Chapter 15 (pp. 498-515)

Benzene and Aromaticity

Suggested Problems:

15.4, 15.10, 15.19, 15.27, 15.31, 15.32, 15.33, 15.35, 15.36, 15.38, 15.41

15A Introduction and Nomenclature

15B Stabilityof Aromatic Compounds/Huckel's Rule

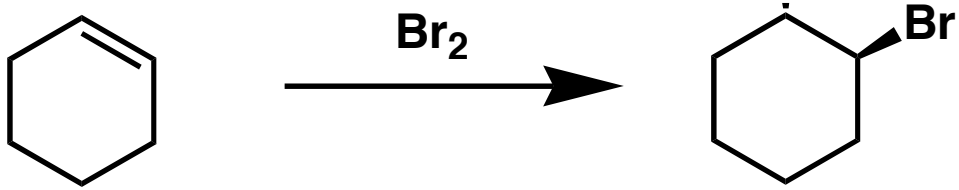
15C Aromatic Ions

15D Aromatic Heterocycles

15E Polycyclic Aromatic Compounds

Effect of Aromatic Stabilization on Reactions with Benzene

ADDITION



Bonds broken	Bonds made
π bond Br-Br bond	2 C-Br

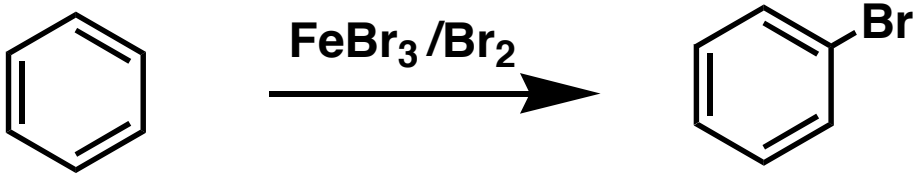
No reaction

If reaction occurred

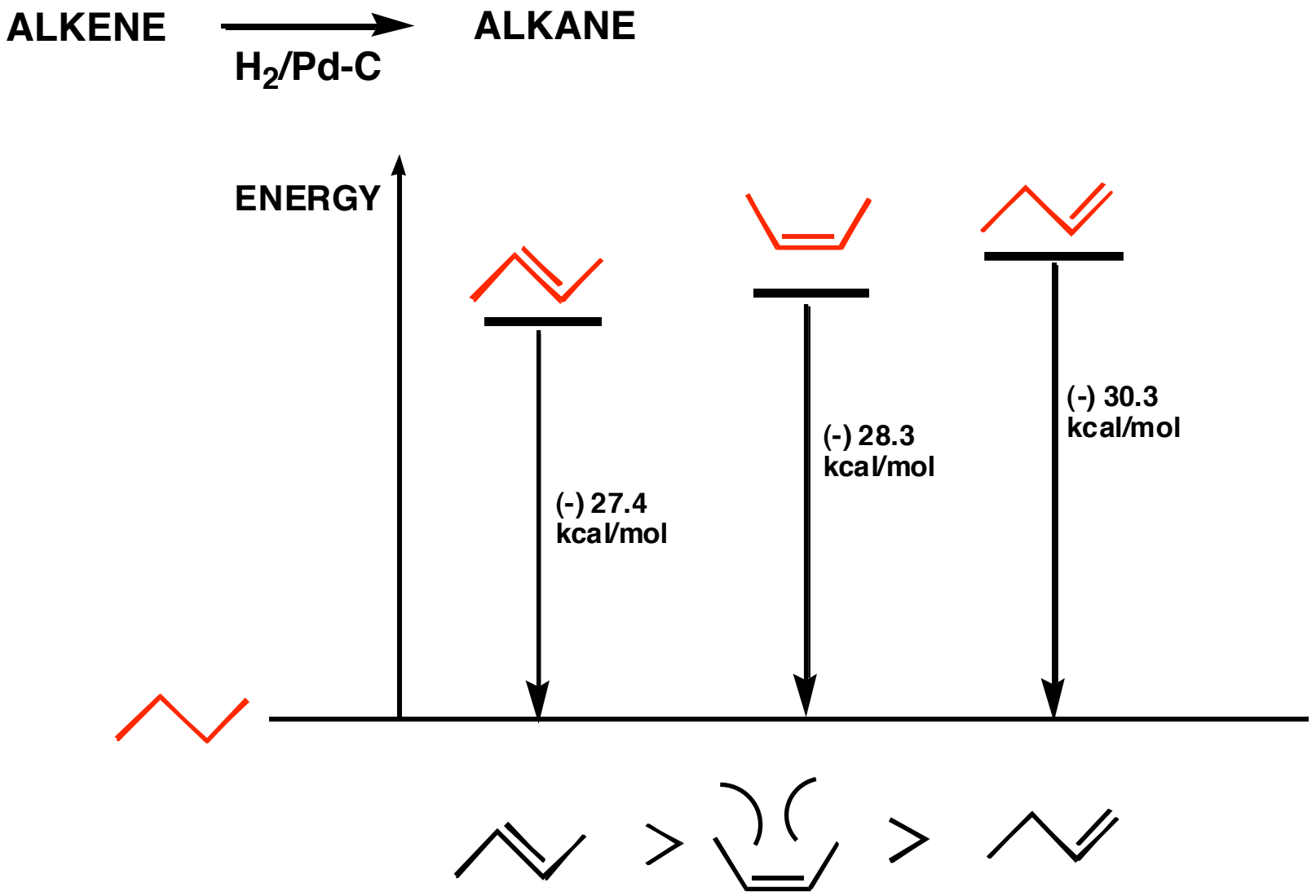
Bonds broken	Bonds made
π bond Br-Br bond	2 C-Br

