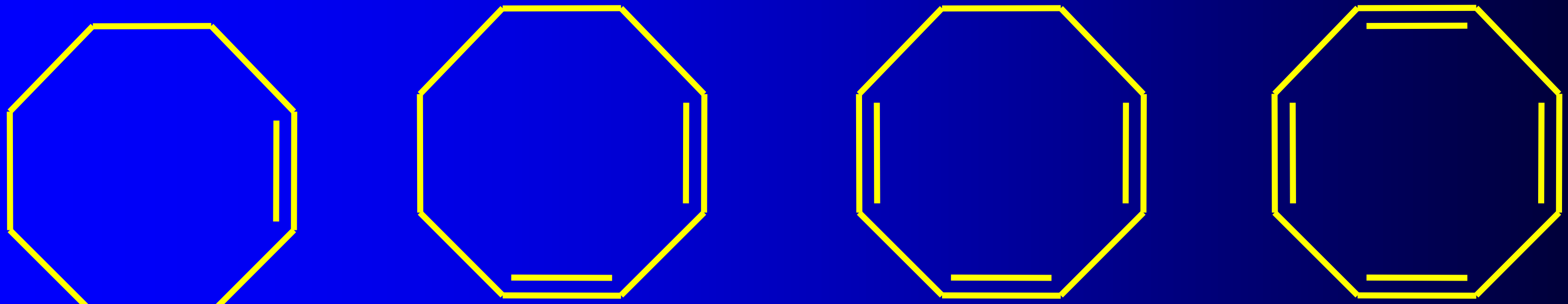


208

heat of hydrogenation of benzene is 152 kJ/mol less than 3 times heat of hydrogenation of cyclohexene

Heats of Hydrogenation

to give cyclooctane (kJ/mol)

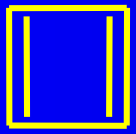


97 205 303 410

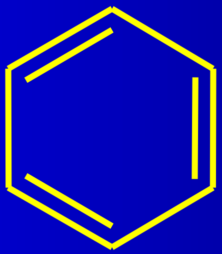
heat of hydrogenation of cyclooctatetraene is more than 4 times the heat of hydrogenation of cyclooctene….no special stability here!

Requirements for Aromaticity

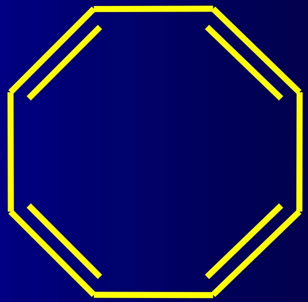
Cyclic conjugation is necessary, *but not sufficient*



not
aromatic



aromatic



not
aromatic

Conclusion

There is still something wrong!!!

There has to be some factor in addition to cyclic conjugation that determines whether a molecule is aromatic or not

Hückel's Rule

The additional factor that influences aromaticity is the *number* of π electrons

Hückel's Ruleb

Among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2\pi$ electrons possess special stability (are aromatic)

Magic Numbers

n	$4n+2$	
0	2	
1	6	benzene!
2	10	
3	14	
4	18	

Hückel's Rule for Aromaticity

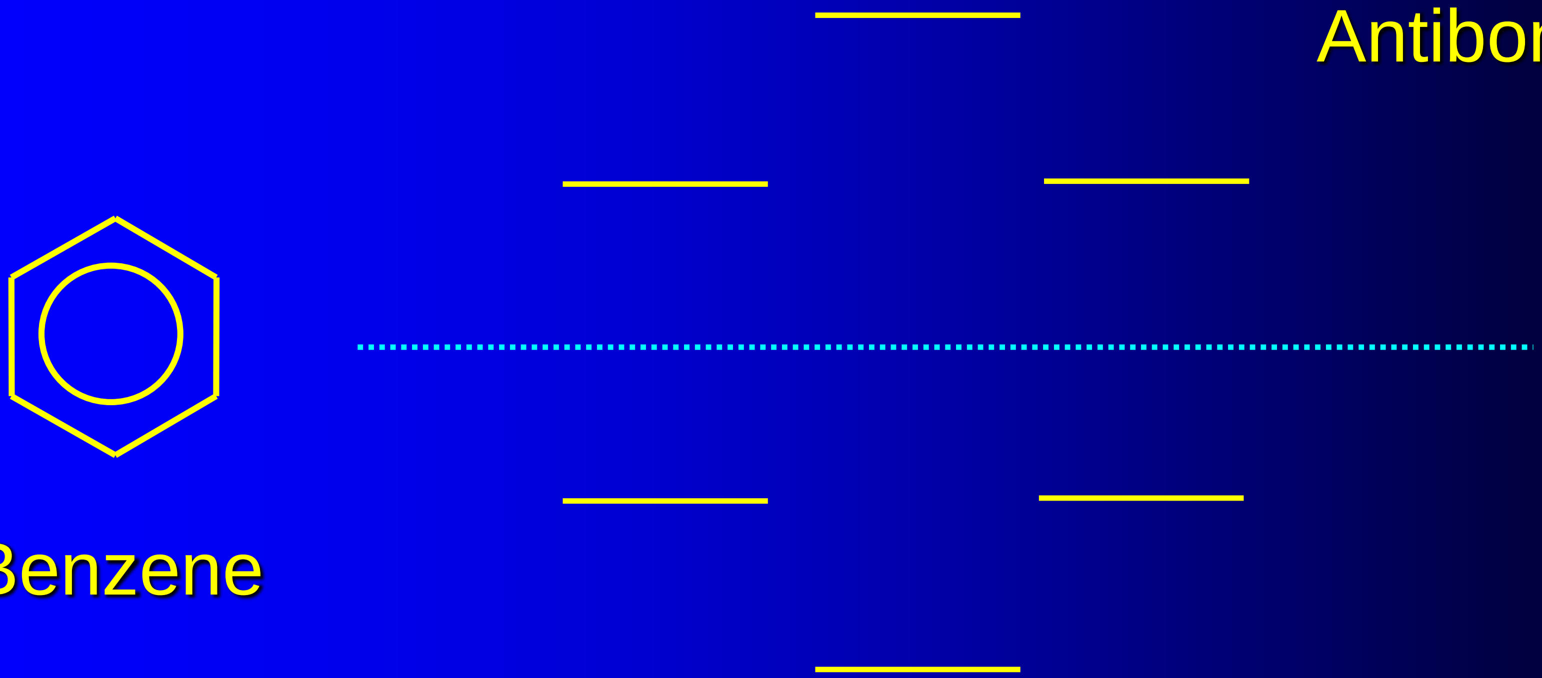
To be Aromatic …a compound must :

