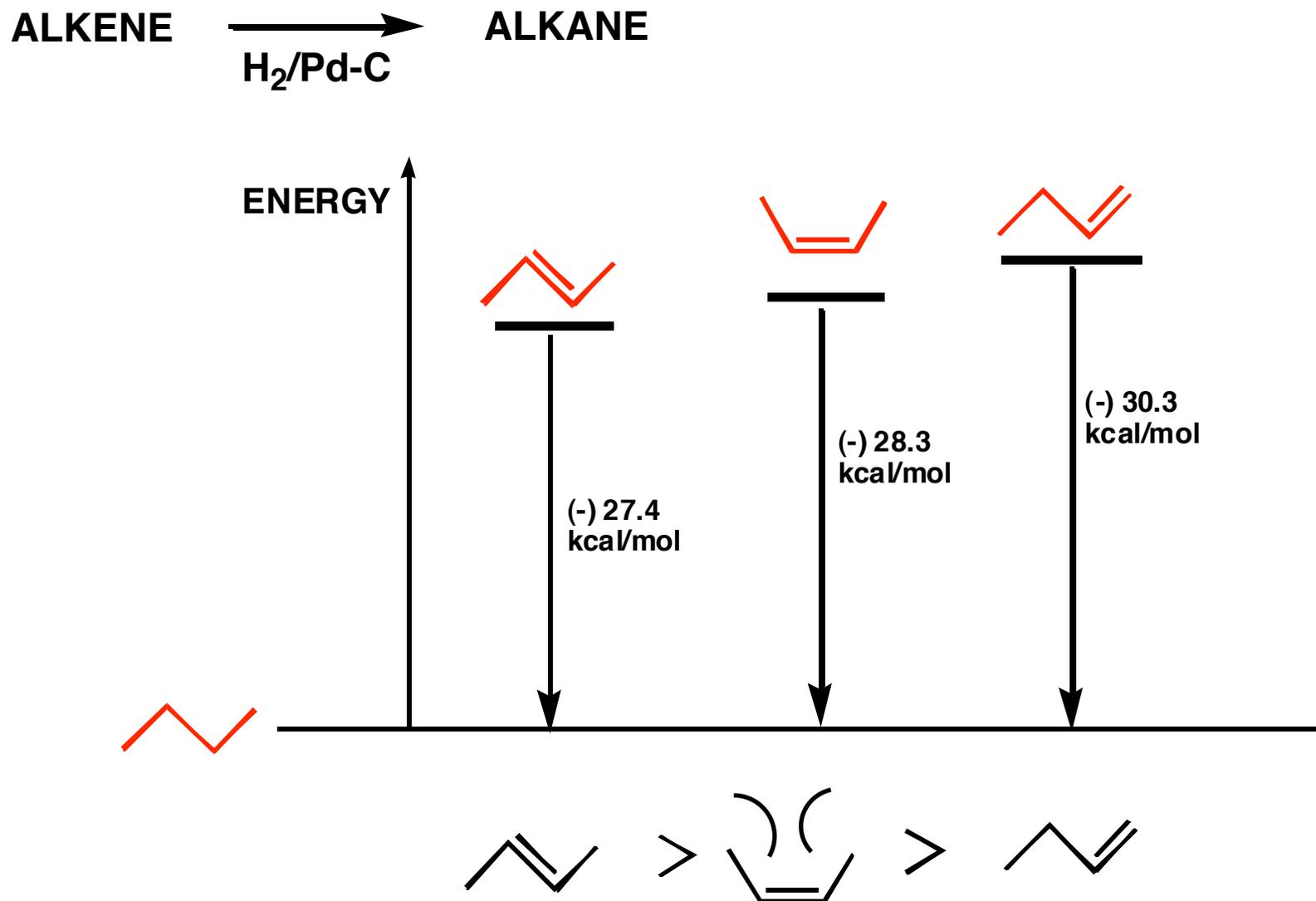
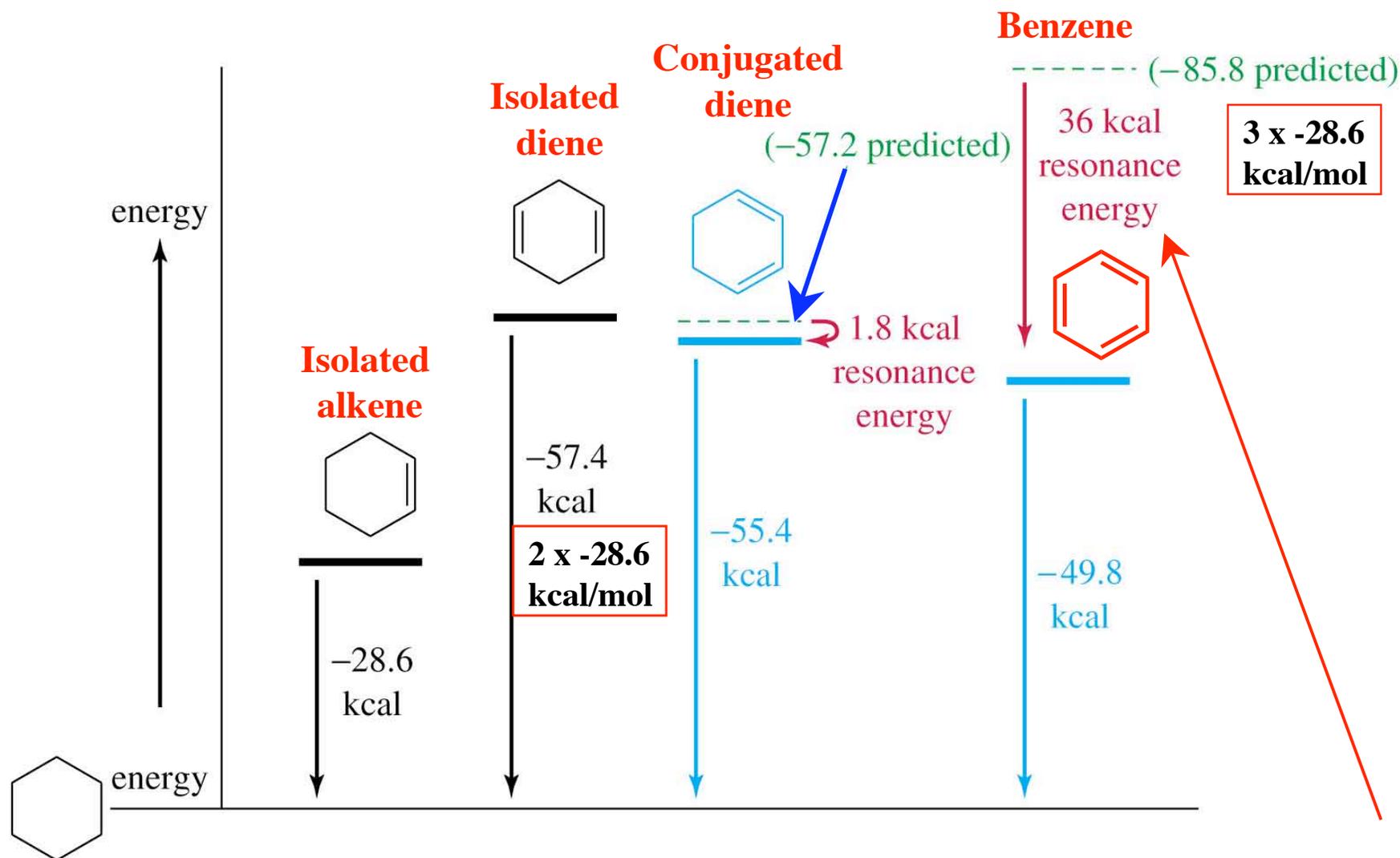