BUT would lose AROMATIC STABILIZATION

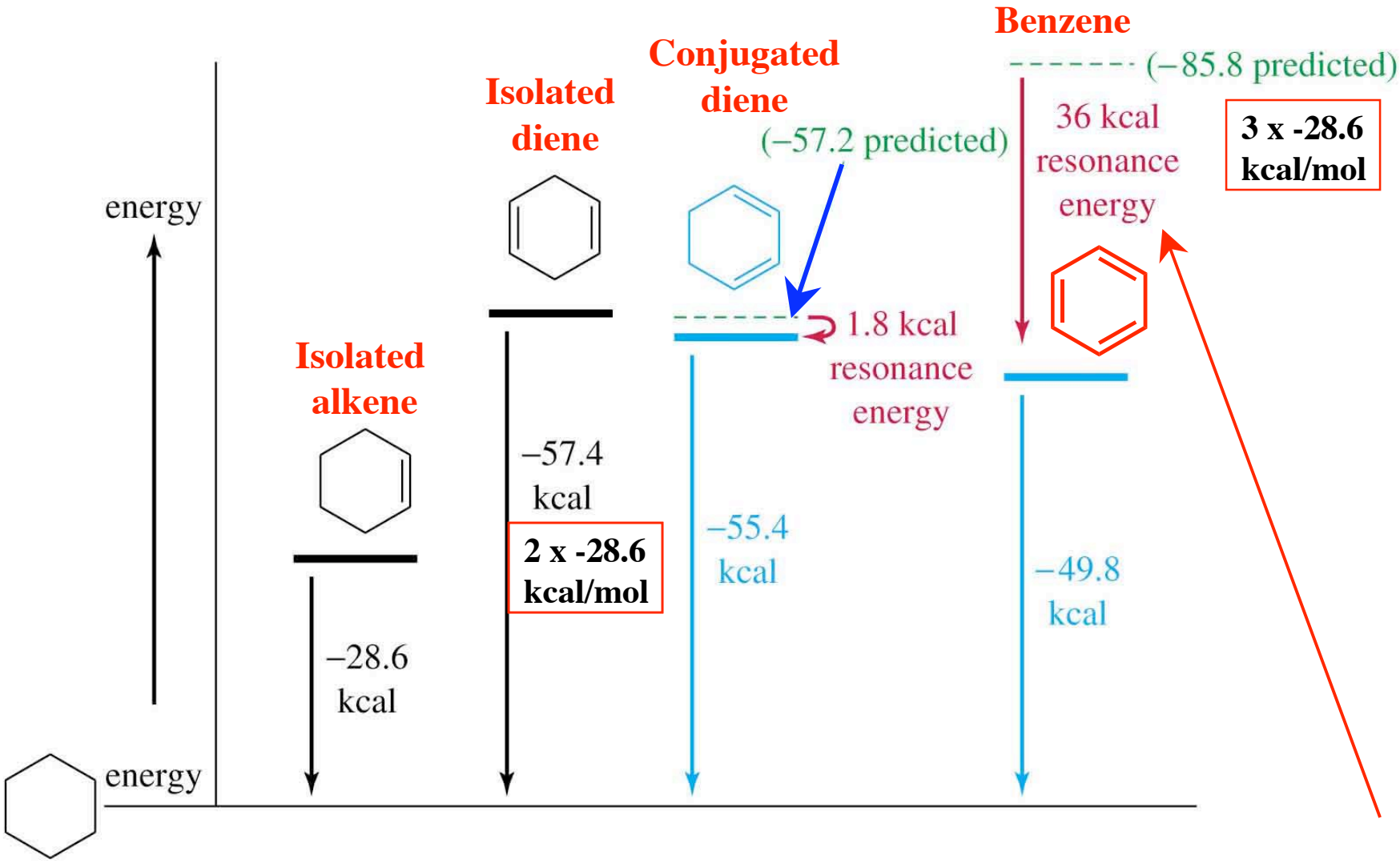
INSTEAD - SUBSTITUTION



Heat evolved upon catalytic hydrogenation (ΔH^{o})
A MEASURE OF ALKENE STABILITY

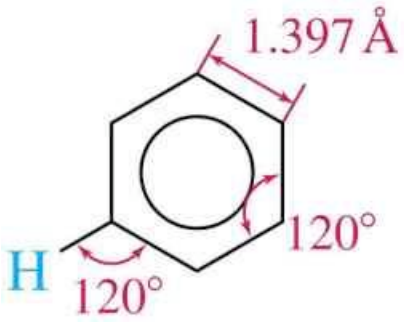


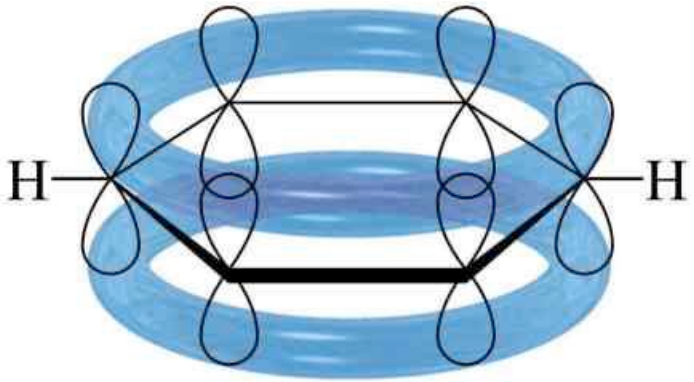
Catalytic hydrogenation of benzene and various cyclohexenes