1. be Cyclic
2. have one P orbital on each atom in the ring
3. be planar or nearly so to give orbital overlap
4. have a closed loop of 4n+2 pi electrons in the cyclic arrangement of p orbitals

Hückel's Rule

Actually and inadvertently defines a condition for cyclic molecules in which the bonding molecular orbitals are filled and there are no electrons in non-bonding or antibonding orbitals …. roughly analogous to the “rare gas” condition for atomic orbitals…

π-MOs of Benzene



Antibonding

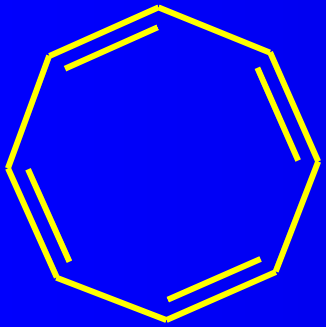
Benzene

Bonding

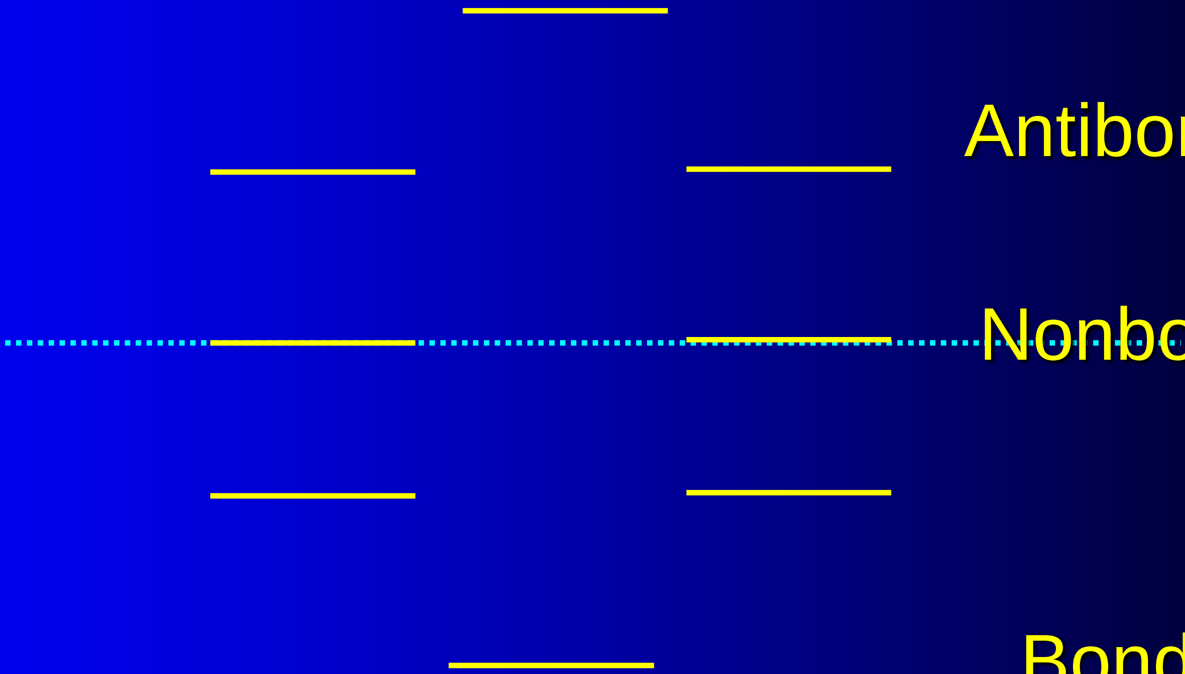
6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

π-MOs of Cyclooctatetraene



Cyclo-octatetraene



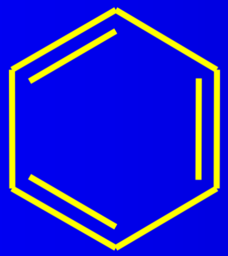
Antibonding

Nonbonding

Bonding

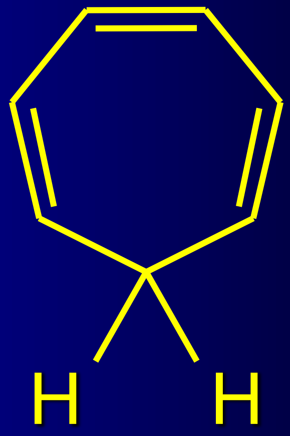
Only Completely Conjugated Polyenes can be Aromatic

