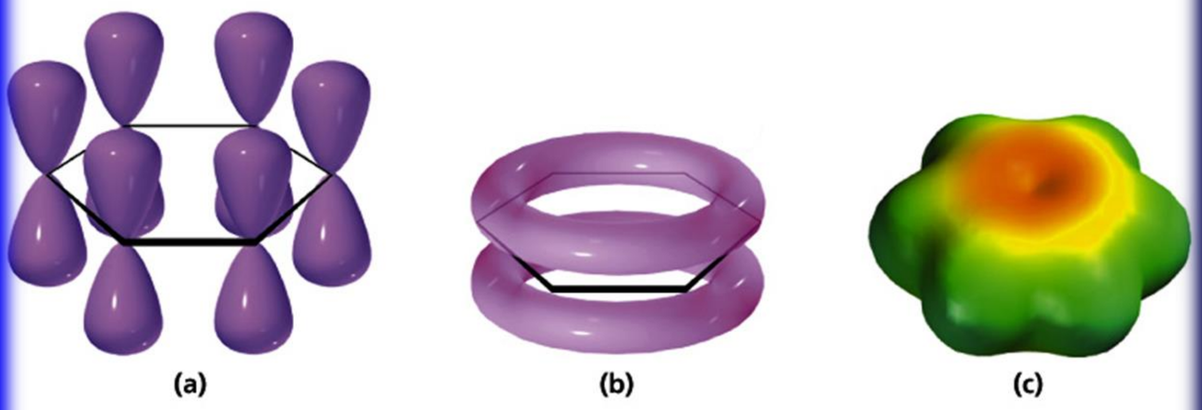
Lecture 9

Aromatics



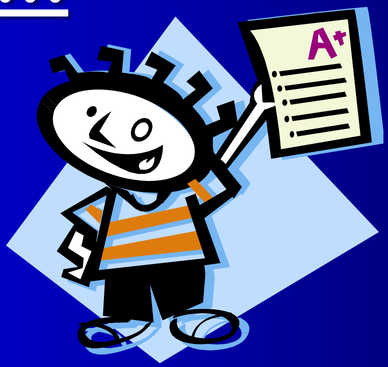
February 16, 2016

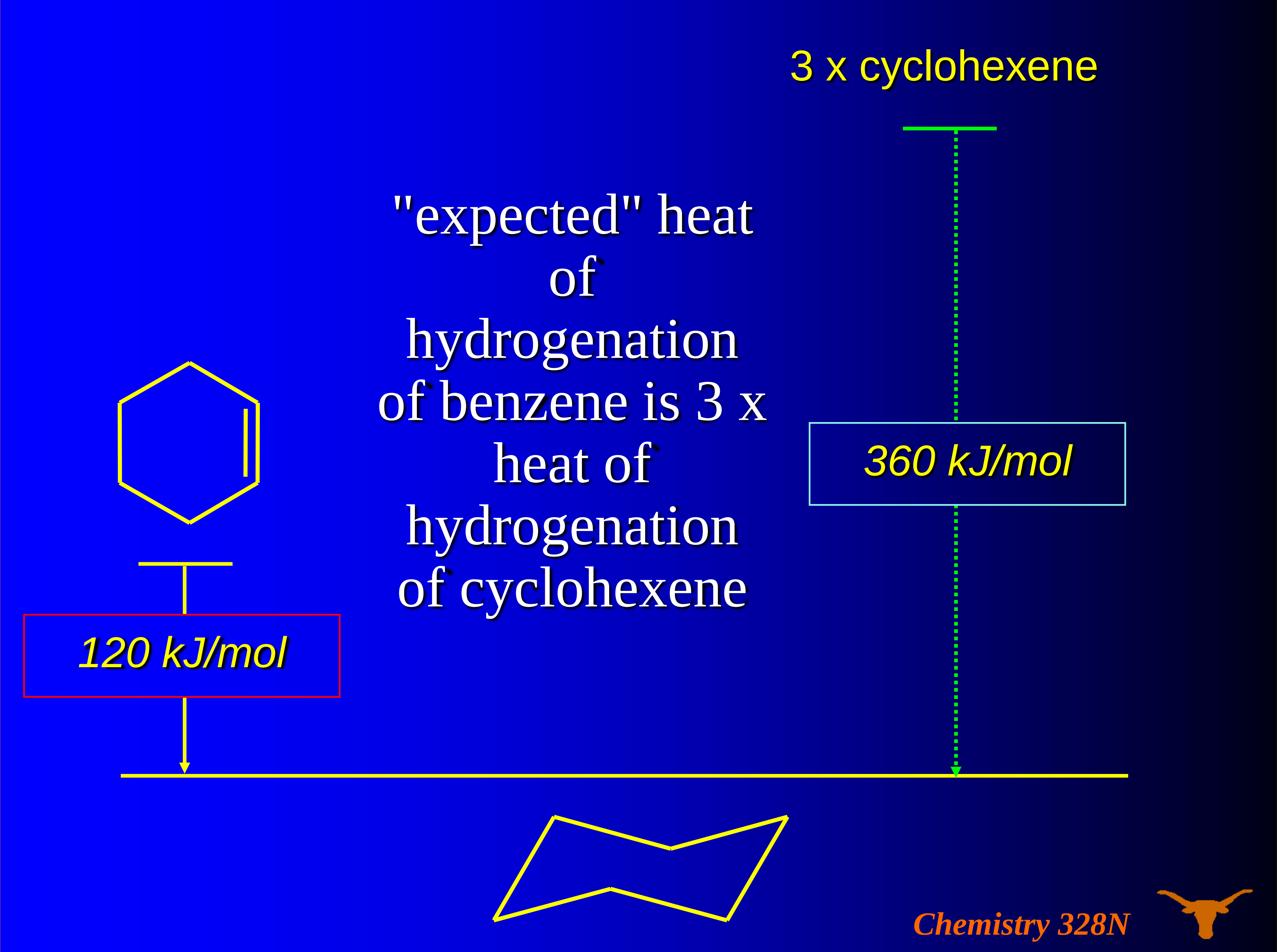
Chemistry 328N

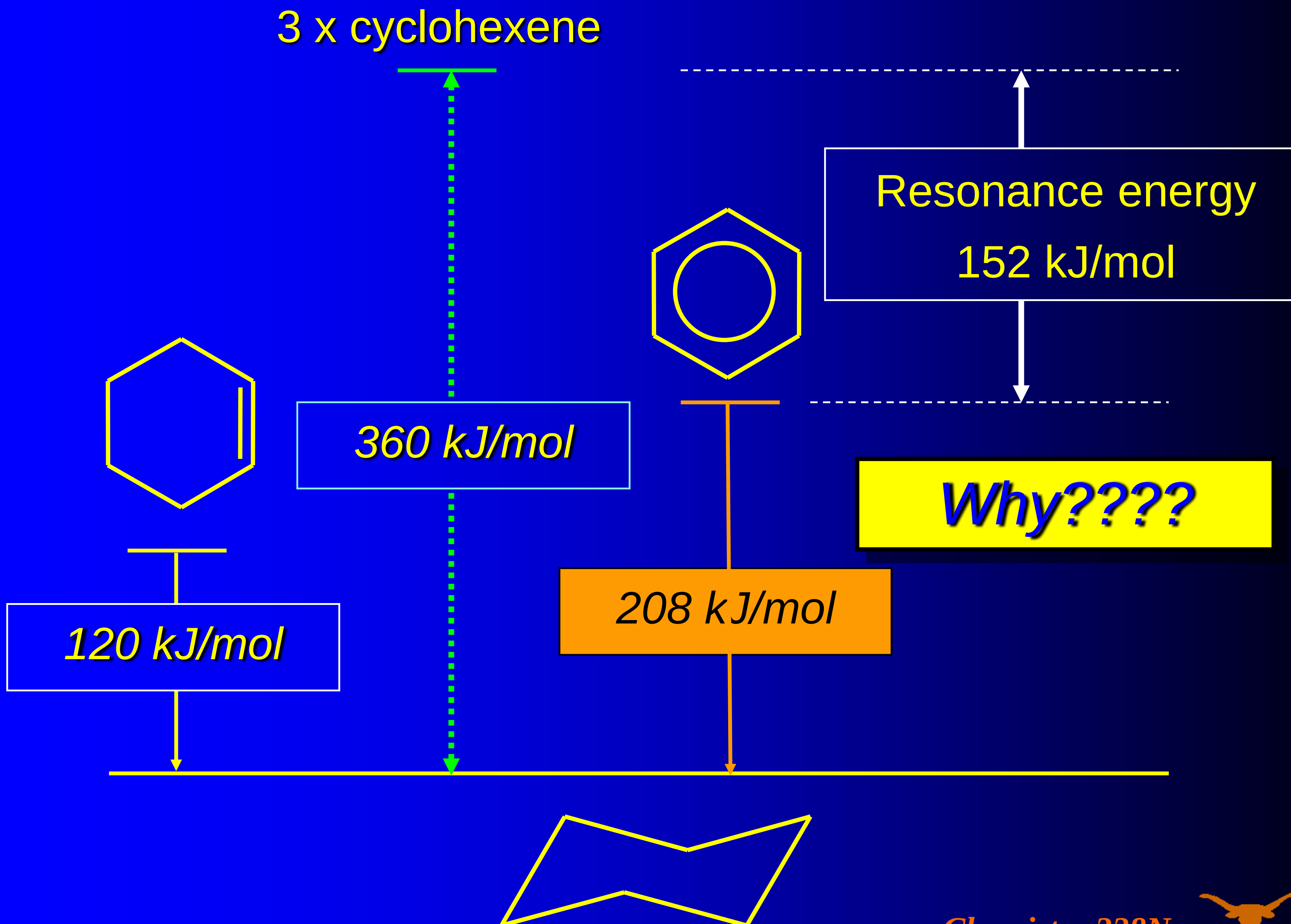
First Midterm Exam

- When: Wednesday, 2/17
- When: 7-9 PM (please do not be late)
- Where: WEL 3.502…enter from Inner Campus Drive
- What: Covers material through Thursday’s lecture
- Remember: Homework problems!!
- Practice: Old exams will be posted on the web site
- Review Sessions: Mon Pharm 2.110, Tue Painter 4.42.
- Please…bring pencils, an eraser and a calculator only and …….**Do a good job!!!**