Heat evolved upon catalytic hydrogenation (ΔH°) A MEASURE OF ALKENE STABILITY

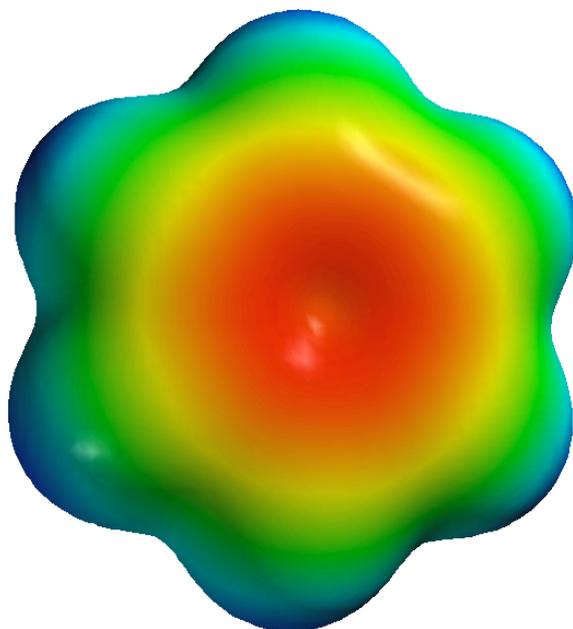
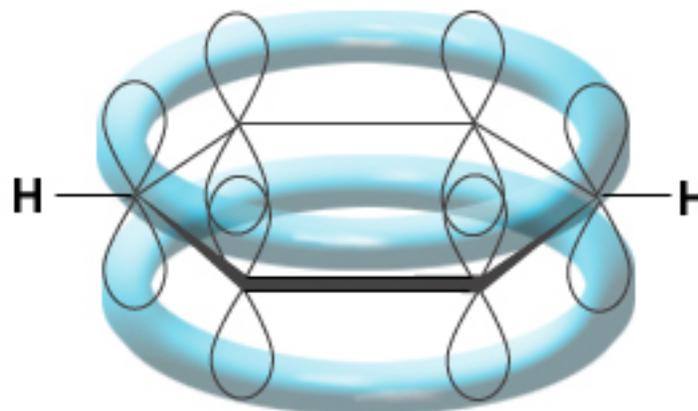
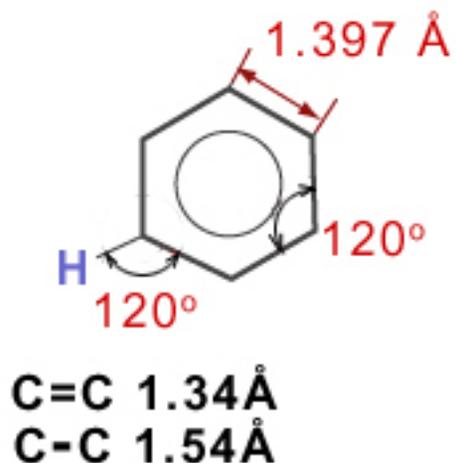