6 π electrons;
completely conjugated



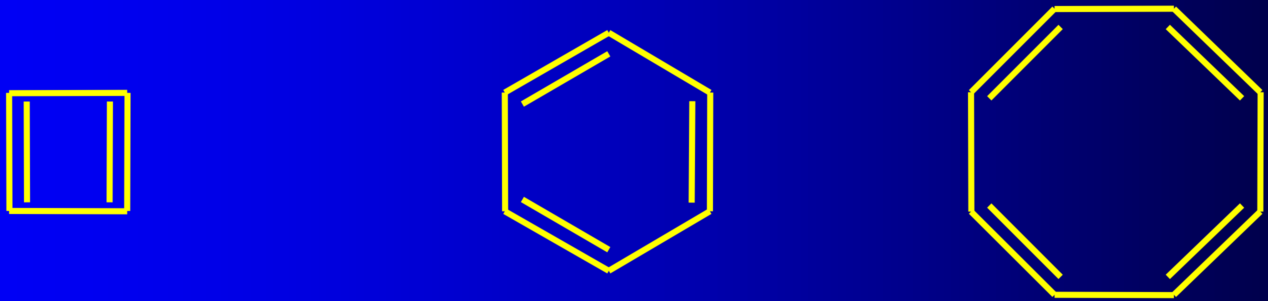
aromatic

6 π electrons;
not completely
conjugated



not
aromatic

π-Electron Requirement for Aromaticity



4 π electrons

not
aromatic

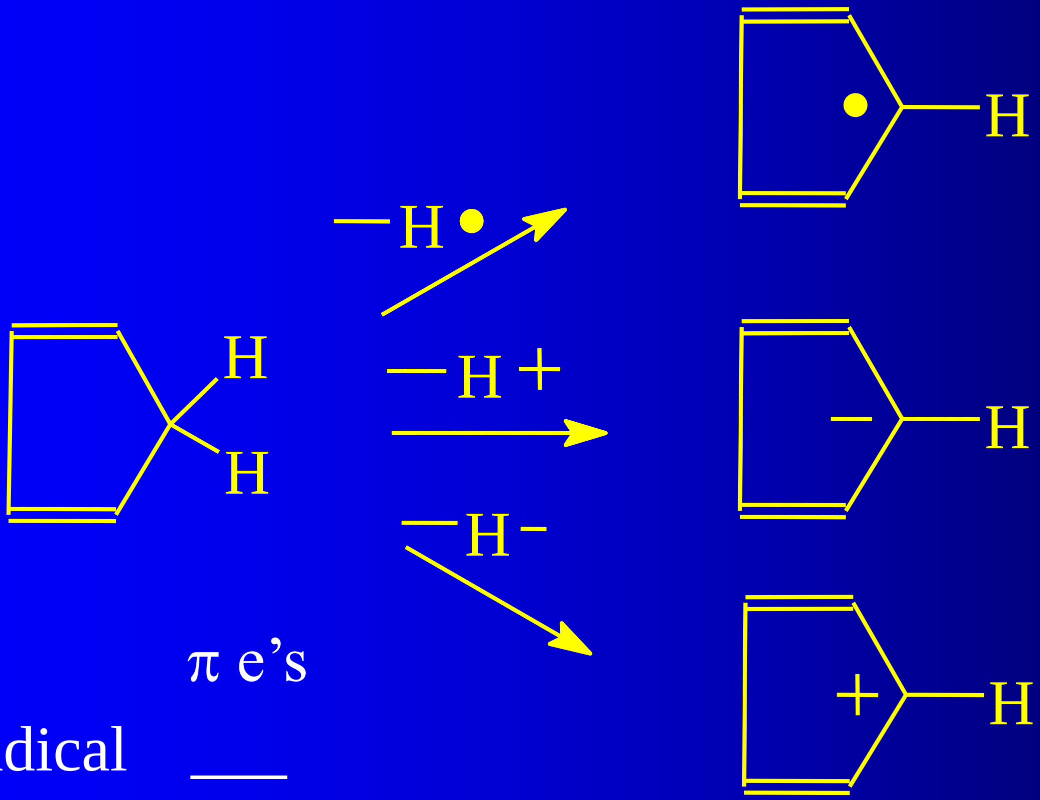
6 π electrons

aromatic

8 π electrons

not
aromatic

Aromatic Ions



Radical

Anion

Cation

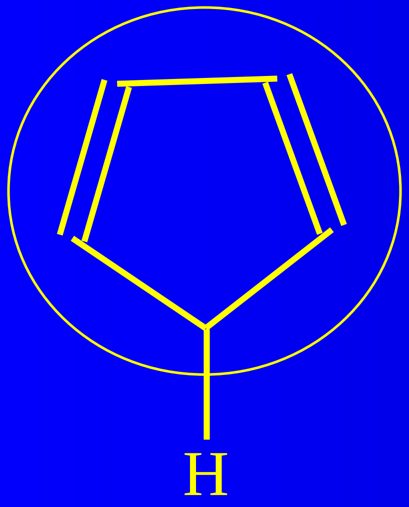
π e's

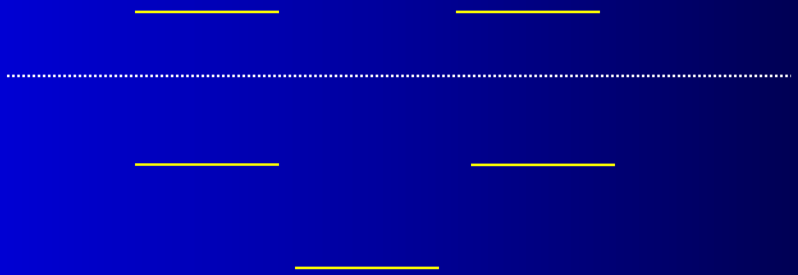
Radical ___

Cation ___

Anion ___

Cyclopentadiene





Let’s fill these for each case, radical, anion and cation