I will bother you! ☺




3 x cyclohexene
"expected" heat of hydrogenation of benzene is 3 x heat of hydrogenation of cyclohexene
360 kJ/mol
120 kJ/mol
Chemistry 328N


3 x cyclohexene
Resonance energy
152 kJ/mol
360 kJ/mol
Why????
208 kJ/mol
120 kJ/mol

The answer comes from MO Theory

1. But I hate MO stuff …it is confusing……☹

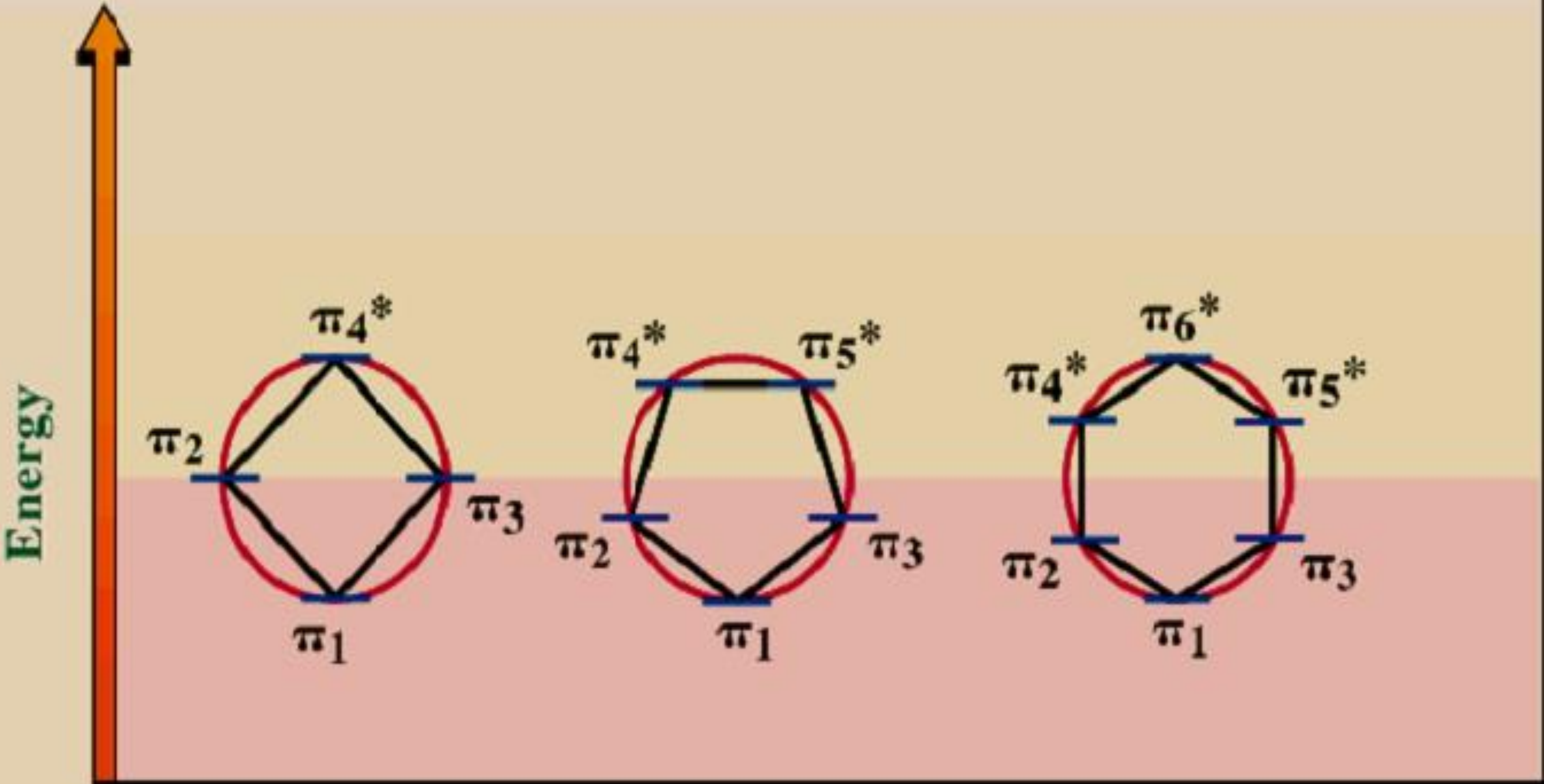
2. How do you even know how many MOs there are??

3. How do you know the relative energies of these MO's???

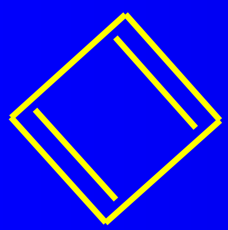
For Cyclic Structures Frost Circles…a Great Trick

- Inscribe a polygon of the same number of sides as the ring to be examined such that one of the vertices is at the bottom of the ring
- 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

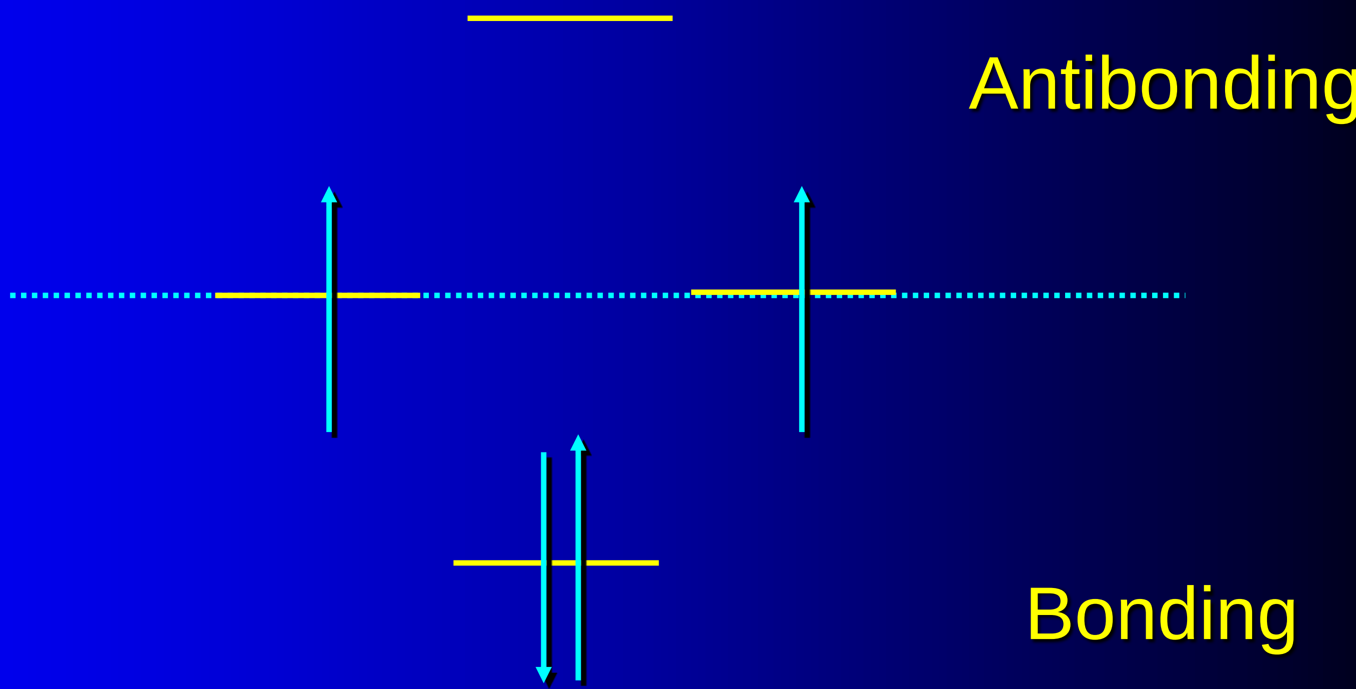
Frost circles for cyclic, fully conjugated 4-,5- and 6-membered rings



π-MOs of Cyclobutadiene (square planar)



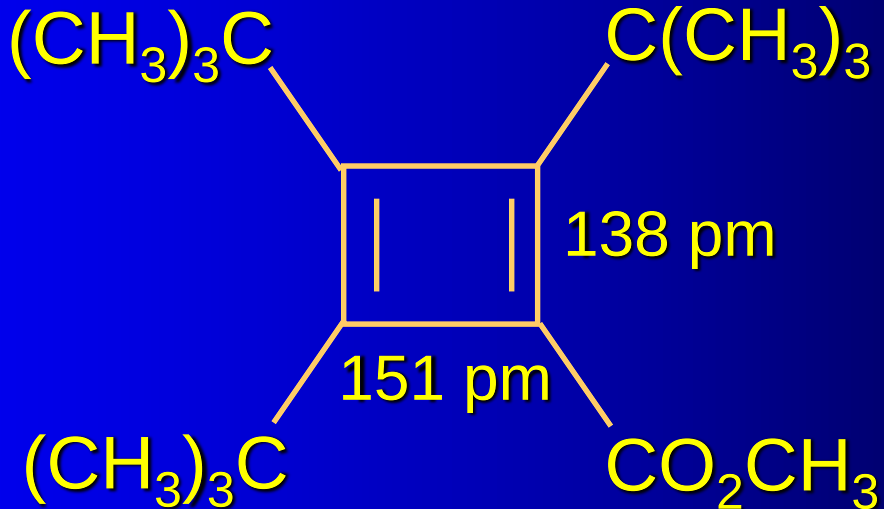
Cyclo-
butadiene



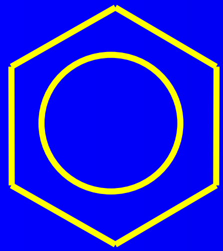
4 π electrons; bonding orbital is filled; other 2 π electrons singly occupy two nonbonding orbitals