Catalytic hydrogenation of benzene and various cyclohexenes



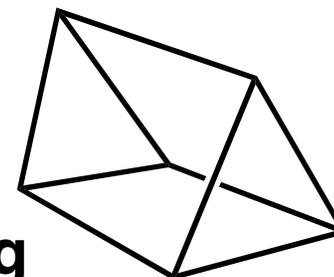
Magnitude of aromatic stabilization = 36 kcal/mol

Benzene (C_6H_6) is not “cyclohexatriene!”



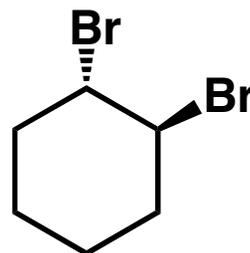
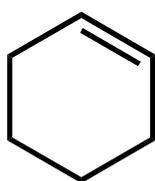
Each sp^2 hybridized C in the ring has an unhybridized p orbital perpendicular to the ring which overlaps around the ring

1879
Landenberg



EFFECT OF AROMATIC STABILIZATION ON REACTIONS OF BENZENE (and other aromatic compounds)

ADDITION

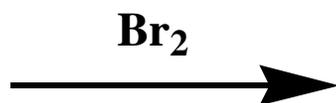


Bonds
broken

□ bond
Br-Br bond

Bonds
made

2 C-Br

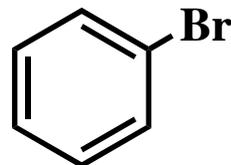
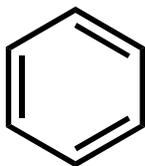


No reaction

If reaction occurred

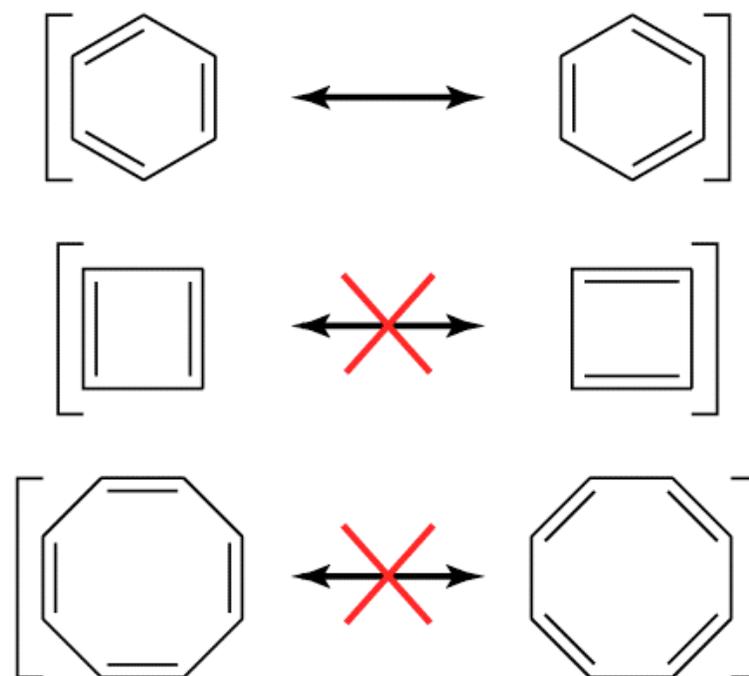
□ bond
Br-Br bond
BUT would also lose
AROMATIC
STABILIZATION