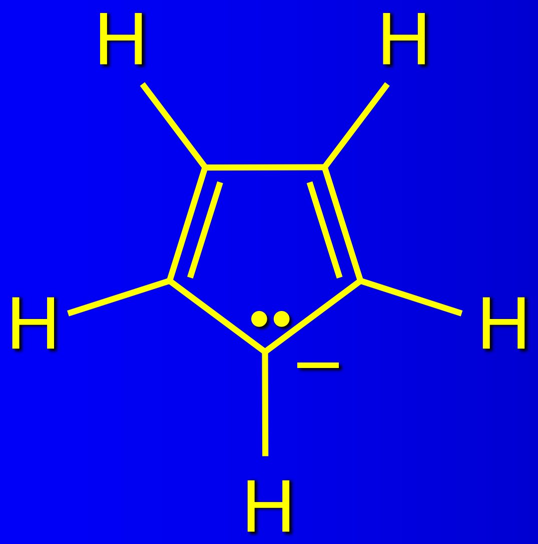
π e’s

Radical ____

Cation ____

Anion ____

Cyclopentadienide Anion

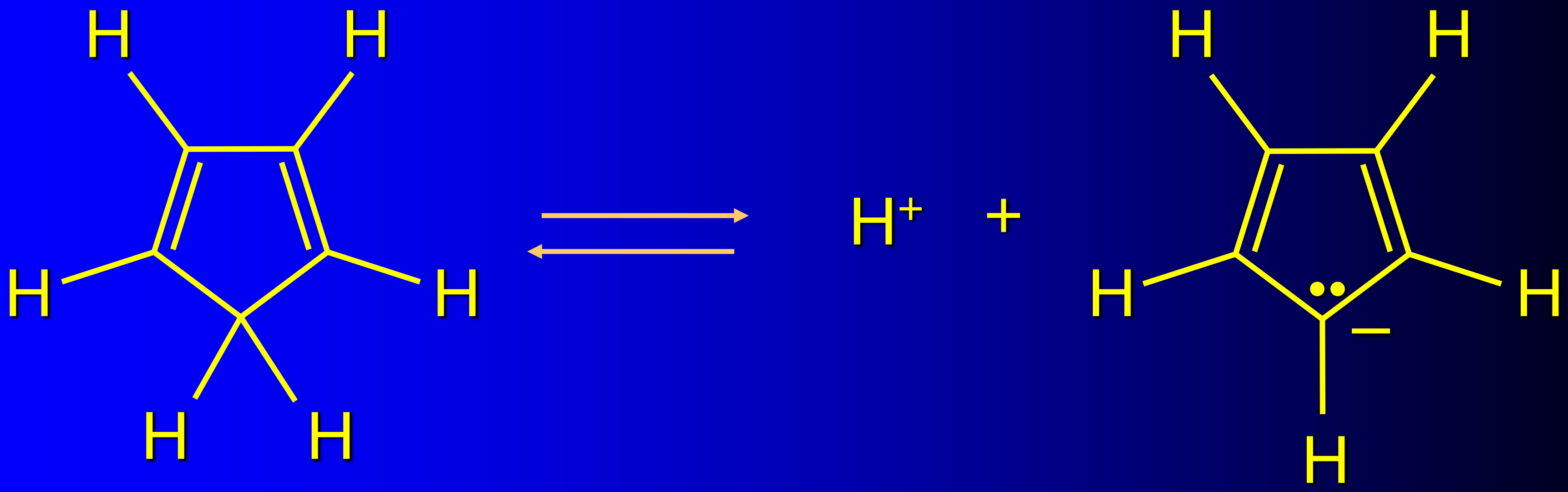


6 π electrons delocalized over 5 carbons

negative charge dispersed over 5 carbons

stabilized anion

Acidity of Cyclopentadiene



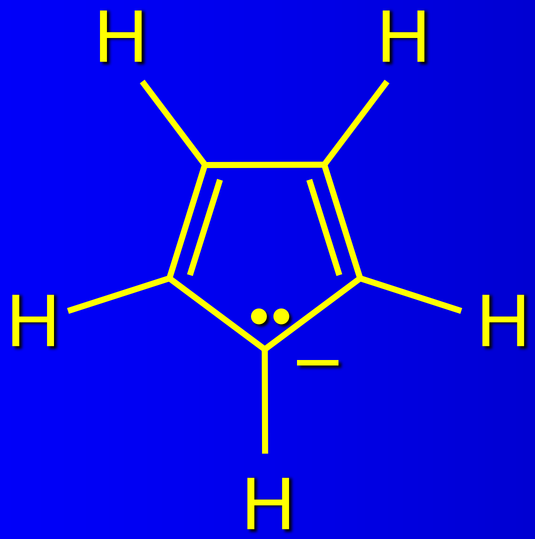
$pK_a = 16$

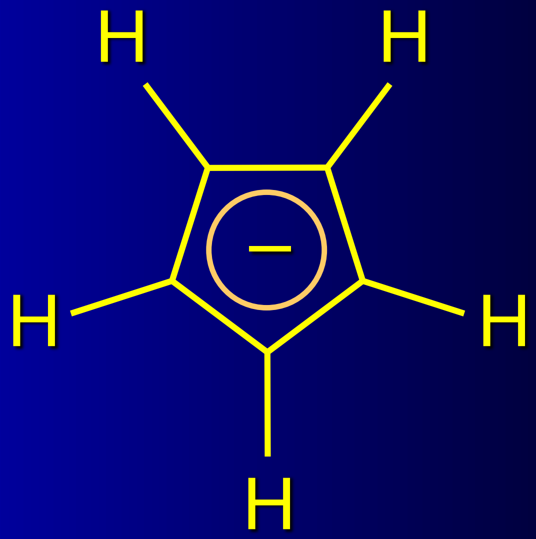
$K_a = 10^{-16}$

Cyclopentadiene is unusually acidic for a hydrocarbon.

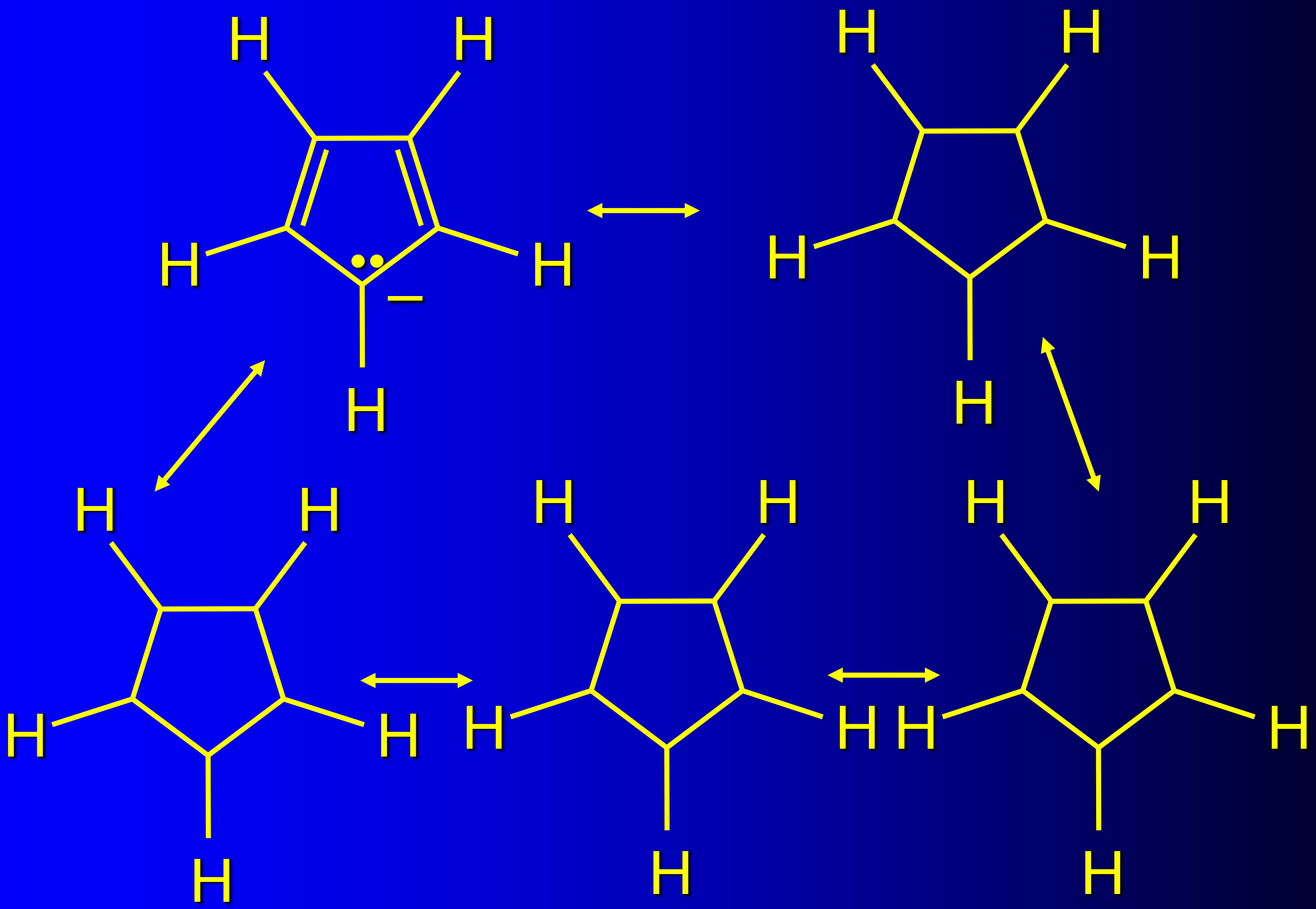
Increased acidity is due to stability of cyclopentadienide anion.