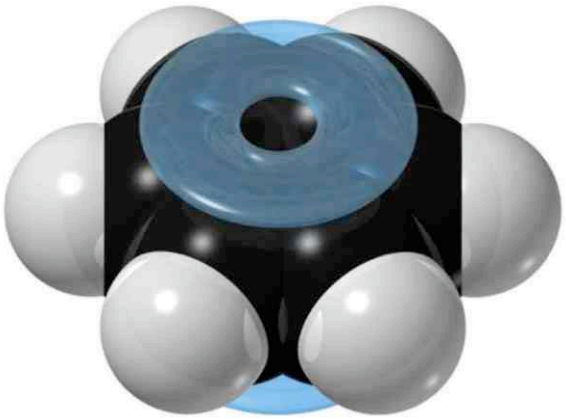


Magnitude of aromatic stabilization = 36 kcal/mol

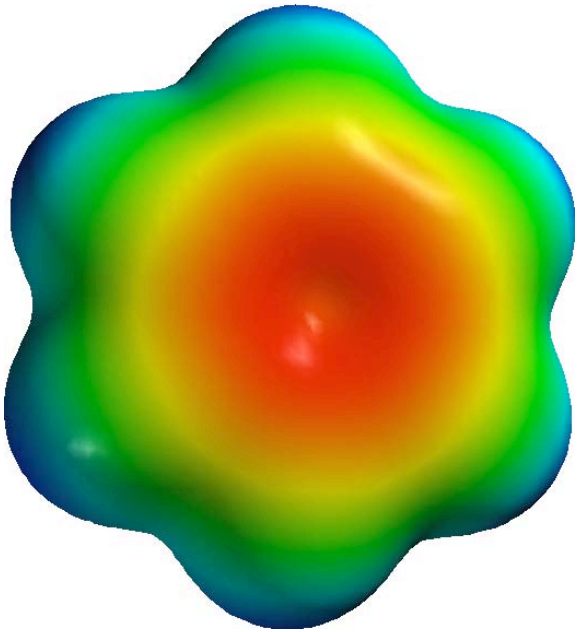
Benzene (C_6H_6) is not "cyclohexatriene!





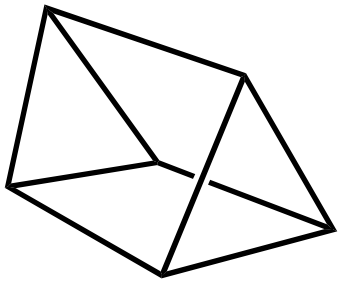


C=C 1.34Å
C-C 1.54Å



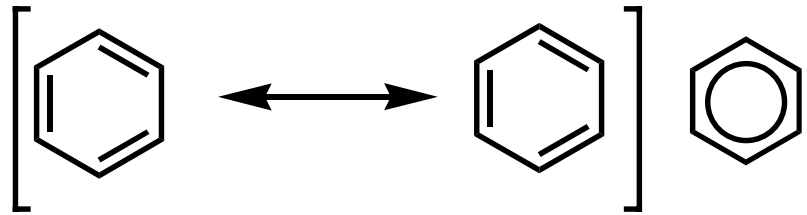
Each sp^2 hybridized C in the ring has an unhybridized p orbital perpendicular to the ring which overlaps around the ring

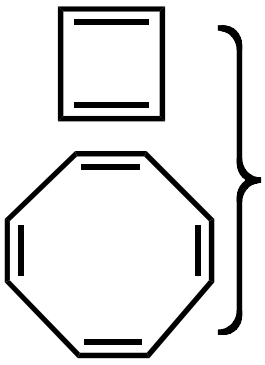
1879
Landenberg



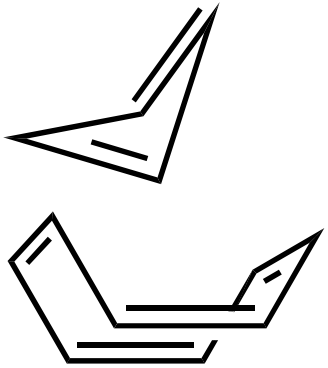
Criteria for Aromaticity

1. Cyclic
2. Unhybridized p orbital in continuous cyclic system
3. Able to adopt a planar geometry
4. Fulfills Huckel's Rule and includes (4n + 2) electrons
   n = 0, 1, 2, 3, 4…….. (the 2, 6, 10, 14….electrons)





mix of single and double bonds non-planar geometry



•Initially, all cyclic conjugated hydrocarbons were proposed to be aromatic

•However, cyclobutadiene is so reactive that it dimerizes before it can be isolated

•Cyclooctatetraene adds Br_2 readily.

•Look at Molecular Orbitals (MOs) to explain aromaticity in benzene-like molecules

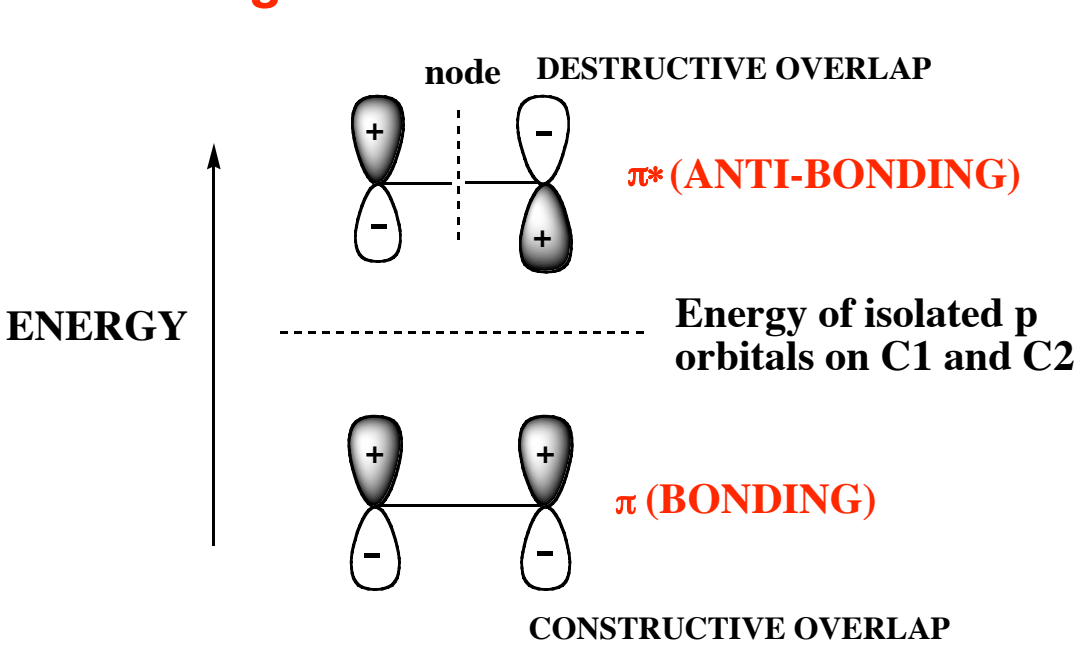
Constructing Molecular Orbitals

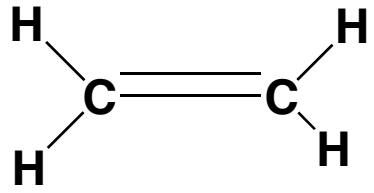
- π molecular orbitals are the sideways overlap of *p* orbitals