Structure of Cyclobutadiene

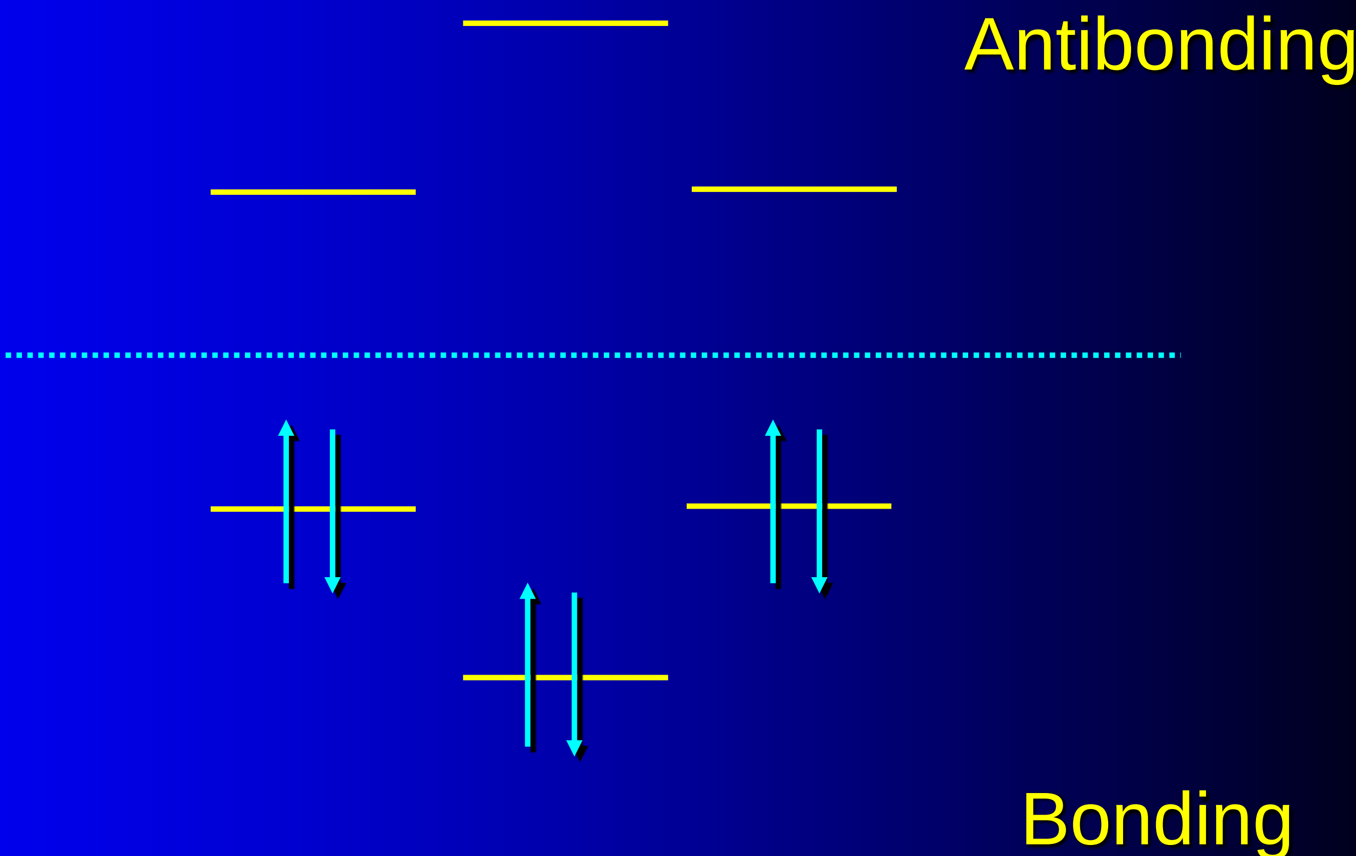
structure of a stabilized derivative is characterized by alternating short bonds and long bonds



π-MOs of Benzene



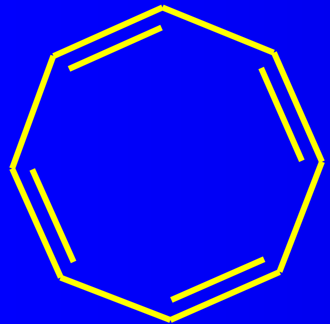
Benzene



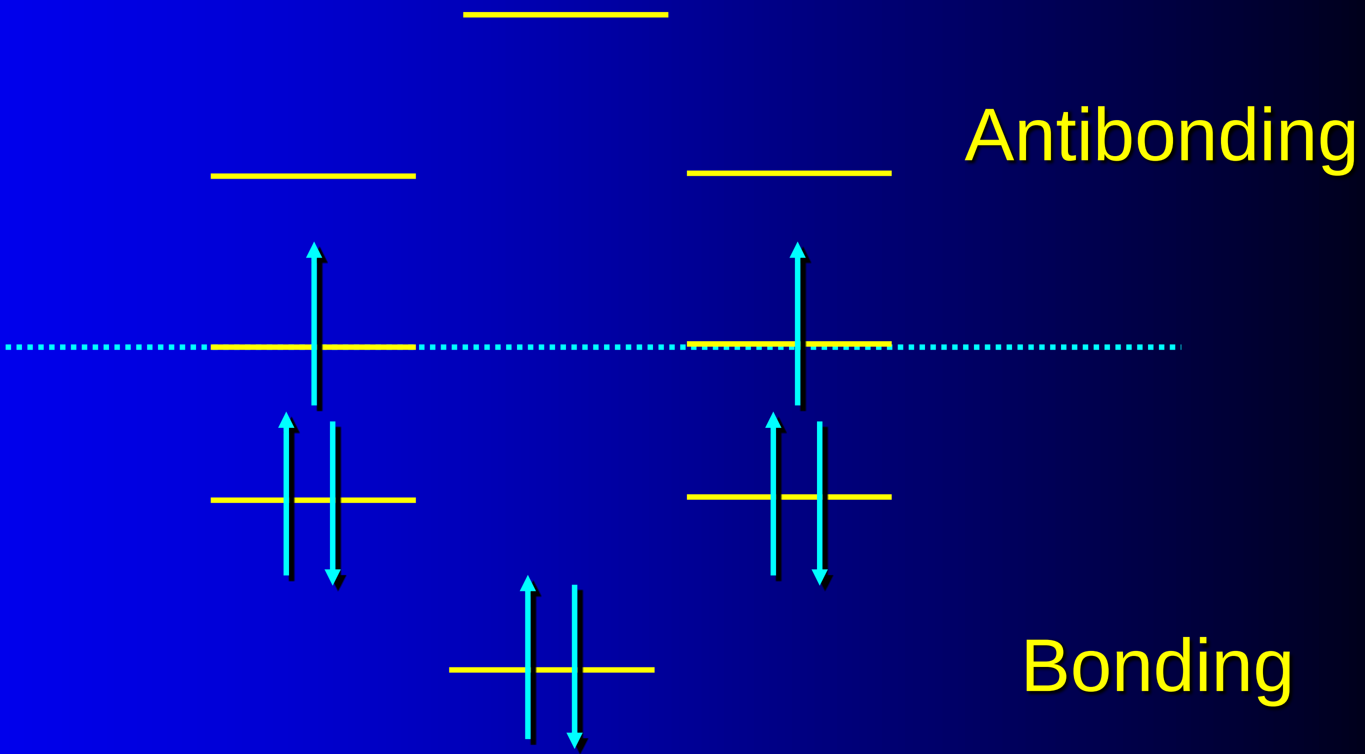
6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

π-MOs of Cyclooctatetraene (square planar)



Cyclo-
octatetraene



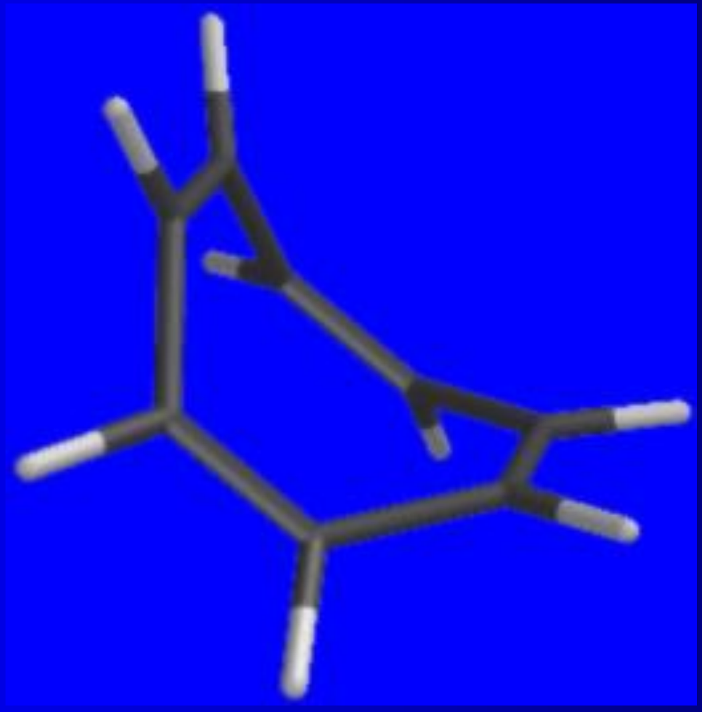
8 π electrons

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

Structure of Cyclooctatetraene

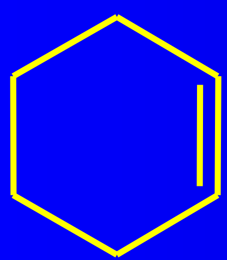
cyclooctatetraene is not planar

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

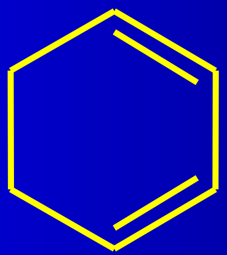


Heats of Hydrogenation

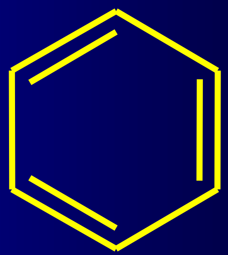
to give cyclohexane (kJ/mol)