Cyclopentadienide Anion

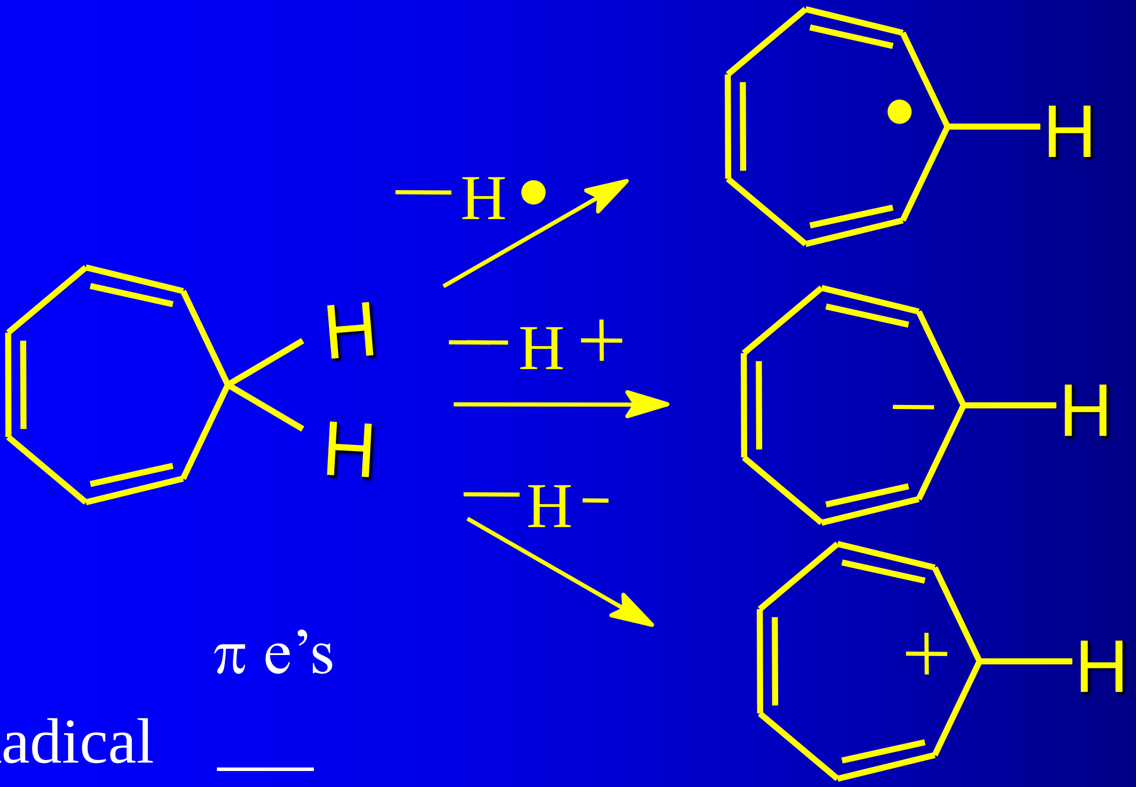




Let’s Move Electrons



Cycloheptatriene



Radical

Anion

Cation

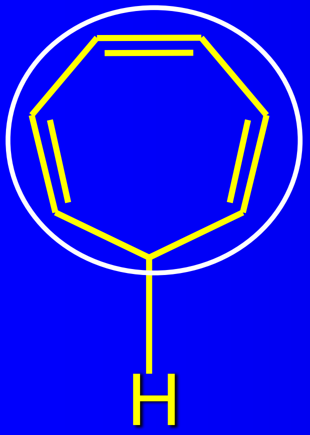
π e's

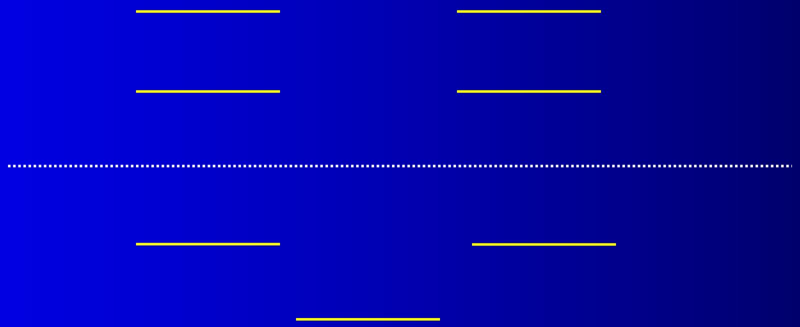
Radical ___

Cation ___

Anion ___

Cycloheptatriene

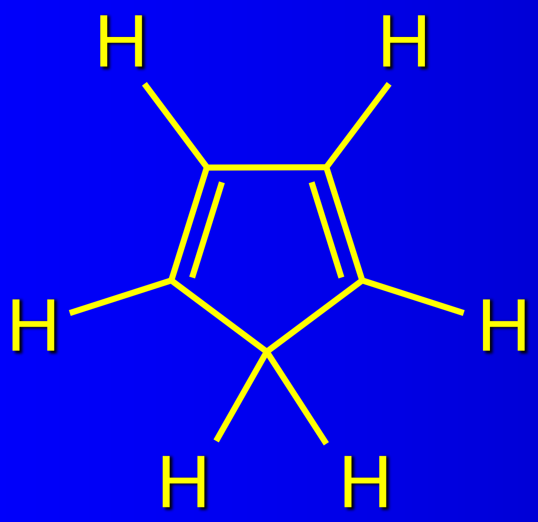


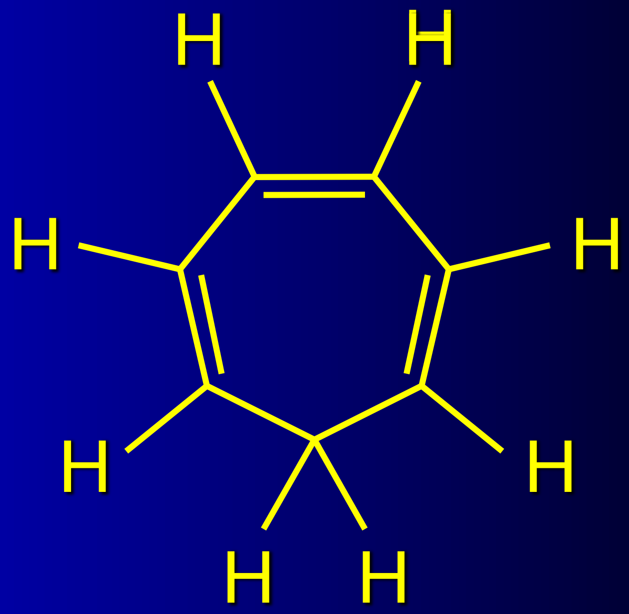


Let's fill these for each case, radical, anion and cation

	π e's
Radical	___