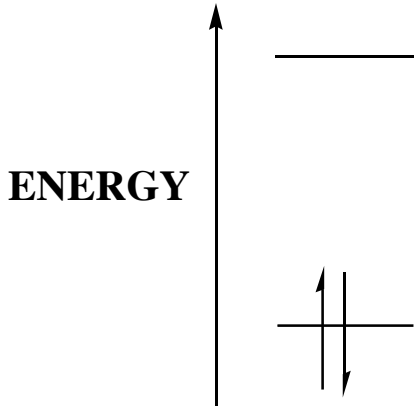
- *p* orbitals have 2 lobes. Plus (+) and minus (-) indicate the opposite phases of the wave function, not electrical charge

- When lobes overlap constructively, (+ and +, or - and -) a bonding MO is formed

- When + and - lobes overlap, waves cancel out and a node forms; antibonding MO

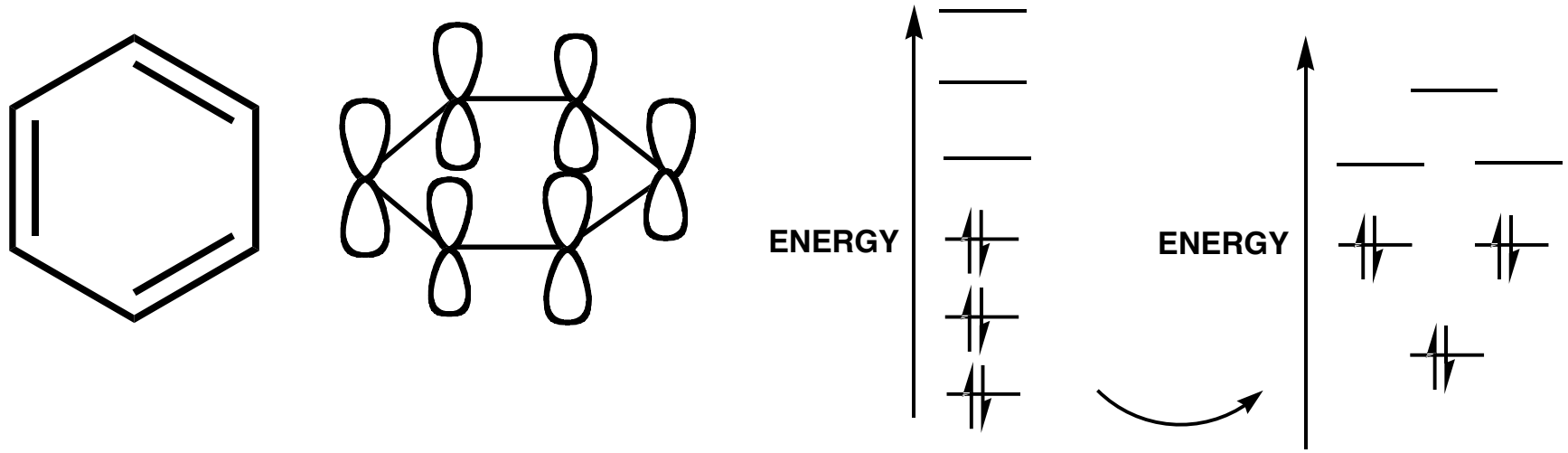






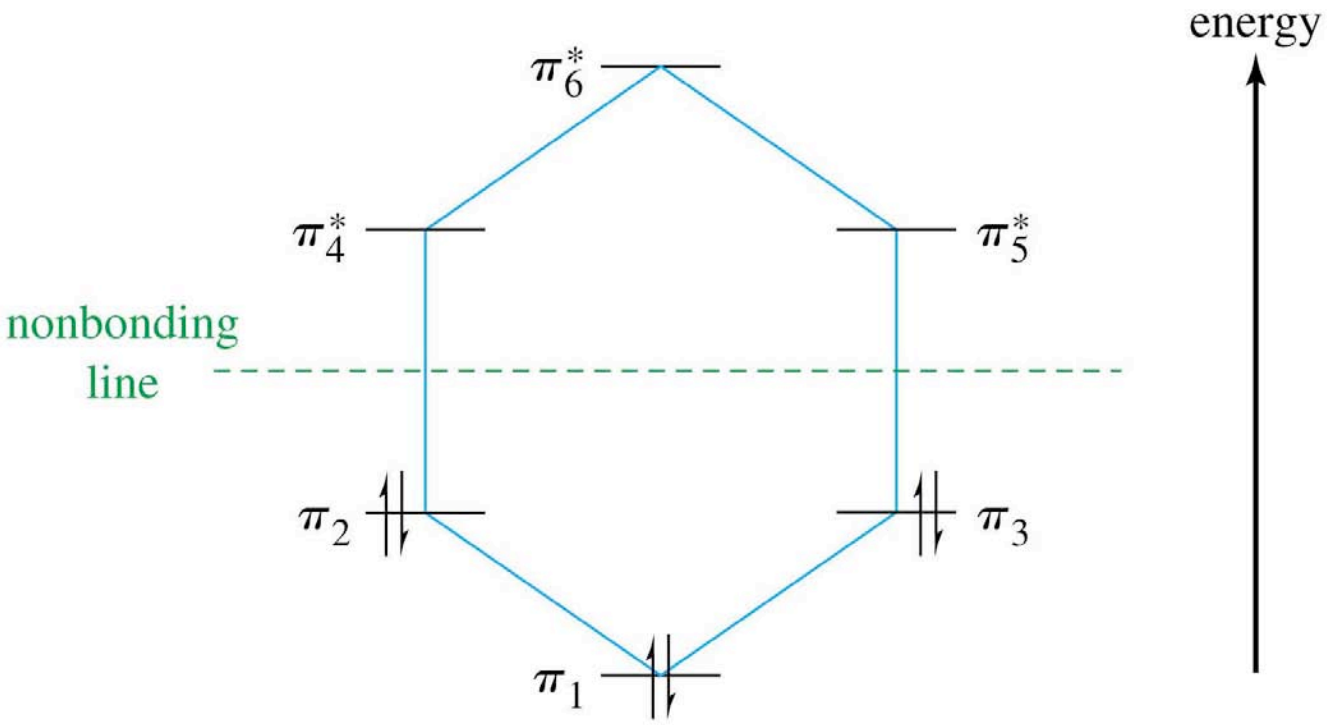
MO Rules for Benzene

- Six overlapping p orbitals must form six molecular orbitals
- Three will be bonding, three antibonding
- Lowest energy MO will have all bonding interactions, no nodes
- As energy of MO increases, the number of nodes increases
- System symmetric so 2 pairs of degenerate orbitals



Energy Diagram for Benzene