INSTEAD - SUBSTITUTION



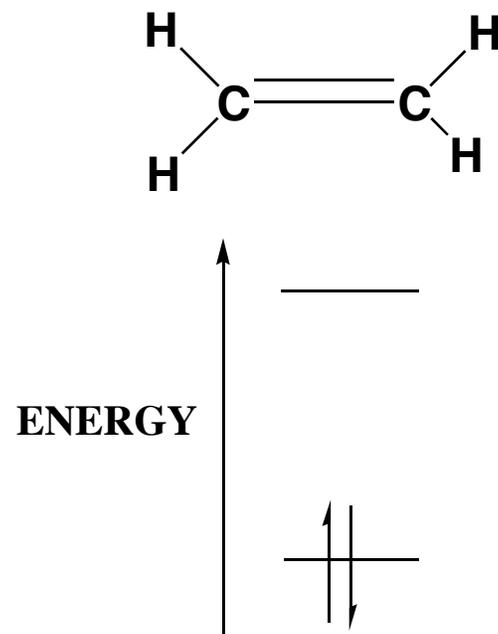
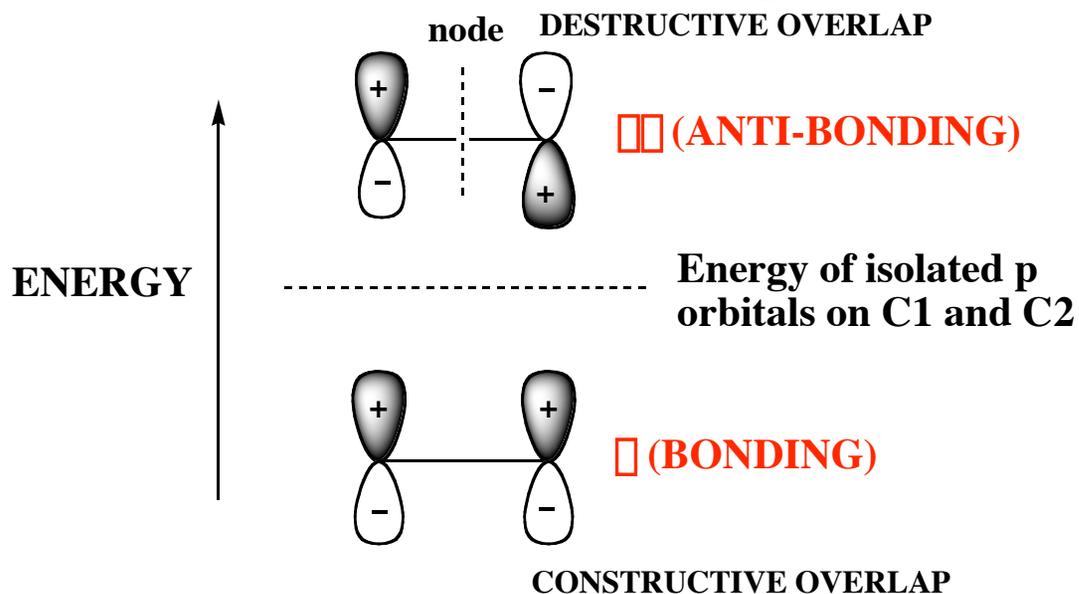
Annulenes

- Initially, all cyclic conjugated hydrocarbons were proposed to be aromatic.
- However, cyclobutadiene is so reactive that it dimerizes before it can be isolated.
- And cyclooctatetraene adds Br_2 readily.
- Look at Molecular Orbitals (MO's) to explain aromaticity in benzene-like molecules.



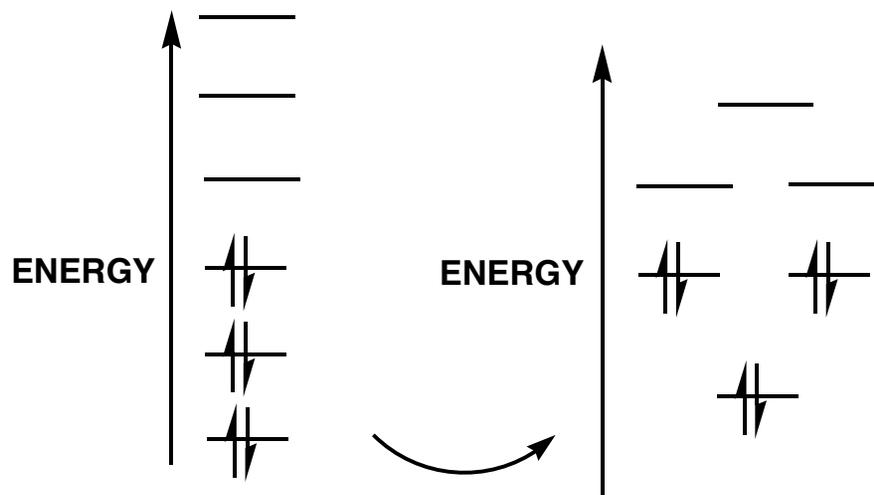
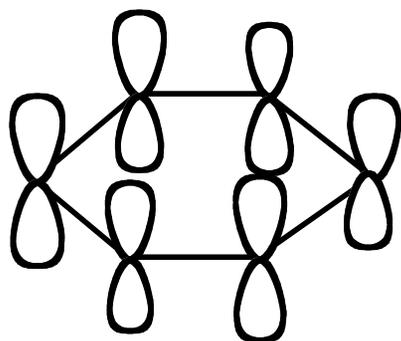
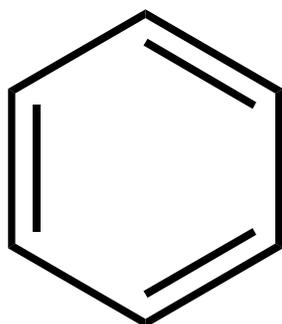
Constructing Molecular Orbitals