Cation	___
Anion	___

Compare Acidities of Cyclopentadiene and Cycloheptatriene





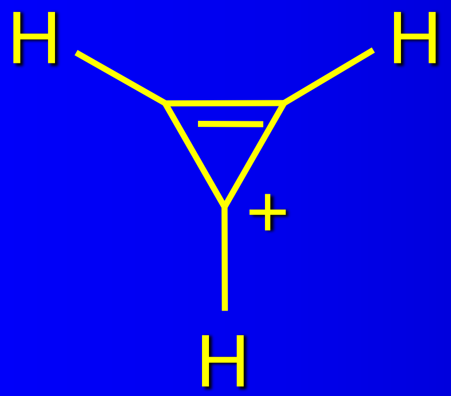
pK_a = 16

$K_a = 10^{-16}$

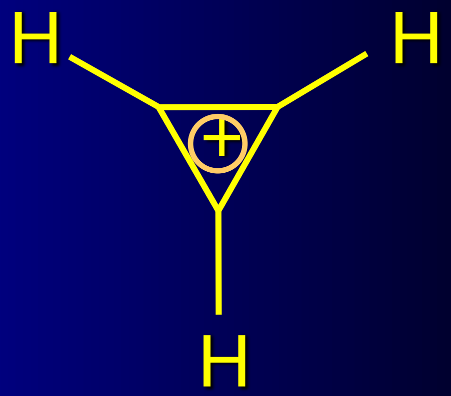
pK_a = 36

$K_a = 10^{-36}$

Cyclopropenyl Cation



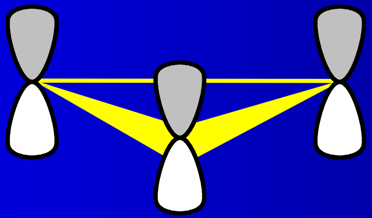
also written as

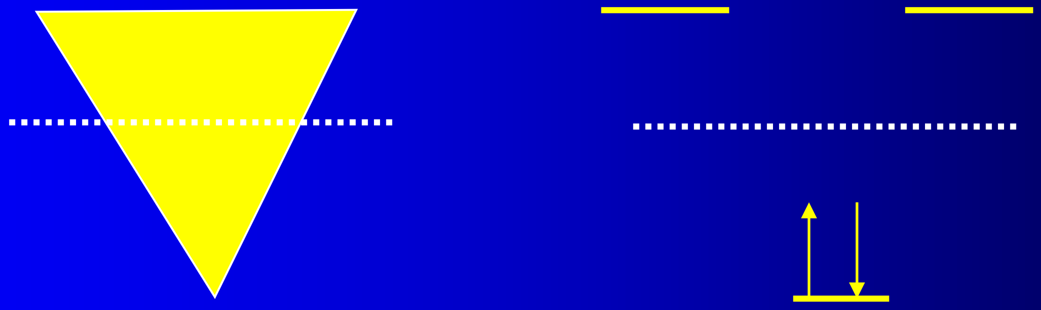


$$n = 0$$

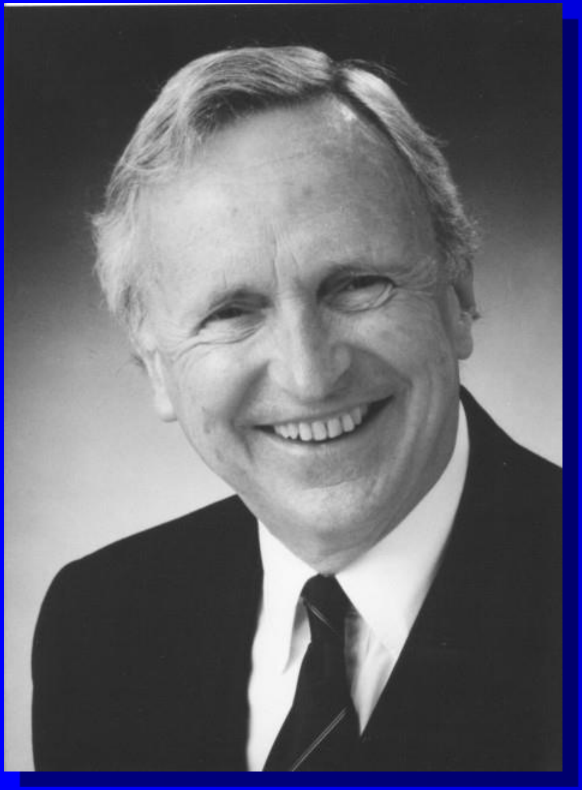
$$4n + 2 = 2\ \pi \text{ electrons !!}$$