6 atomic orbitals - 6 molecular orbitals
System symmetric so 2 pairs of degenerate orbitals



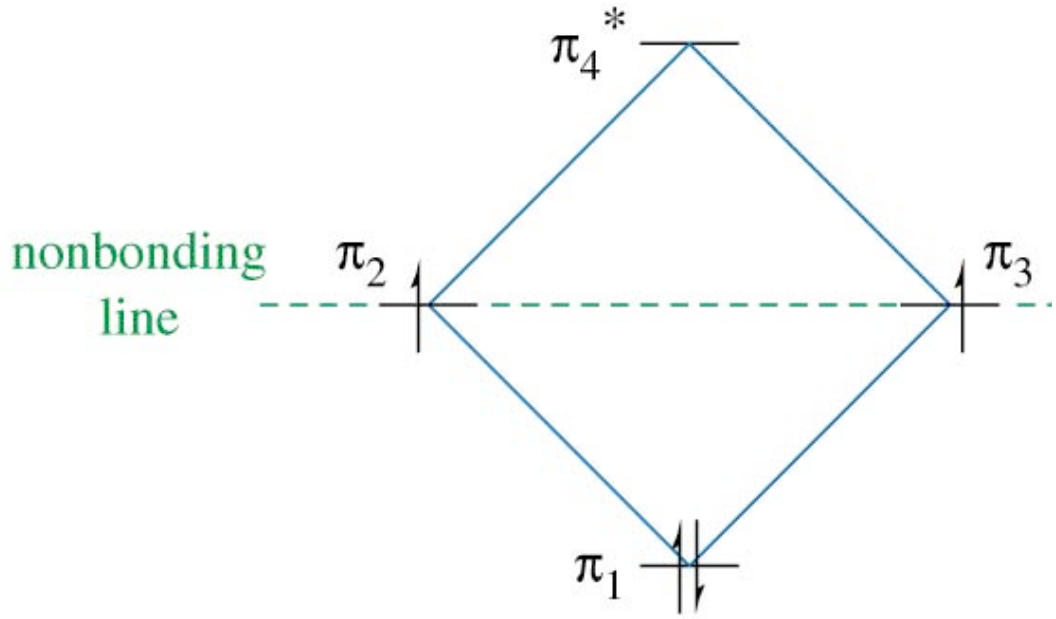
The six electrons fill three bonding pi orbitals.

All bonding orbitals are filled ("closed shell"), an extremely stable arrangement (AROMATIC STABILIZATION).

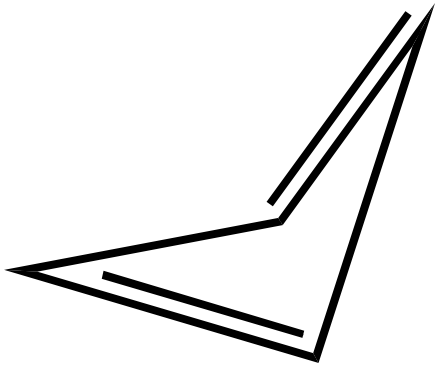
Energy Diagram for Cyclobutadiene

Following Hund's rule, two electrons are in separate orbitals because they are at same energy.

Most stable if filled with an electron pair (as with benzene)

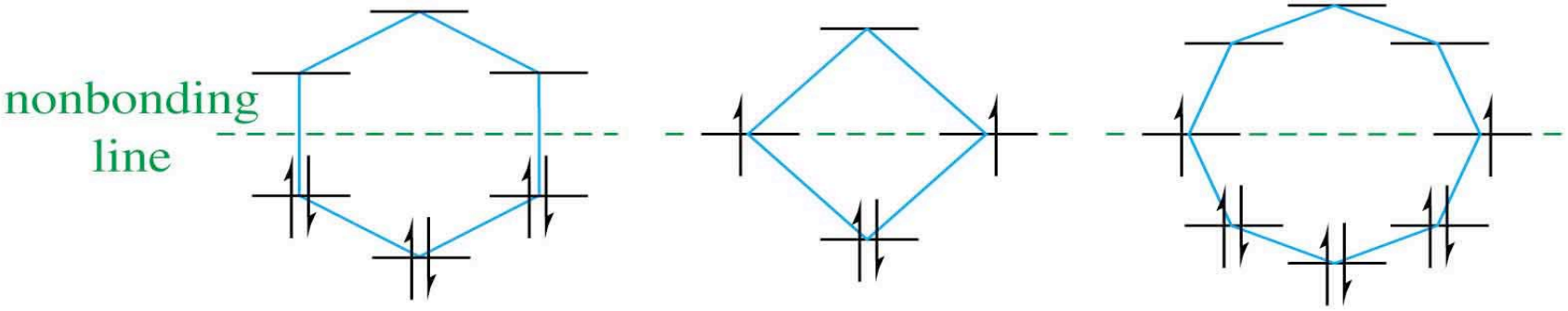


If cyclobutadiene adopted a coplanar geometry - two of the molecular orbitals would each have a single unpaired electron - very unstable. Applies to any (4 n) system
Cyclobutadiene is ANTIAROMATIC