120



231

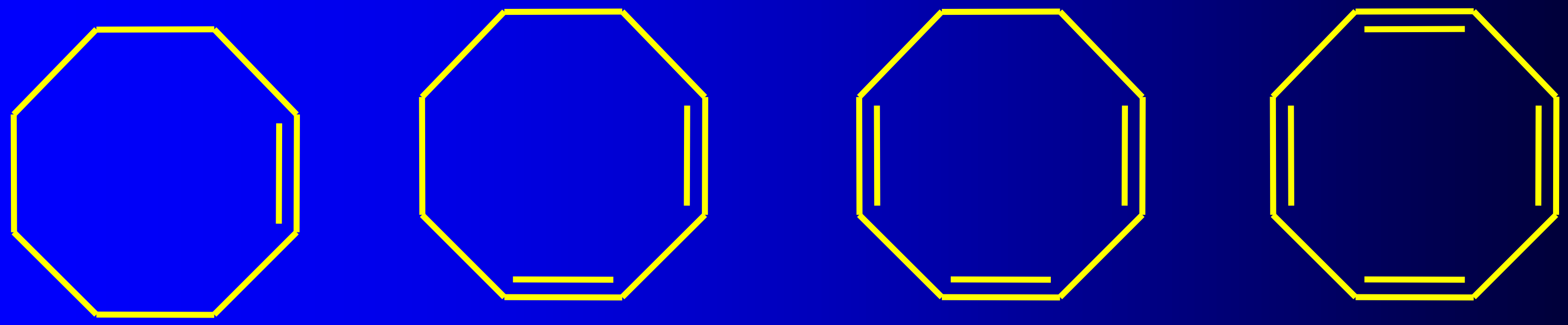


208

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)

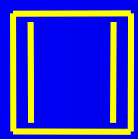


97 205 303 410

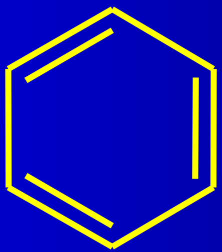
heat of hydrogenation of cyclooctatetraene is more than 4 times the heat of hydrogenation of cyclooctene….no special stability here!

Requirements for Aromaticity

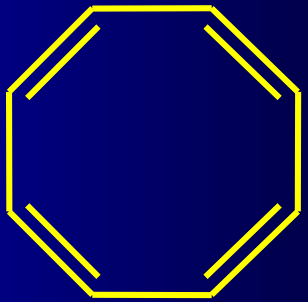
Cyclic conjugation is necessary, *but not sufficient*



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

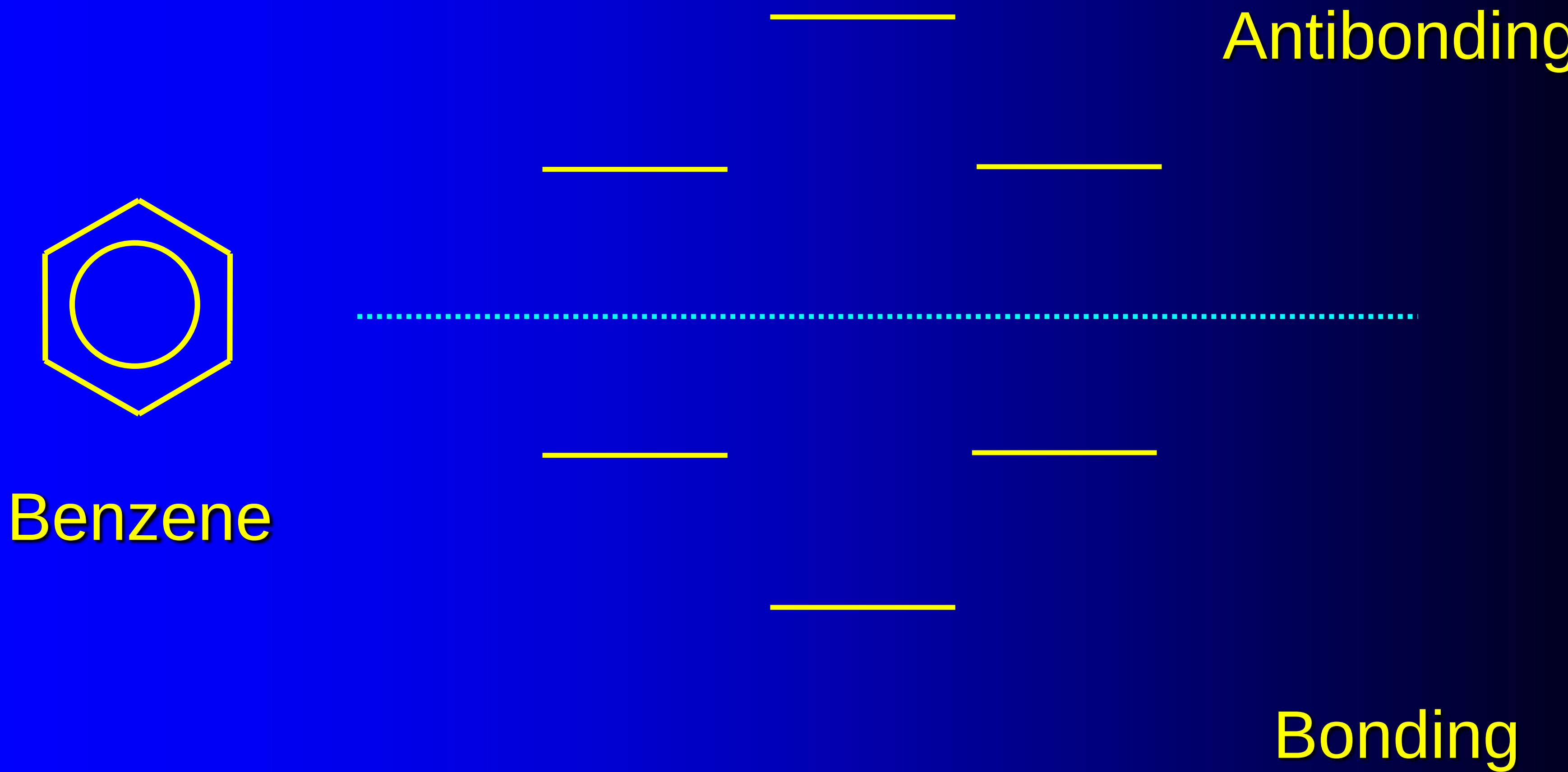
To be Aromatic …a compound must :

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…

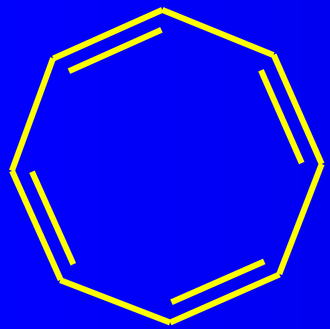
π-MOs of Benzene



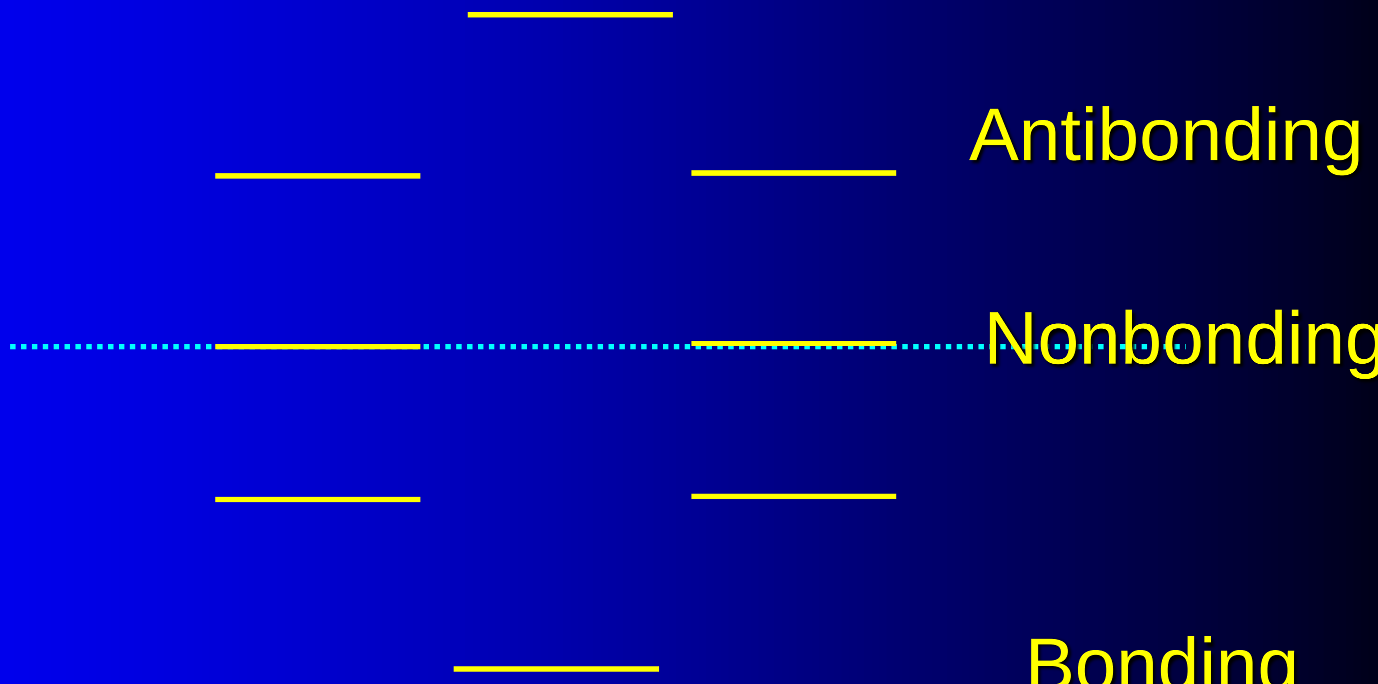
6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