n = 0 (4n+2 = 2) fills a bonding MO





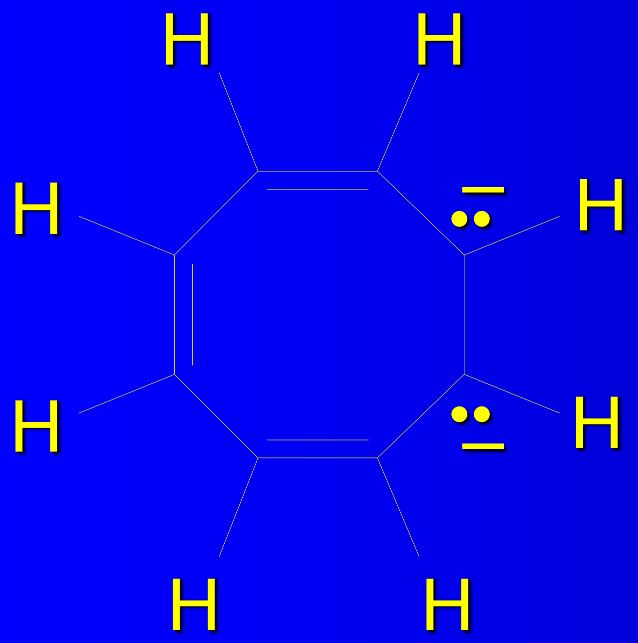
Discovery of Cyclopropylium Cation



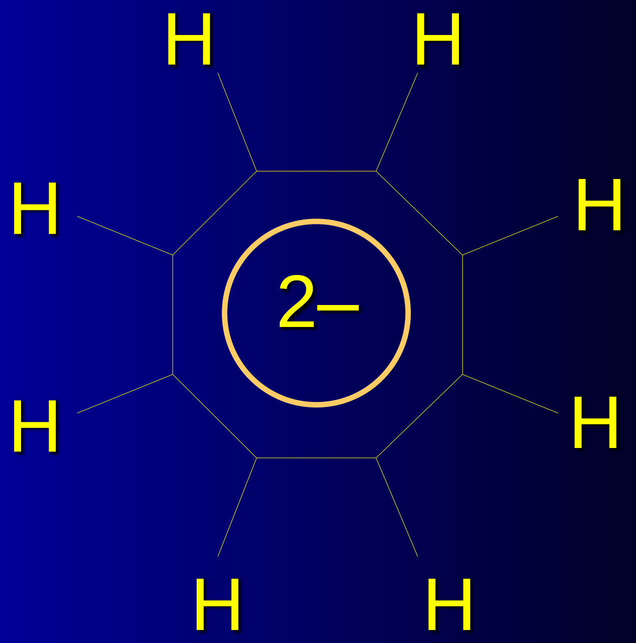
Ron Breslow 1931 -

While still in his twenties, Breslow made two groundbreaking contributions to mechanistic organic chemistry. His synthesis of a cyclopropenyl cation generalized the concept of aromaticity to cyclic systems with only 2 **π**-electrons. This work was bolstered by showing that cyclopropenyl anions and cyclopentadienyl cations, each with 4n **π**-electrons in a cyclic array, are anti-aromatic (a term Breslow coined).

Cyclooctatetraene Dianion



also written as

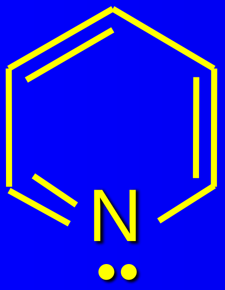


$n = 2$

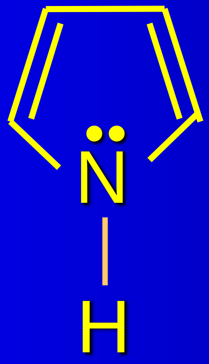
$4n + 2 = 10\ \pi$ electrons

Heterocyclic Aromatic Compounds

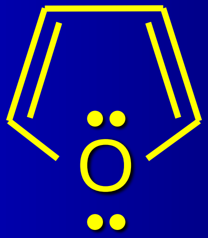
Heterocyclic Aromatic Compounds



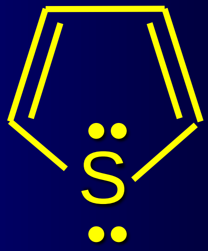
Pyridine



Pyrrole

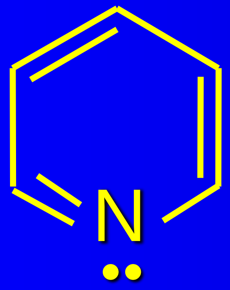


Furan



Thiophene

Heterocyclic Aromatic Compounds
and
Hückel's Rule



Pyridine

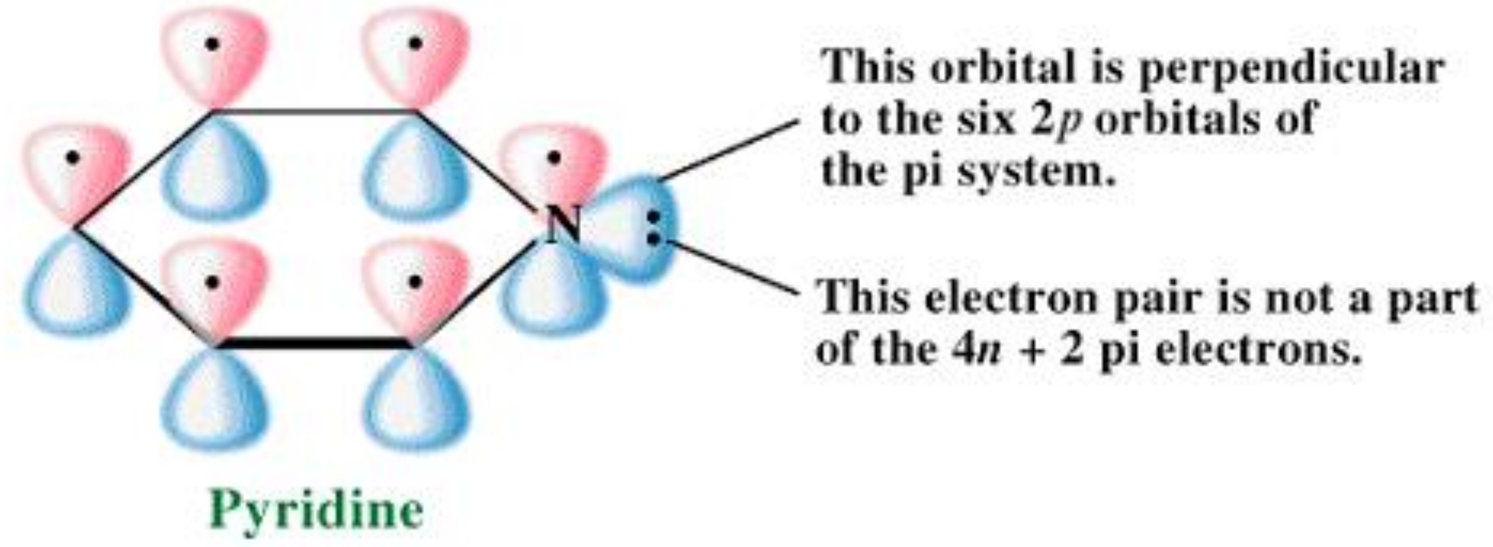
6 π electrons in ring

lone pair on nitrogen is in an

sp^2 hybridized orbital;

not part of π system of ring

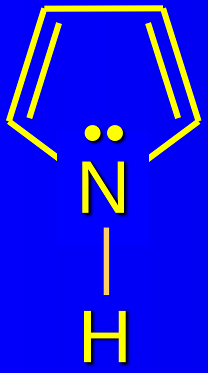
Hückel and Pyridine



This orbital is perpendicular to the six 2p orbitals of the pi system.

This electron pair is not a part of the $4n + 2$ pi electrons.

