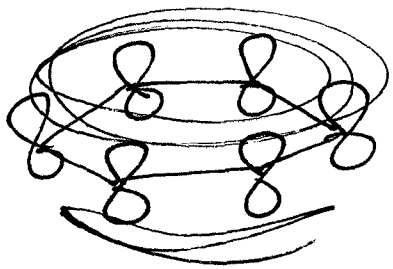
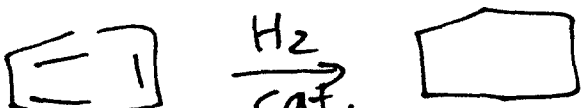
Benzene is flat, all bonds are same length, observably v. stable / nonreactive.



circular overlapping π e' cloud above + below the plane of the ring.

$\Delta H = 28.6$ kcal/mol (120 kJ/mol)

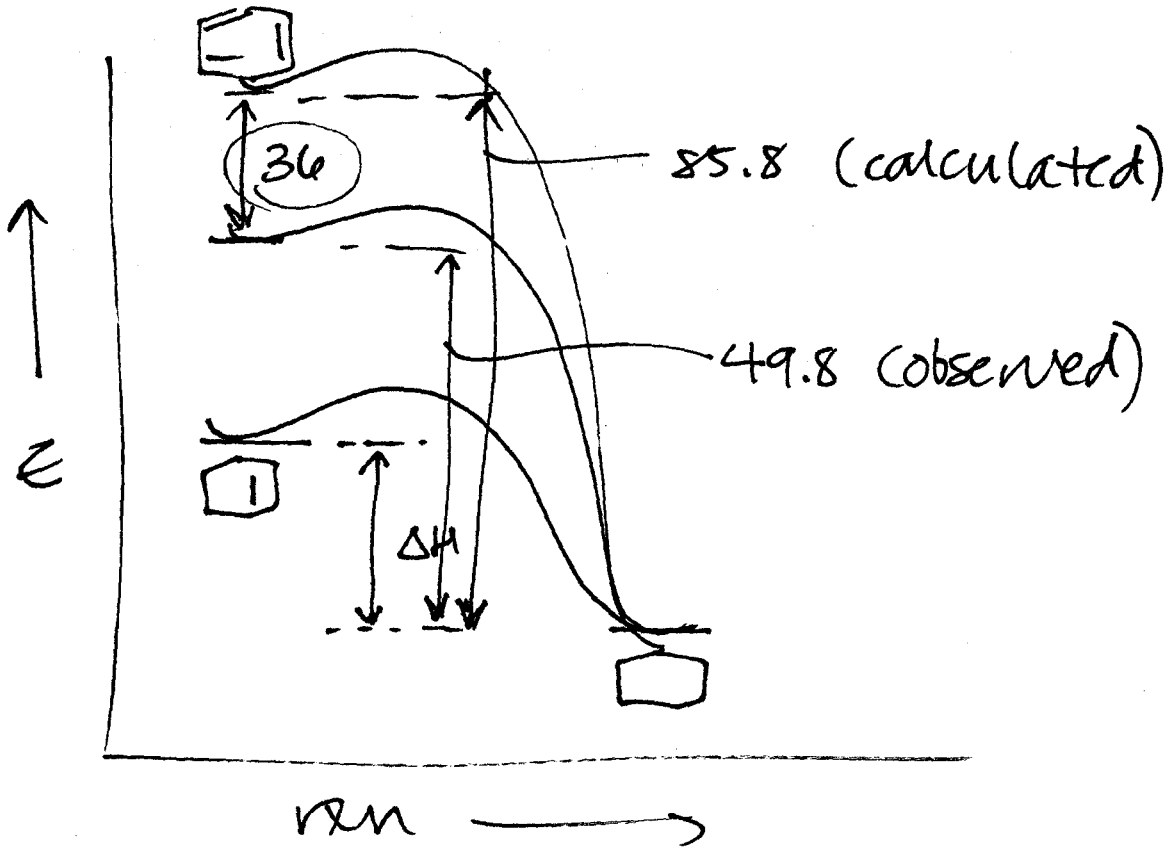


"1,3,5-cyclohexatriene"