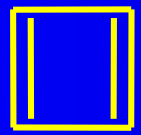
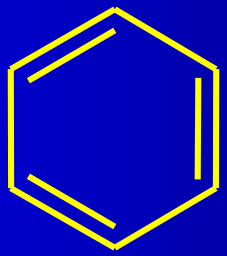
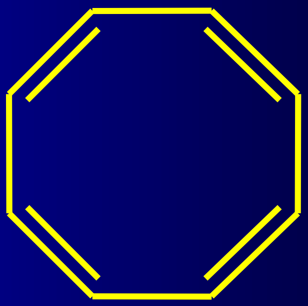
π-MOs of Cyclooctatetraene



Cyclo-
octatetraene

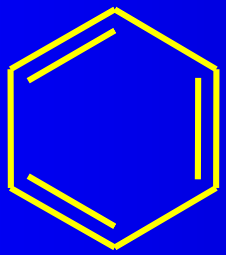


π-Electron Requirement for Aromaticity

4 π electrons	6 π electrons	8 π electrons
		
not aromatic	aromatic	not aromatic

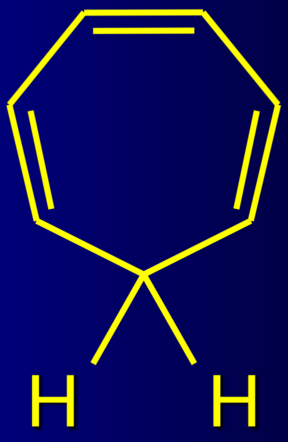
Only Completely Conjugated Polyenes can be Aromatic

6 π electrons;
completely conjugated



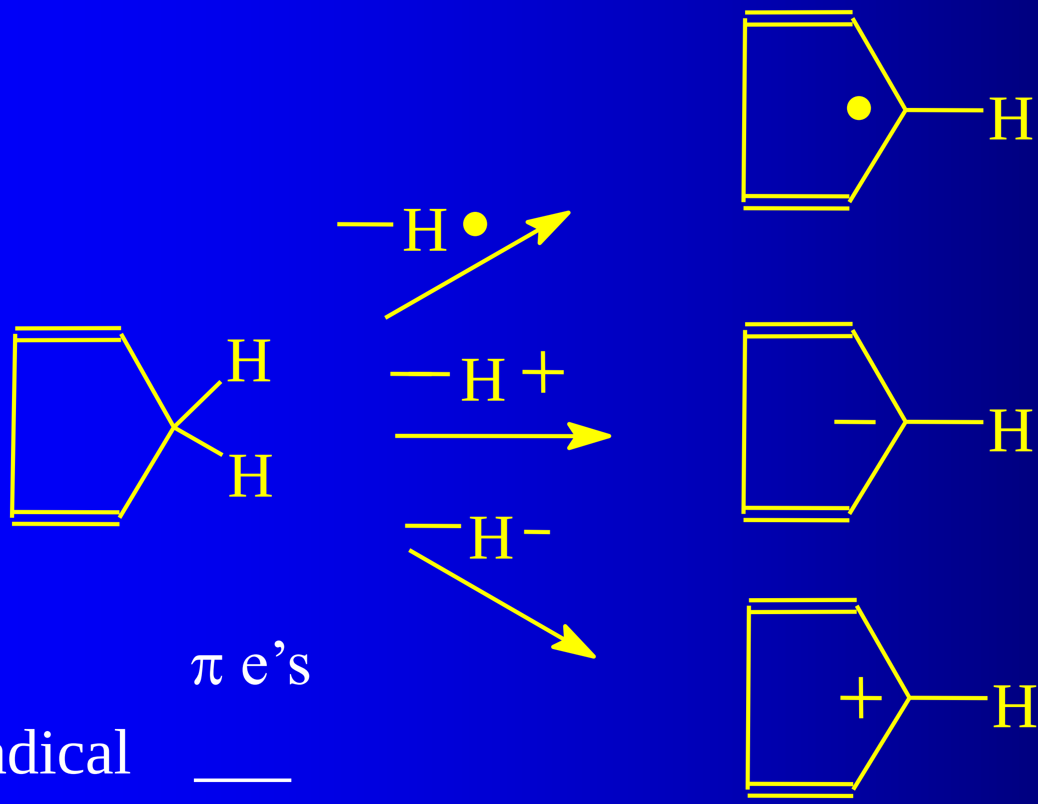
aromatic

6 π electrons;
not completely
conjugated



not
aromatic

Aromatic Ions



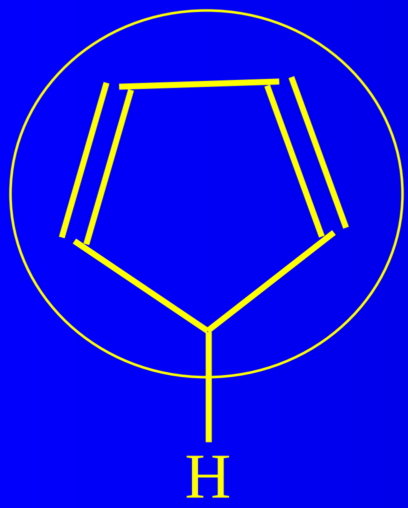
Radical

Anion

Cation

	π e's
Radical	___
Cation	___
Anion	___

Cyclopentadiene



π e’s

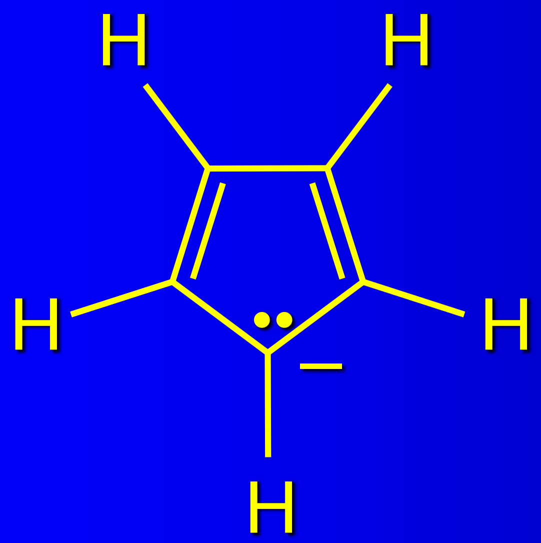
Radical ___

Cation ___

Anion ___

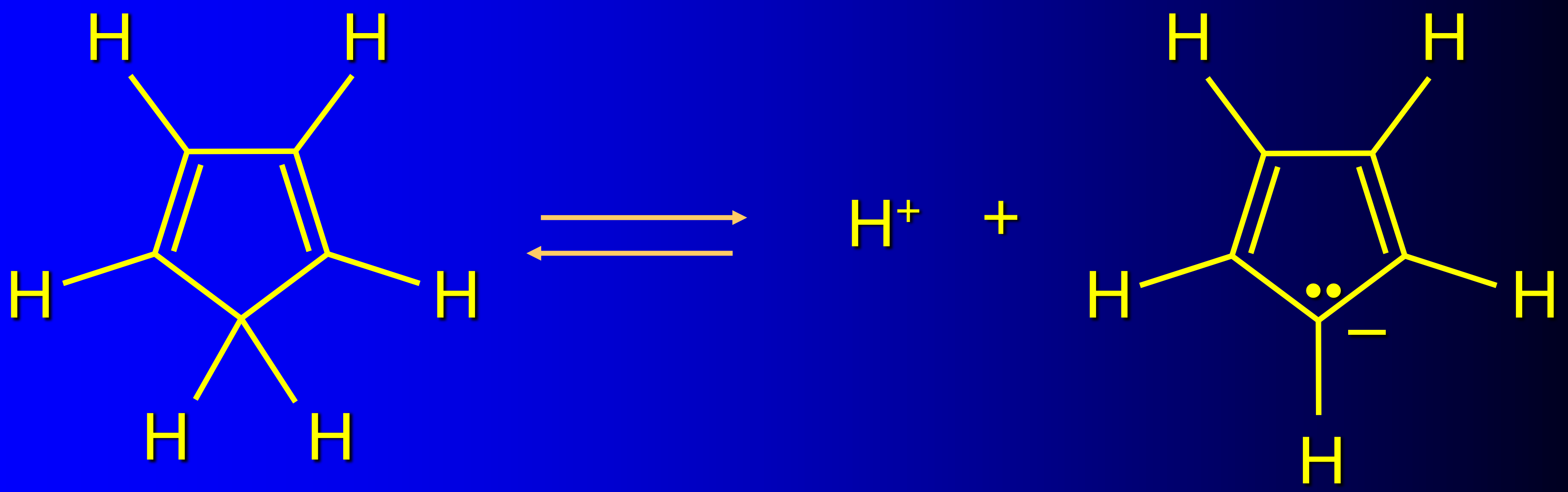
Let’s fill these for each case, radical, anion and cation