Pyridine

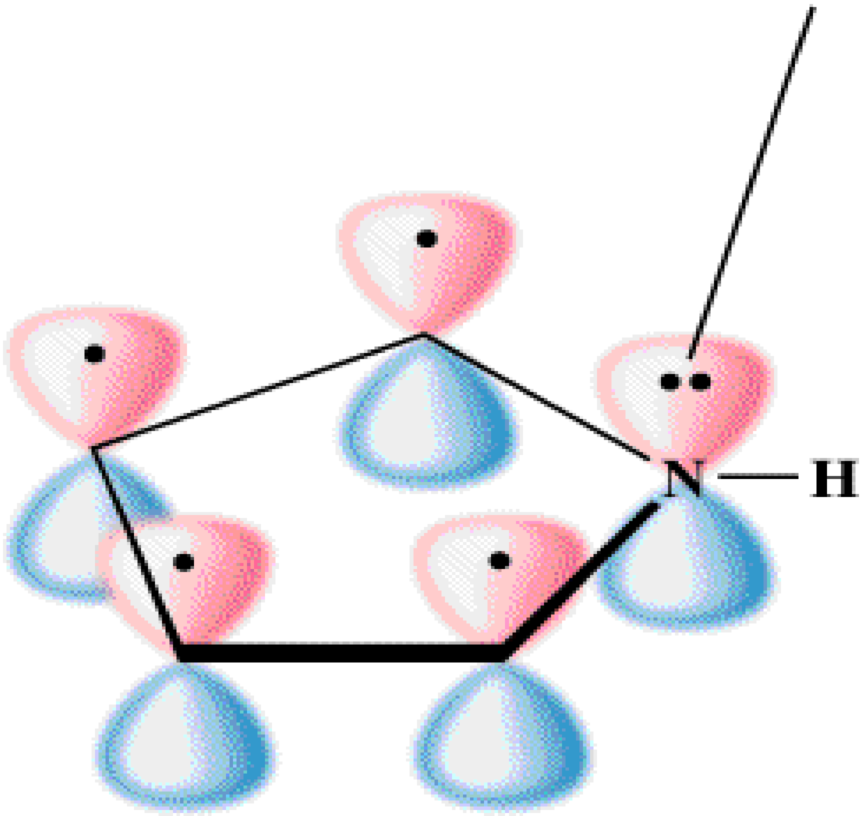


Pyrrole

lone pair on nitrogen must be part of ring π system if ring is to have 6 π electrons

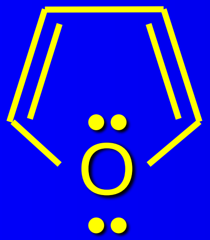
lone pair <u>must be in</u> a *p* orbital in order to overlap with ring π system

Hückel and Pyrrole


This electron pair is a part of the 4*n* + 2 pi electrons.

Pyrrole

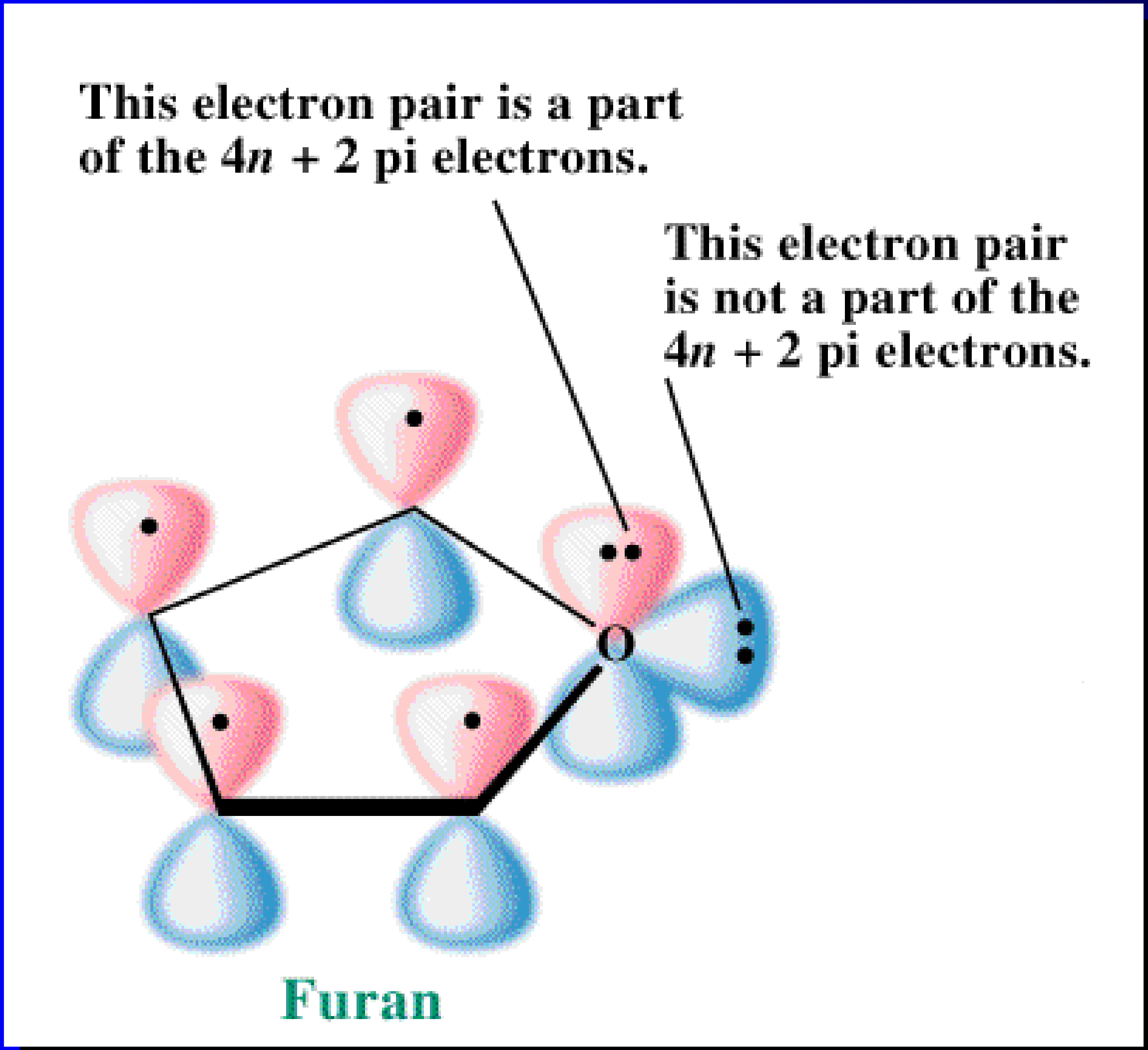
Furan



two lone pairs on oxygen

one pair is in a *p* orbital and is part of ring π system; other is in an sp^2 hybridized orbital and is not part of ring π system

Huckel and Furan



This electron pair is a part of the 4*n* + 2 pi electrons.

This electron pair is not a part of the 4*n* + 2 pi electrons.

Furan