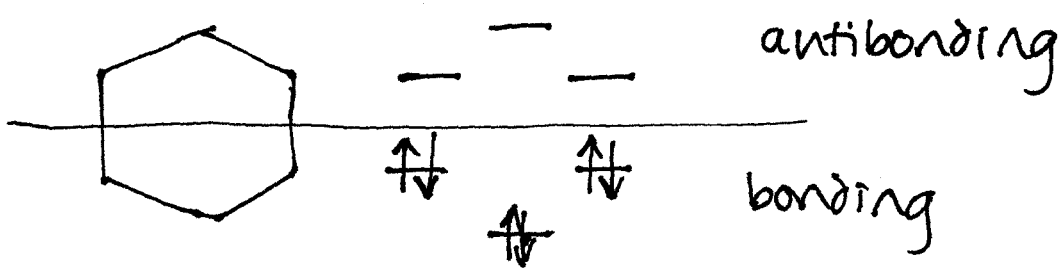
expect $\Delta H = 3 \times 28.6$ kcal/mol
$= 85.8$ kcal/mol (359 kJ/mol)

observe $\Delta H = 49.8$ kcal/mol (208 kJ/mol)

$\Rightarrow$ benzene is **36 kcal/mol** more stable than we expected.



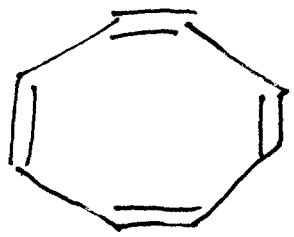
look @ benzene from an MO perspective.



All of the bonding orbitals are full.

CLOSED SHELL - very stable.

Consider 1,3,5,7-cyclooctatetraene (COT)



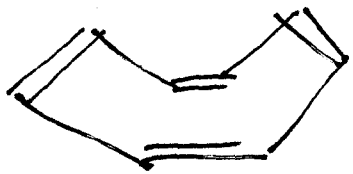
add Br_2/CCl_4 - decolorizes (adds Br_2)

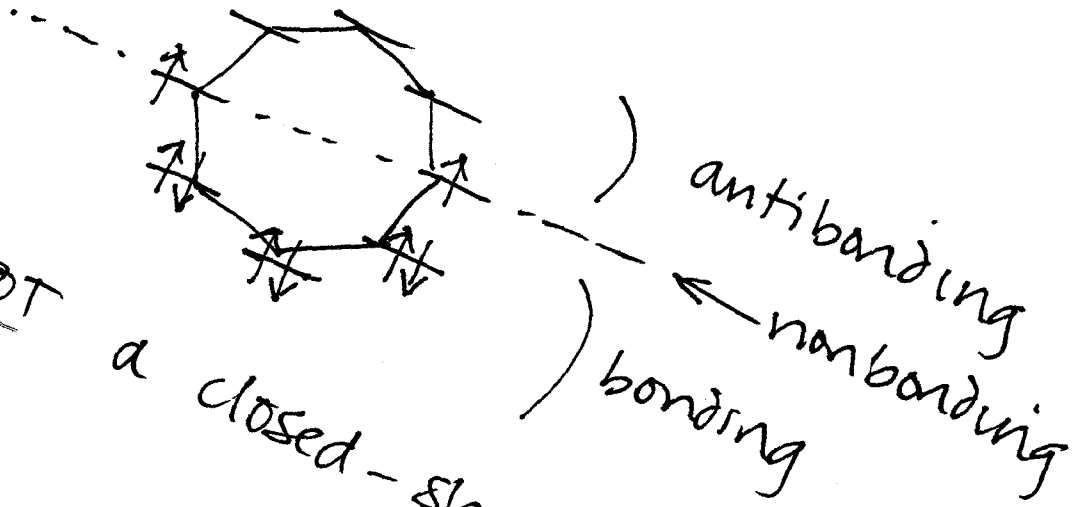
H_2/cat. - fast rxn

aq. $KMnO_4$ - see color change (vic. diol)

etc.

structure analysis shows: NOT planar.





NOT a closed-shell system.

⇒ concept of aromaticity must have something else going on.