Aromatic

Anti-aromatic

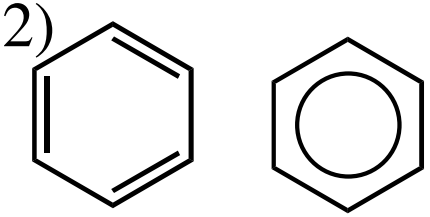


benzene

cyclobutadiene

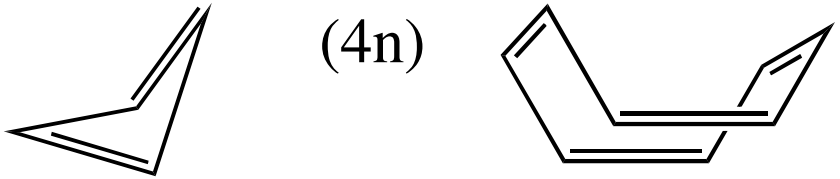
cyclooctatetraene

(4n + 2)



All bond lengths same

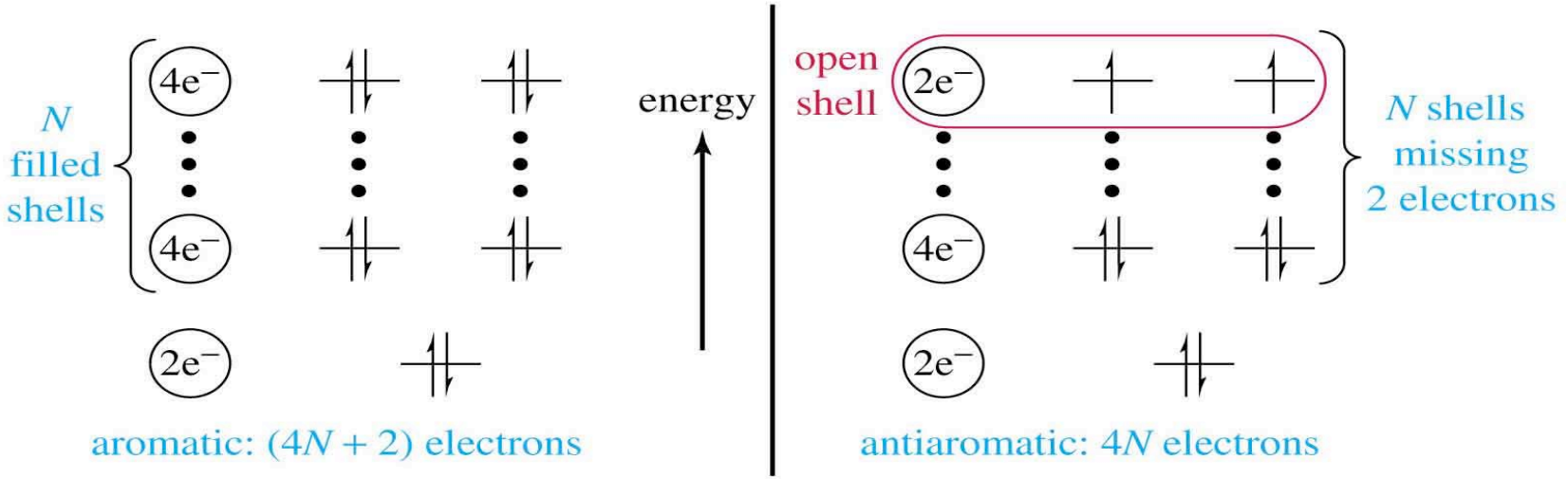
(4n)



Combination of single and double bonds

(vacant orbitals not shown)

(vacant orbitals not shown)