- Pi 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

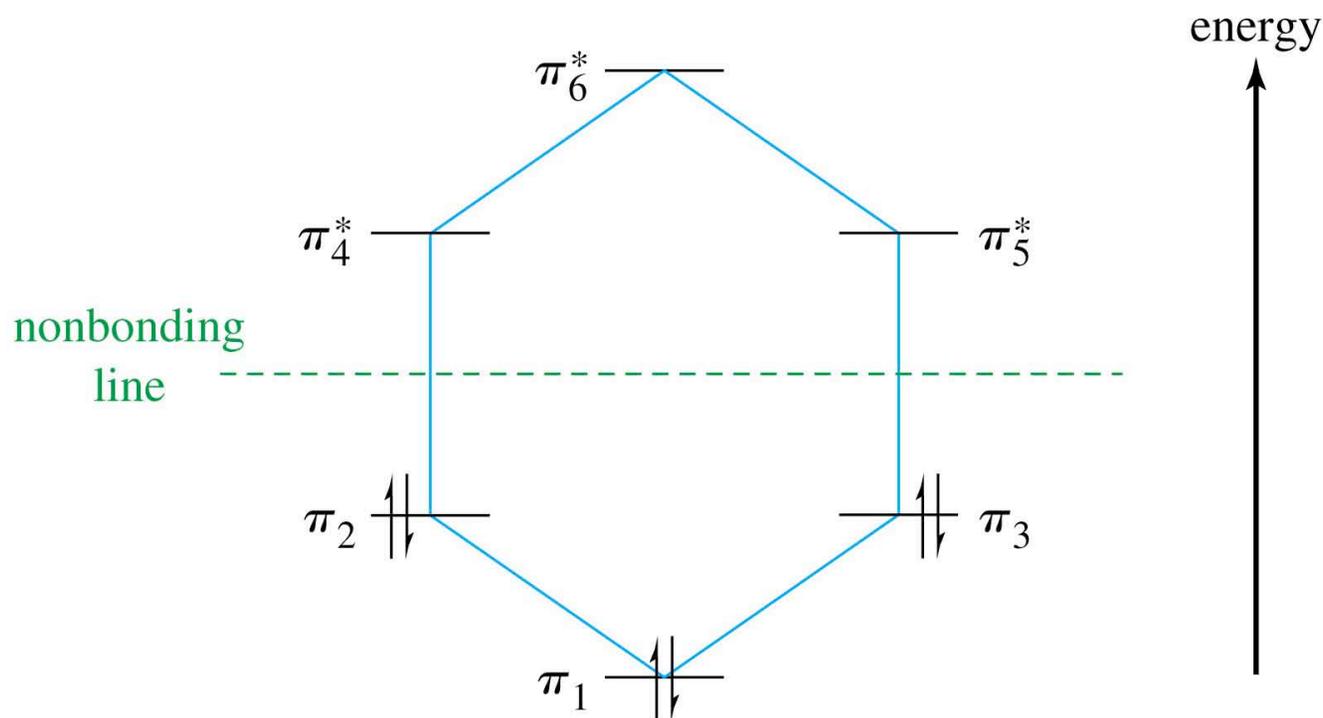


See 16.3 (Wade)

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**).

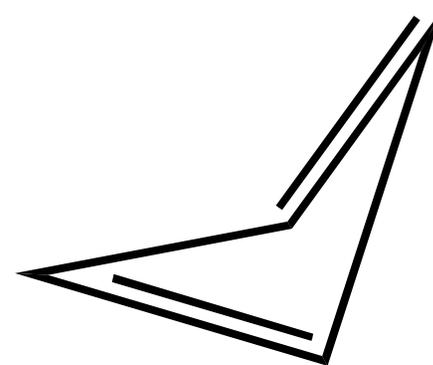
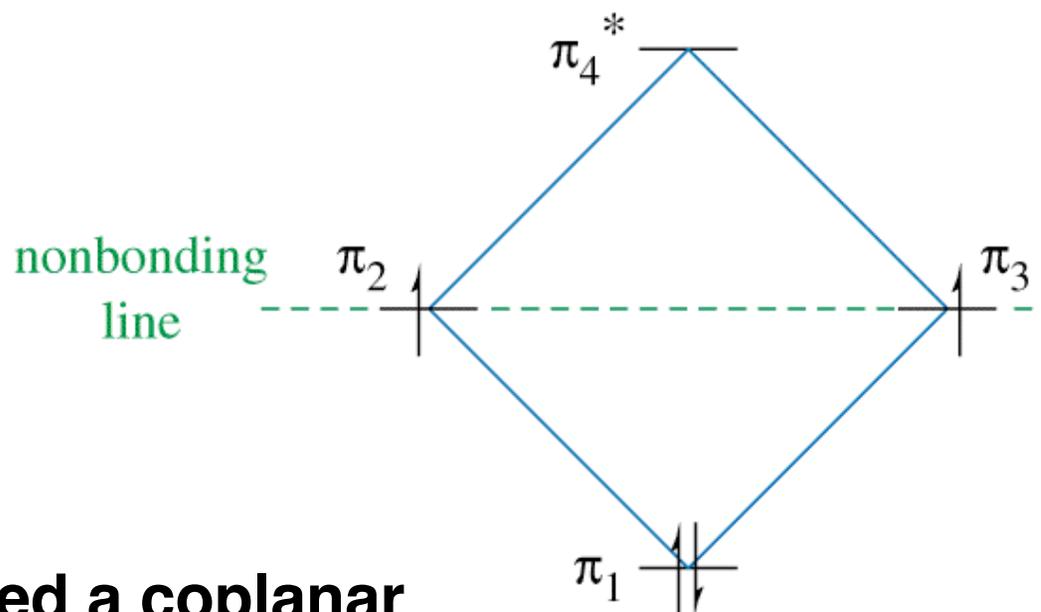
Energy Diagram for Cyclobutadiene