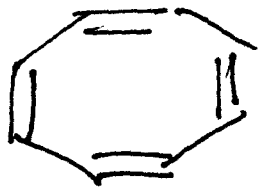
In 1931 Erich Hückel did a lot of math.

conclusion: cyclic systems w/ $4n+2$ π e's (n = integer: 0, 1, 2...) should be <u>aromatic</u>

cyclic systems w/ $4n$ π e's are called <u>antiaromatic</u>.

6 π e's $\quad 4n+2=6 \quad n=1$ integer

*aromatic



8 π e's $\quad 4n+2=8 \quad n=3/2$ not an integer

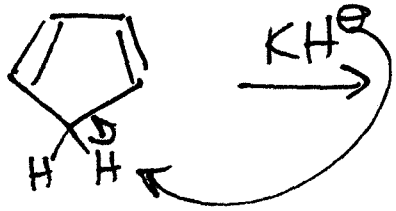
$4n=8 \quad n=2$

* antiaromatic.

4 πe's 4n (n=1) antiaromatic

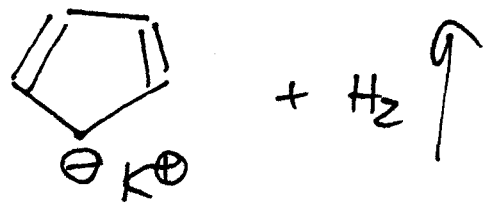
sp^3 carbon

nonaromatic



pka ~15

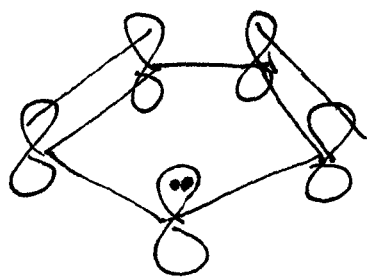
?



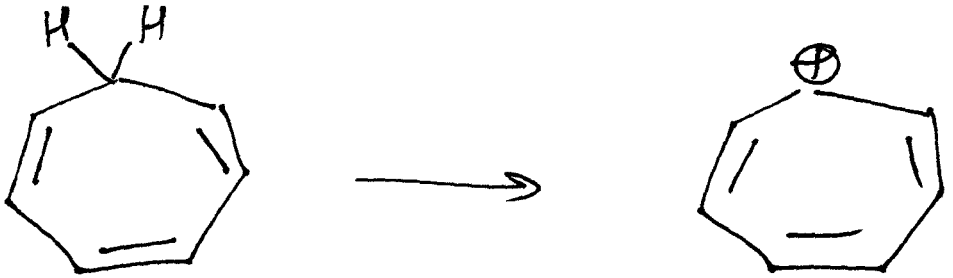
carbon-based cations + anions are sp^2

2 e' from each π bond
2 e' from ⊖ charge

6 e'