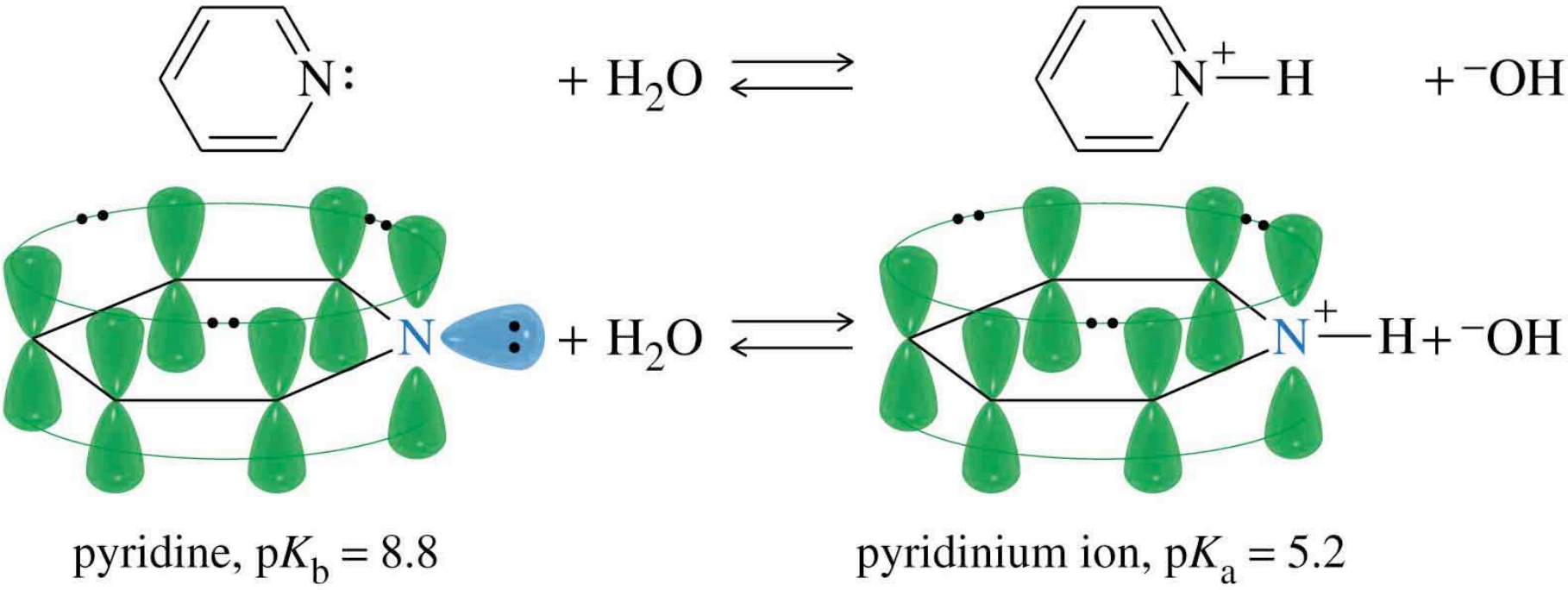


aromatic: (4*N* + 2) electrons

antiaromatic: 4*N* electrons

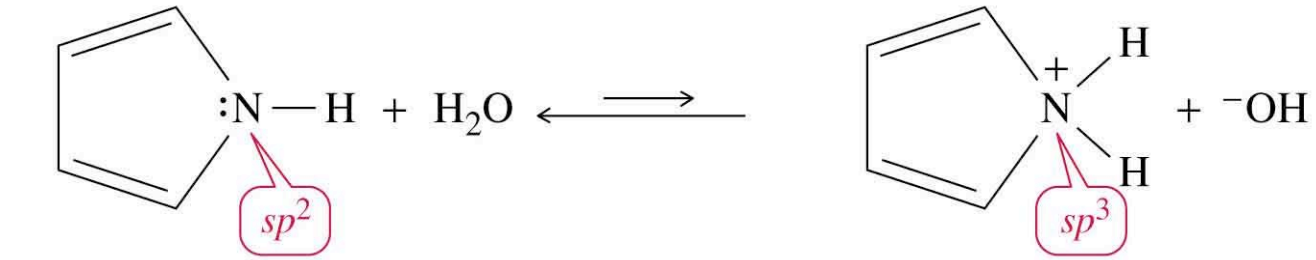
The Acidity of the Pyridinium Ion

- Heterocyclic aromatic compound.
- Nonbonding pair of electrons in sp^2 orbital, so weak base, $pK_b = 8.8$.



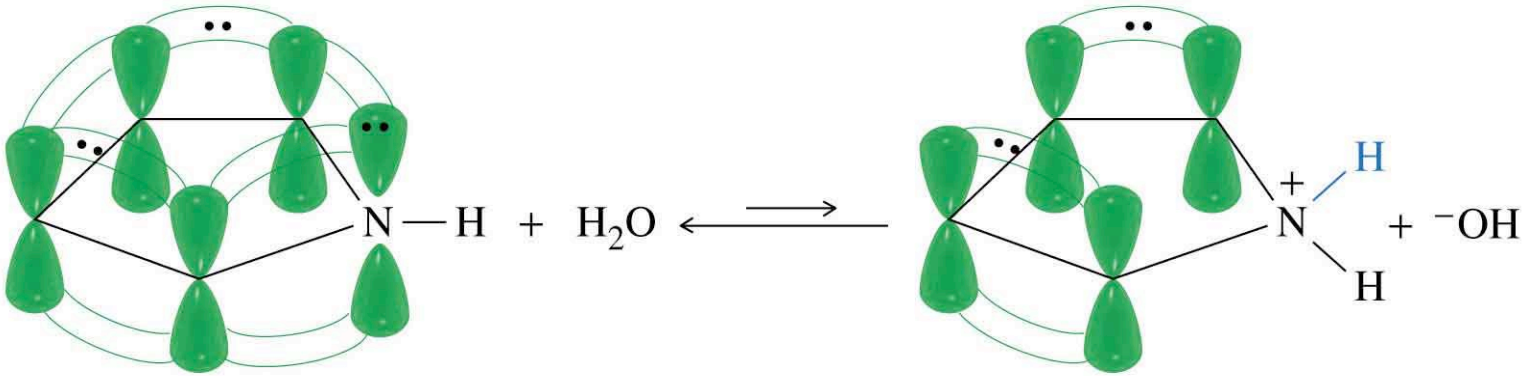
The Acidity of Protonated Pyrrole

Also aromatic, but lone pair of electrons is delocalized: much weaker base.



pyrrole, pK_b = 13.6
(weak base)

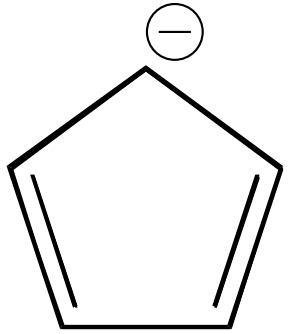
N-protonated pyrrole, pK_a = 0.4
(strong acid)