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)

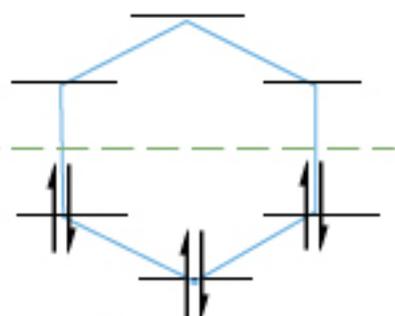
If cyclobutadiene adopted a coplanar geometry - two of the molecular orbitals would each have a single unpaired electron - very unstable. Applies to any $(4n)$ system

Cyclobutadiene is ANTIAROMATIC

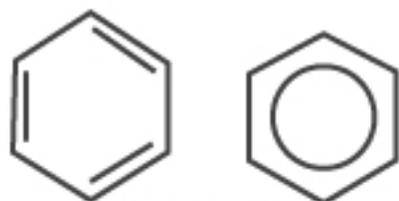


Aromatic

Nonbonding line



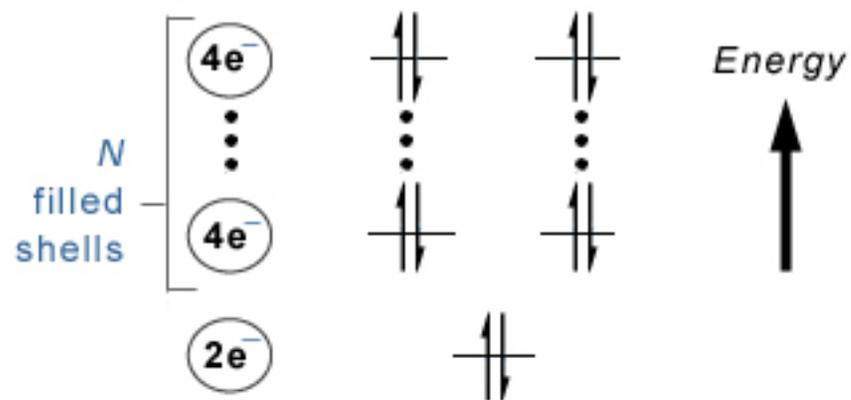
Benzene



$$(4n + 2)$$

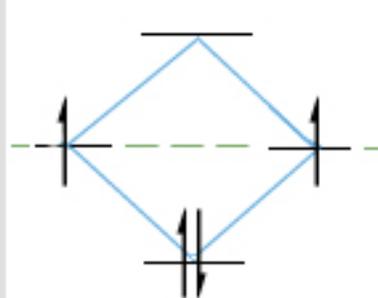
All bonds same length

(vacant orbitals not shown)