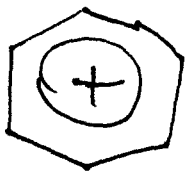


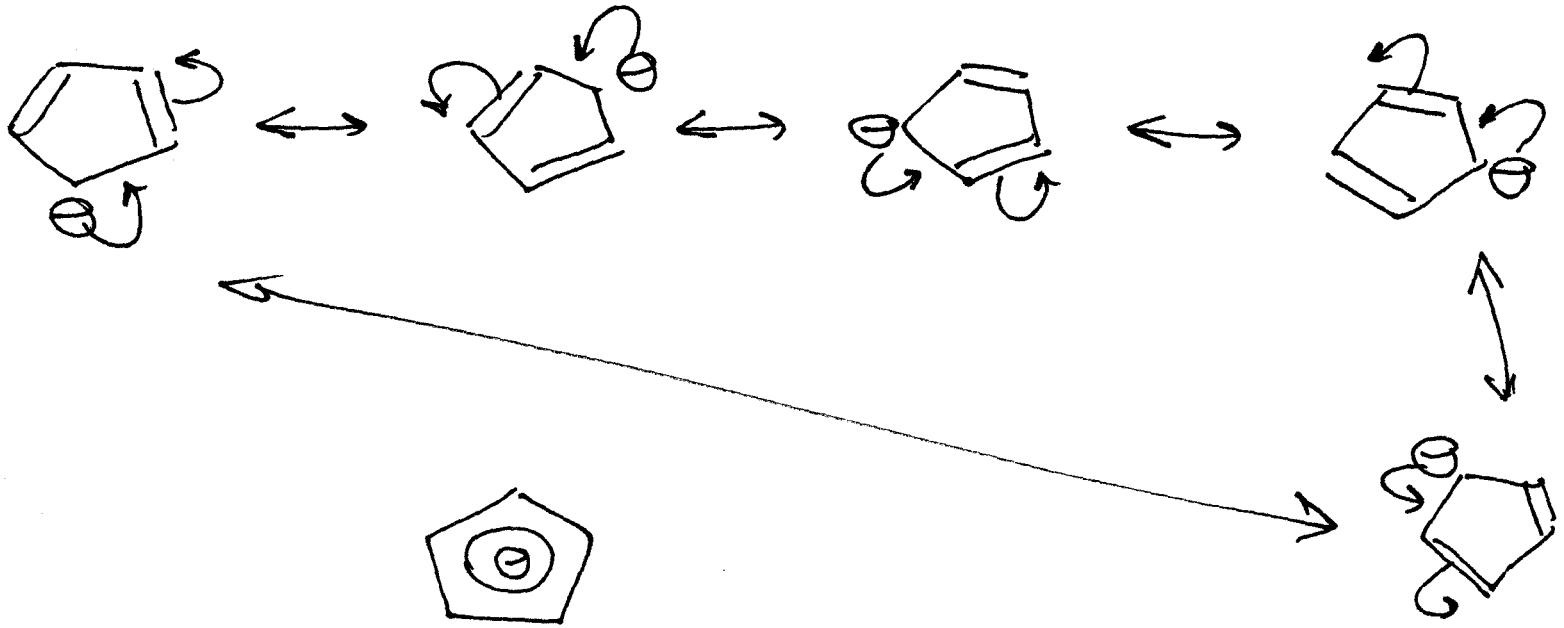
AROMATIC



6 π e's
AROMATIC

cycloheptatriene
(nonaromatic)



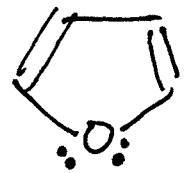


what about heterocyclic compounds?

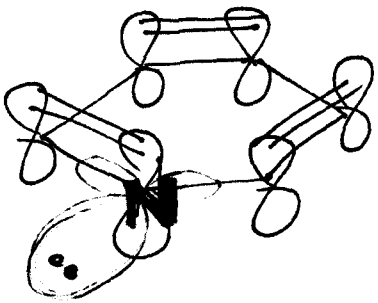
6 π e's
aromatic

pyridine

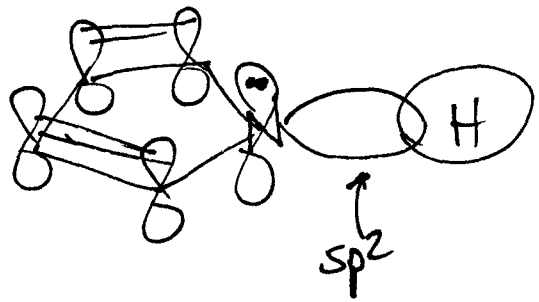
pyrrole

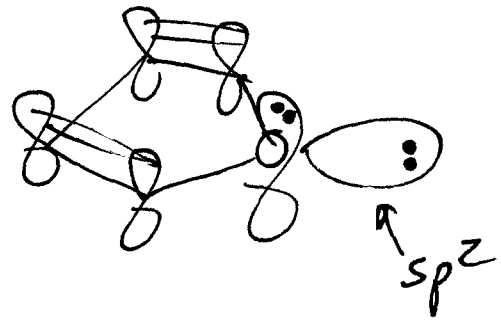


furan



lone pair is in an sp^2 hybrid orbital perp. to plane of p orbs.





6 e'
aromatic

1. Heteroatoms can be sp^2 hybridized if it benefits 'em.
2. If the heteroatom is part of a π bond
   DO NOT COUNT any lone pairs
3. If the heteroatom is NOT part of a π bond
   COUNT ONE lone pair (2 e')