Cyclopentadienide Anion



6 π electrons delocalized
over 5 carbons
negative charge dispersed
over 5 carbons
stabilized anion

Acidity of Cyclopentadiene



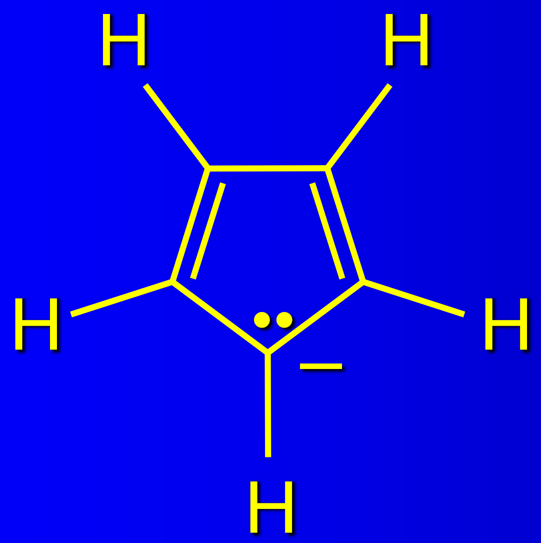
pK_a = 16

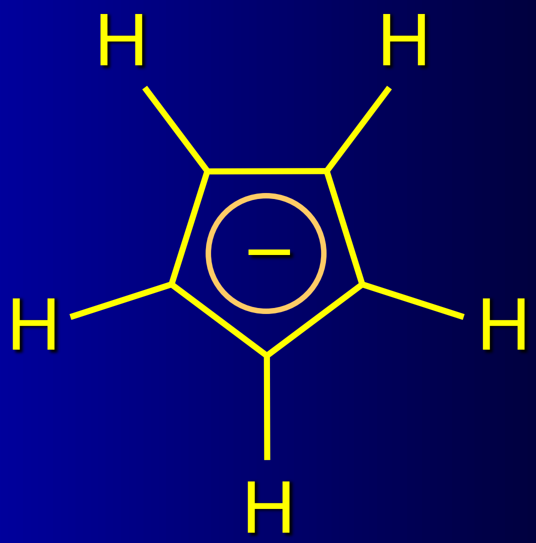
$K_a = 10^{-16}$

Cyclopentadiene is unusually acidic for a hydrocarbon.

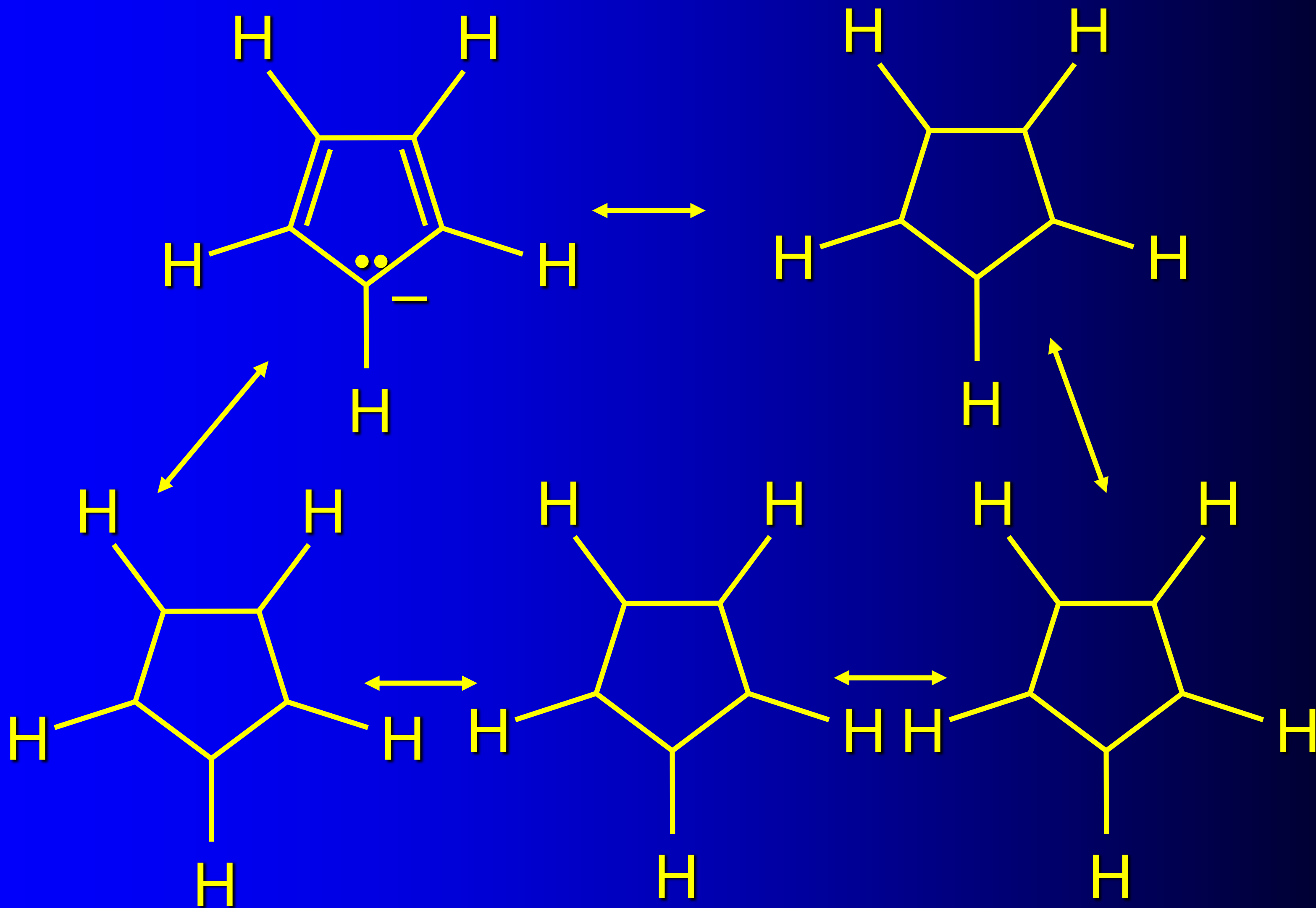
Increased acidity is due to stability of cyclopentadienide anion.