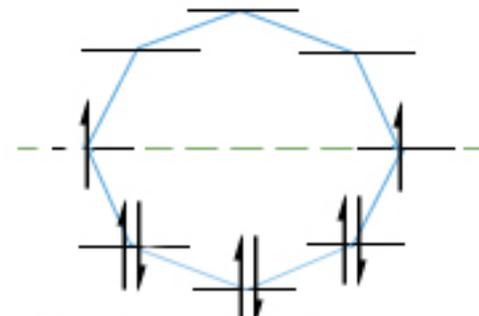


Aromatic: $(4N + 2)$ electrons

Anti-aromatic



Cyclobutadiene



Cyclooctatetraene

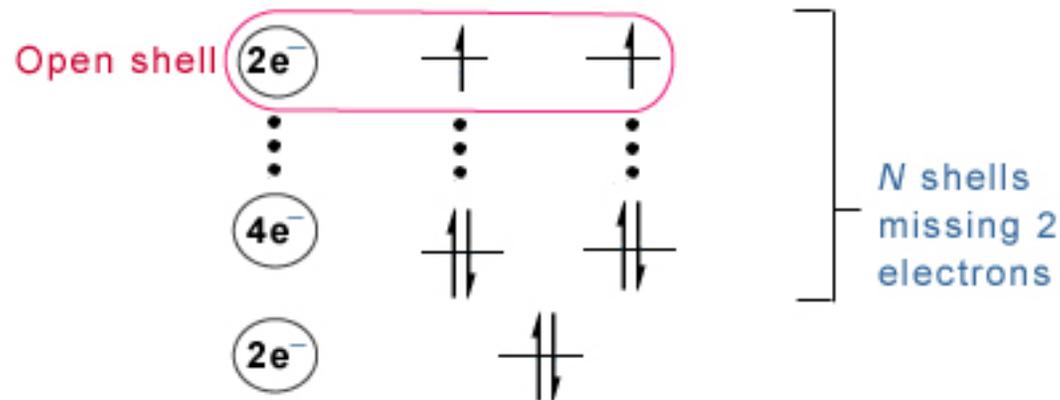


$$(4n)$$

Combination of single and double bonds



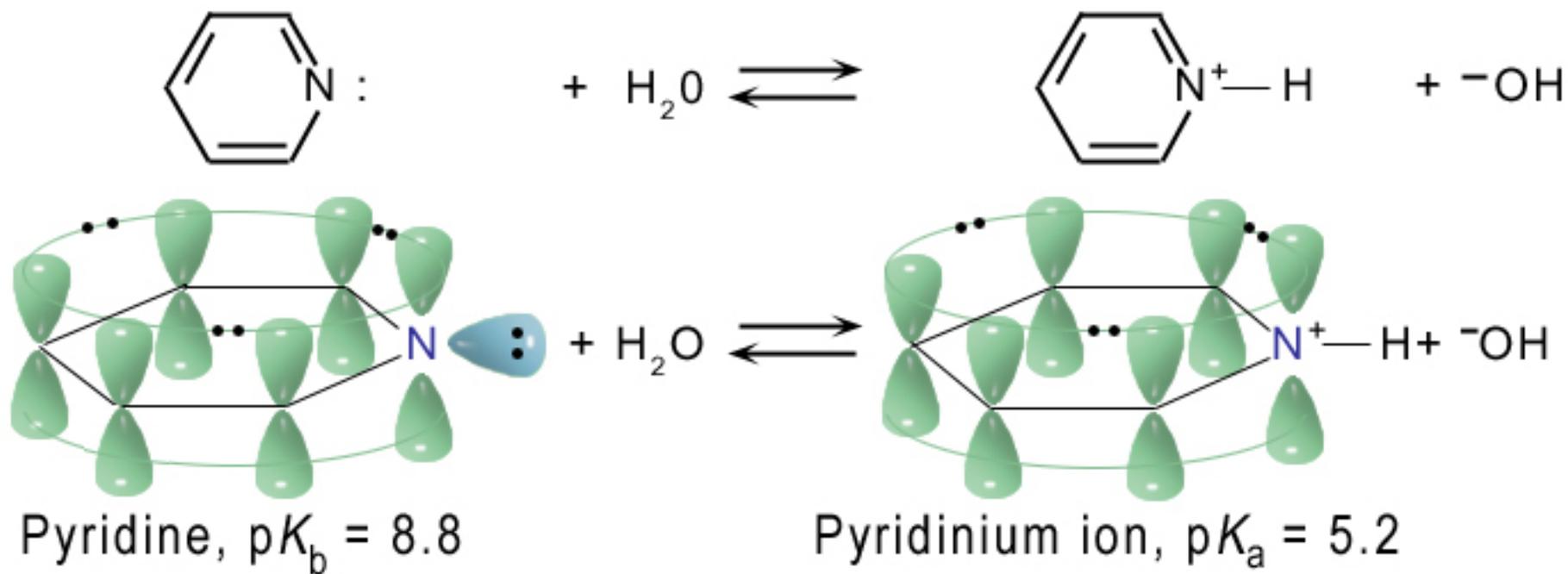
(vacant orbitals not shown)



Anti-aromatic: $4N$ electrons

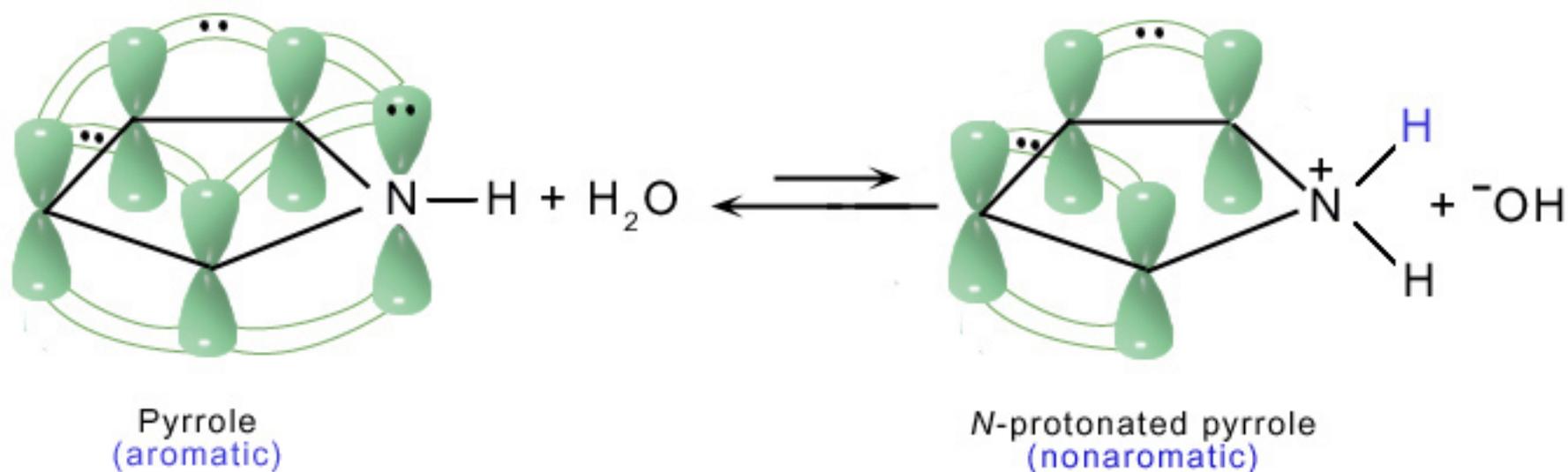
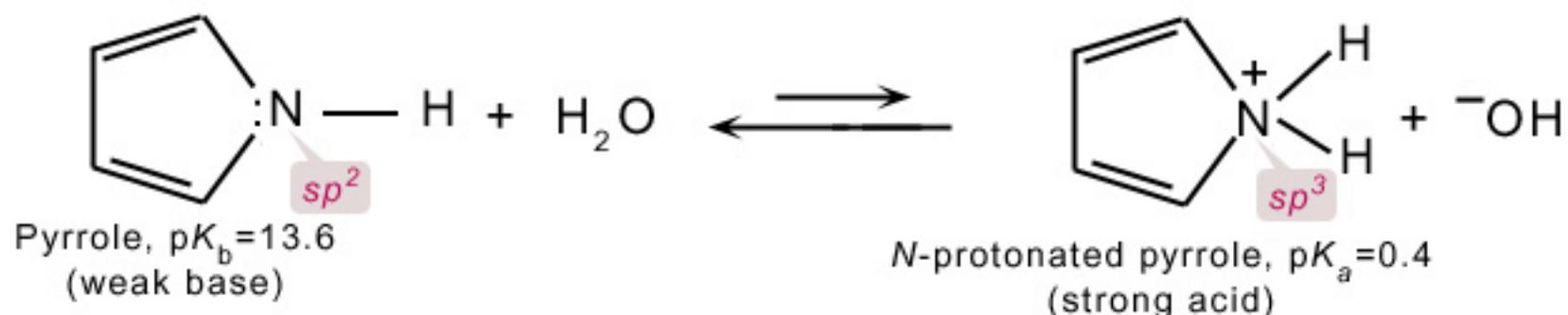
THE ACIDITY OF THE PYRIDINIUM ION