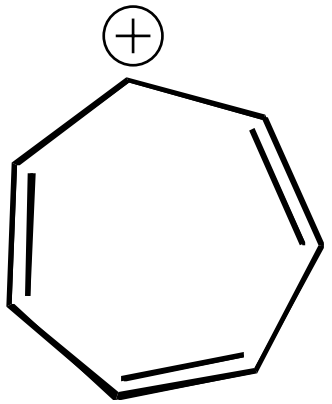


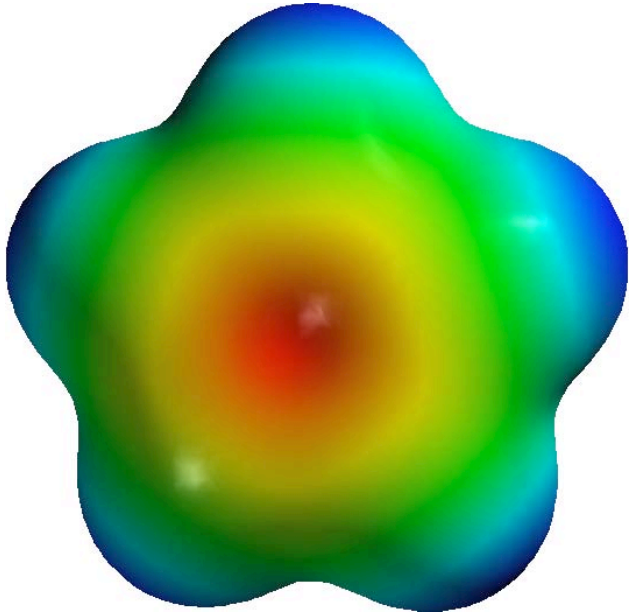
pyrrole
(aromatic)

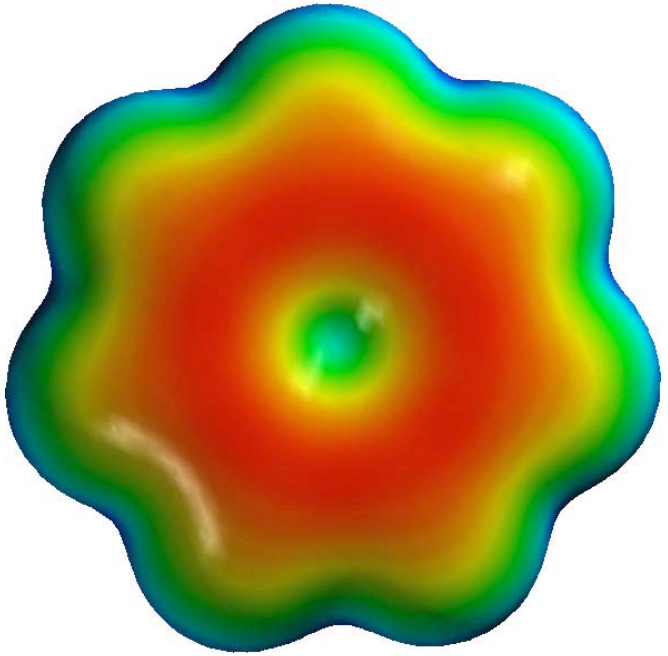
N-protonated pyrrole
(nonaromatic)

Aromatic Cations and Anions

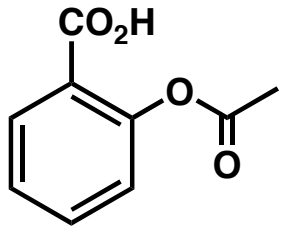




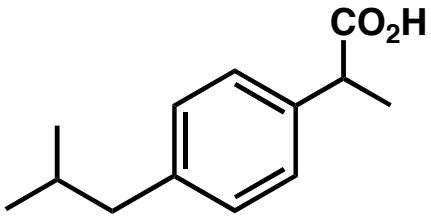




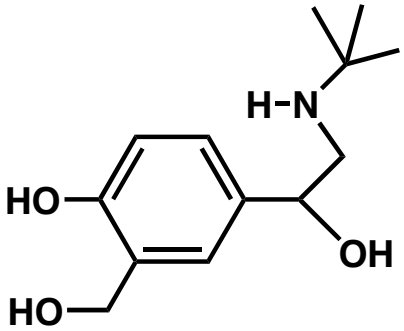
Many Benzene Derivatives are Useful Drugs



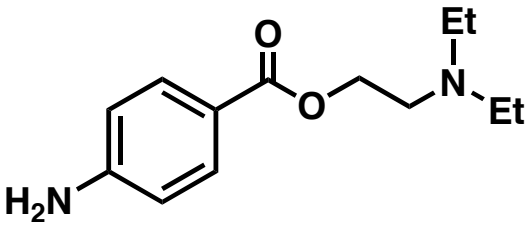
acetyl salicylic acid
ASPIRIN



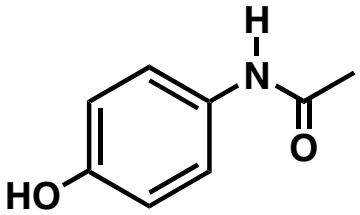
ibuprofen
ADVIL



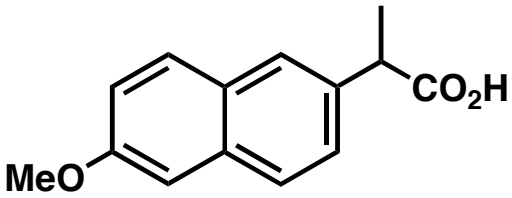
bronchodilator
ALBUTEROL



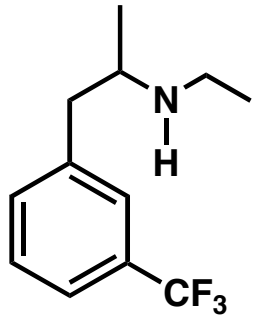
procaine
NOVOCAINE



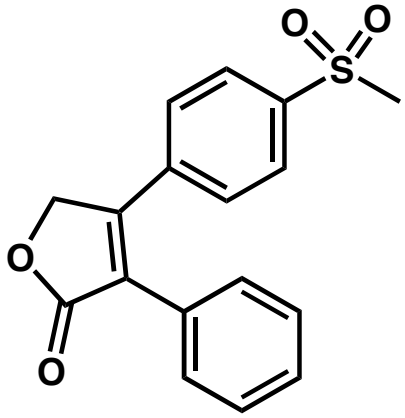
acetaminophen
TYLENOL



naproxen
ALEVE



appetite suppresant
FENFLURAMINE



rocecoxib
VIOXX