Cyclopentadienide Anion

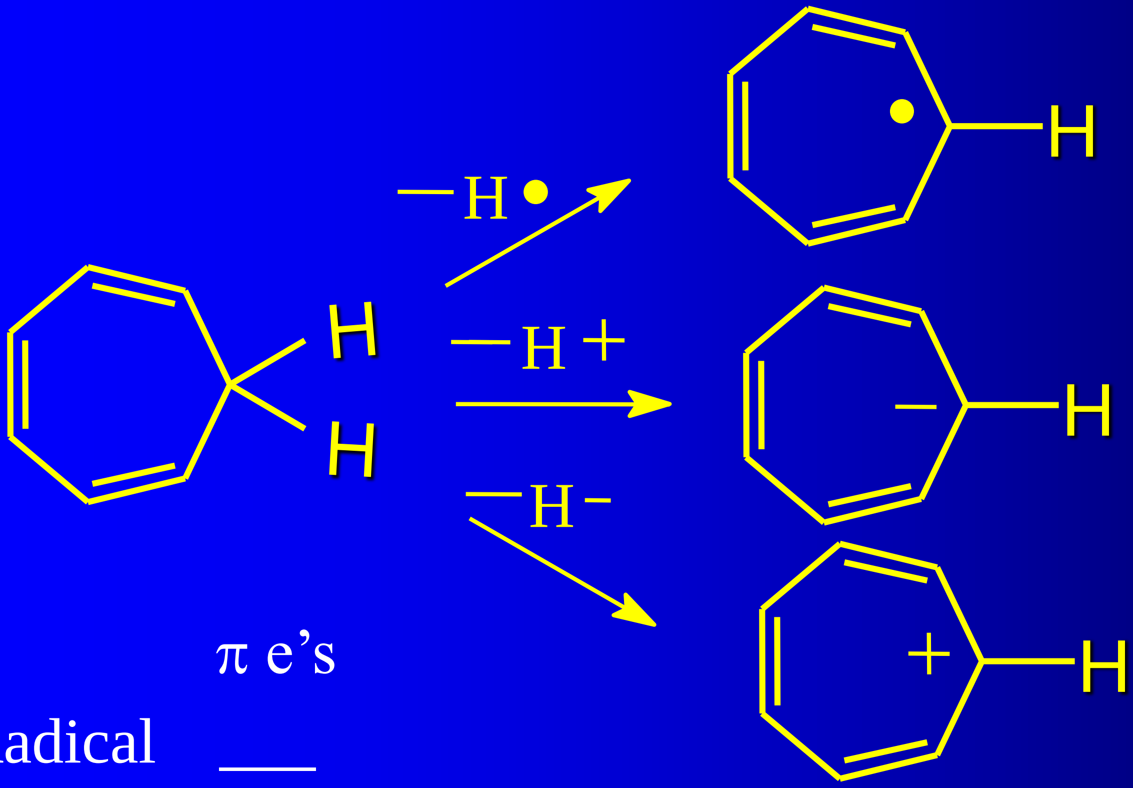




Let’s Move Electrons



Cycloheptatriene



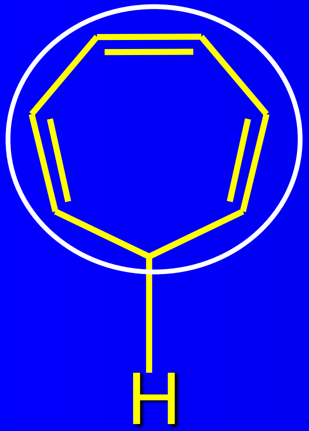
Radical

Anion

Cation

	π e's
Radical	___
Cation	___
Anion	___

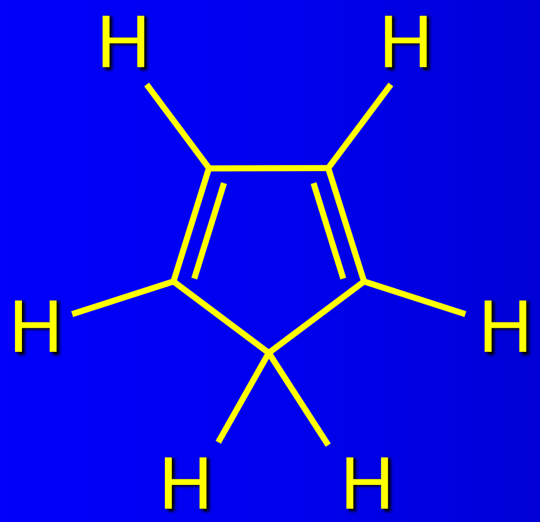
Cycloheptatriene

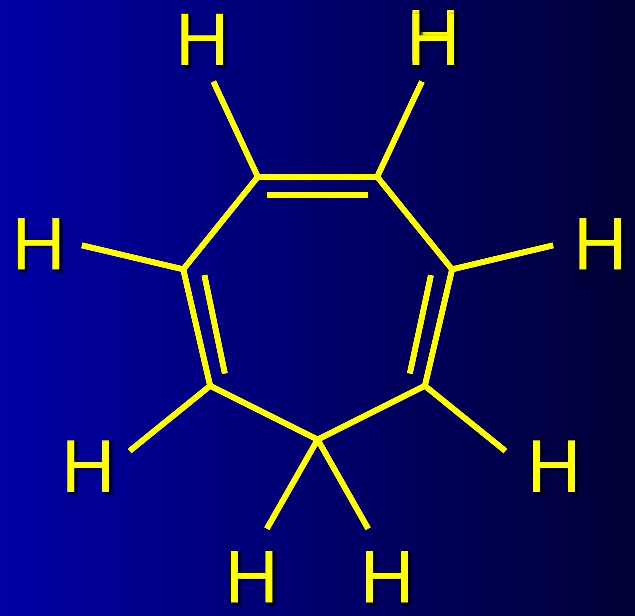


Let's fill these for each case, radical, anion and cation

	π e's
Radical	___
Cation	___
Anion	___

Compare Acidities of Cyclopentadiene and Cycloheptatriene





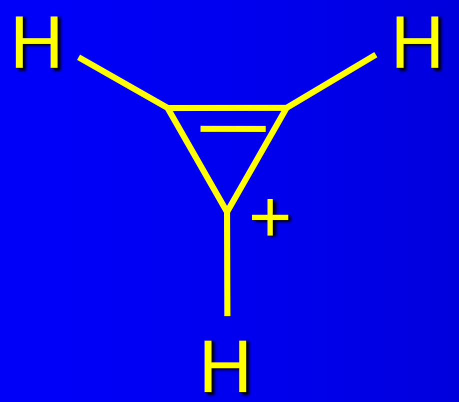
pK_a = 16

$K_a = 10^{-16}$

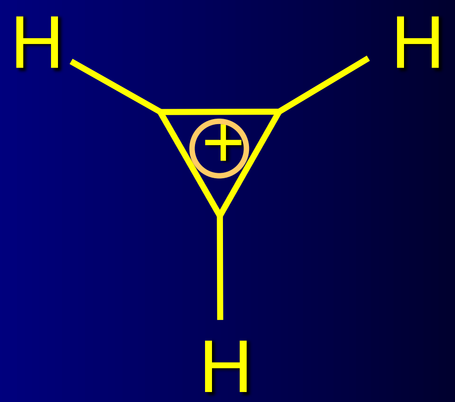
pK_a = 36

$K_a = 10^{-36}$

Cyclopropenyl Cation



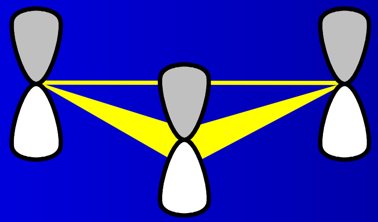
also written as

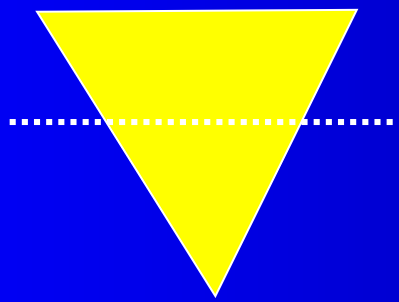


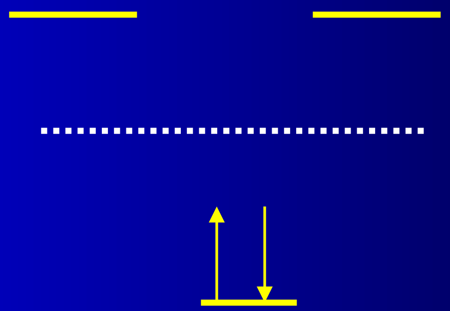
$$n = 0$$

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

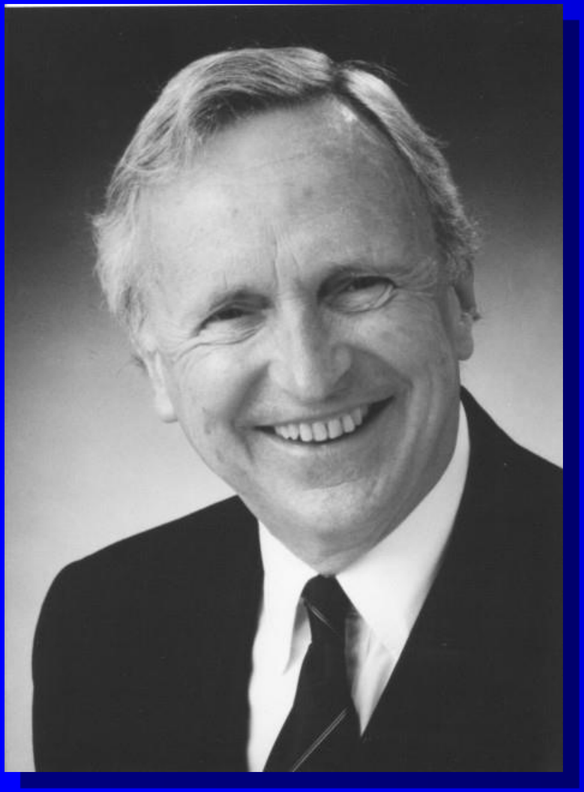
n = 0 (4n+2 = 2) fills a bonding MO







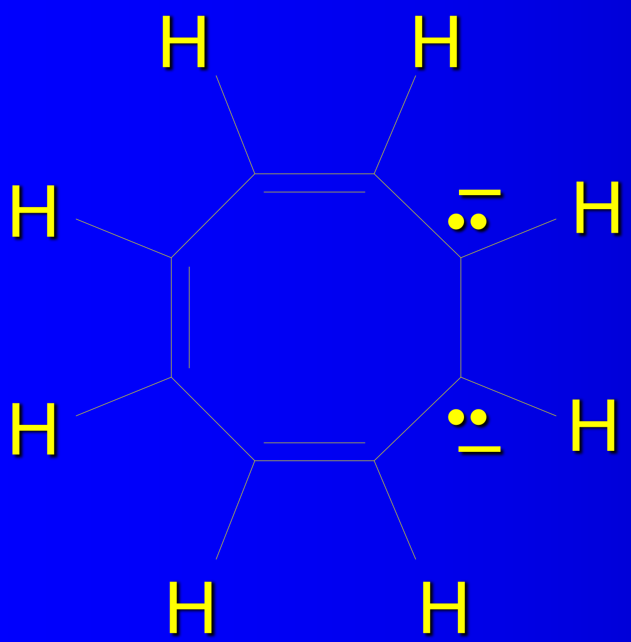
Discovery of Cyclopropylium Cation



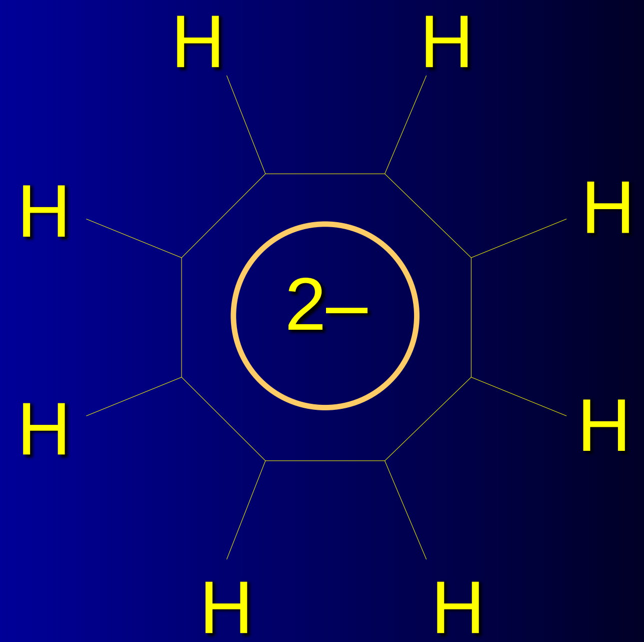
Ron Breslow 1931 -

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

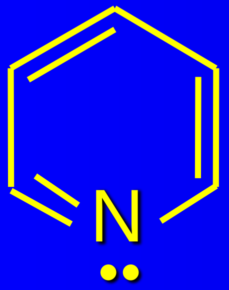


$n = 2$

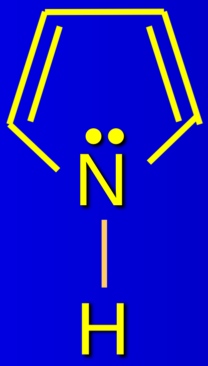
$4n + 2 = 10\ \pi$ electrons

Heterocyclic Aromatic Compounds

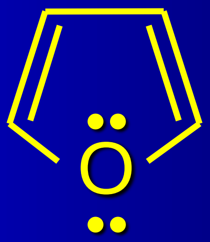
Heterocyclic Aromatic Compounds



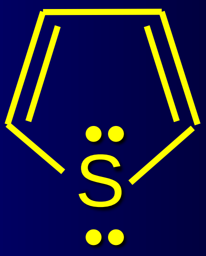
Pyridine



Pyrrole

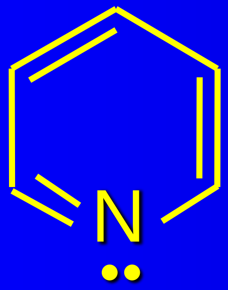


Furan



Thiophene

Heterocyclic Aromatic Compounds and Hückel's Rule

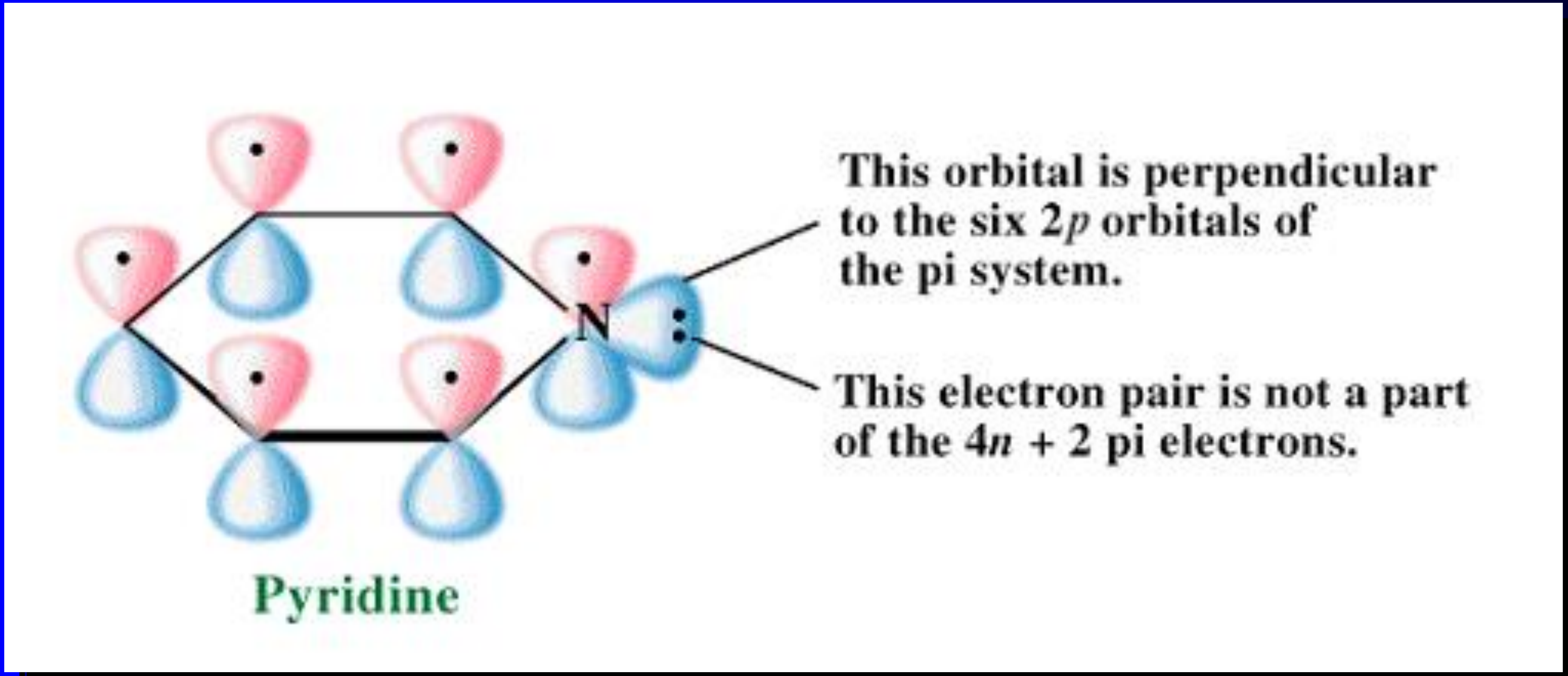


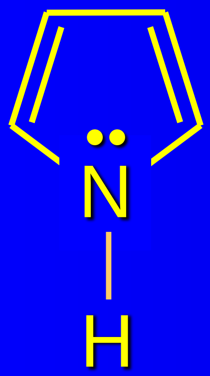
Pyridine

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



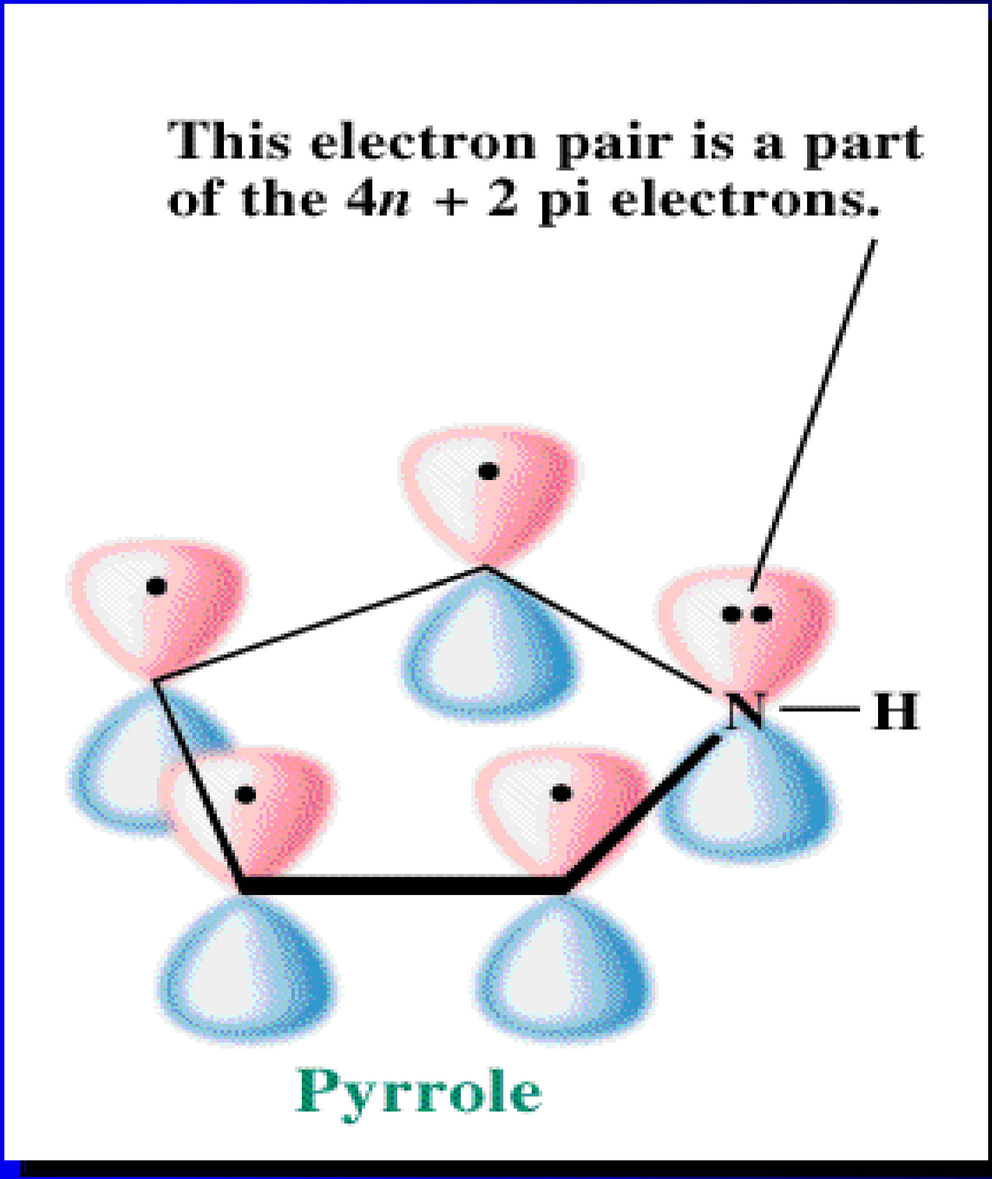


Pyrrole

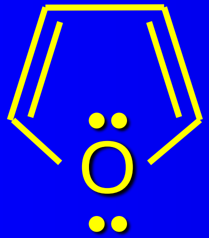
lone pair on nitrogen must be part of ring π system if ring is to have 6 π electrons

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

Hückel and 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