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

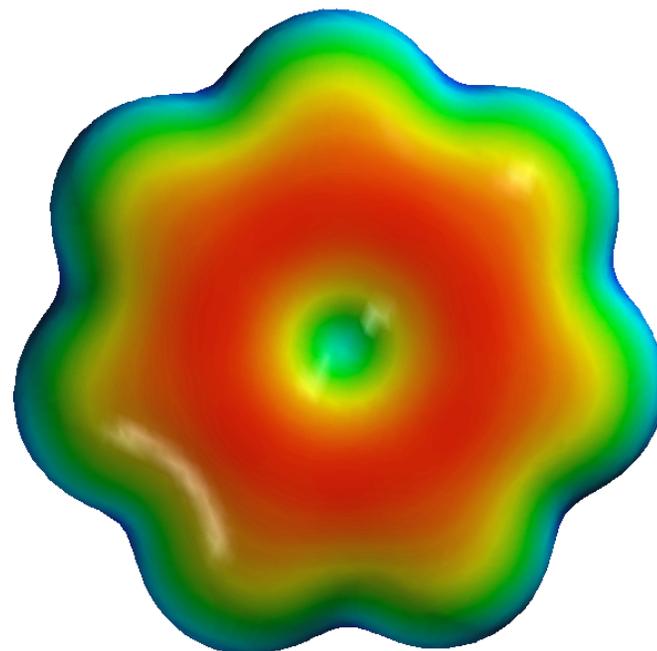
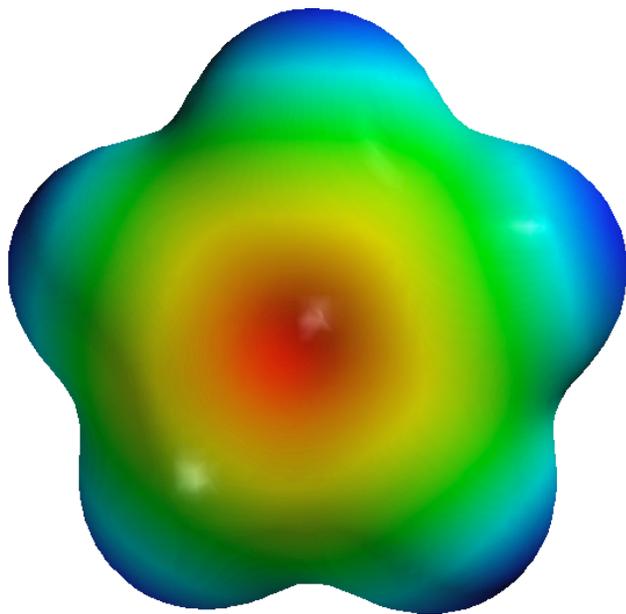
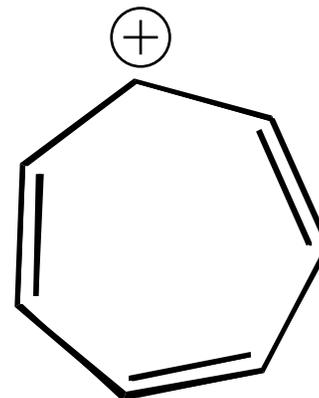
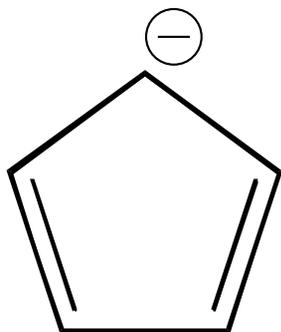


The Acidity of Protonated Pyrrole

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

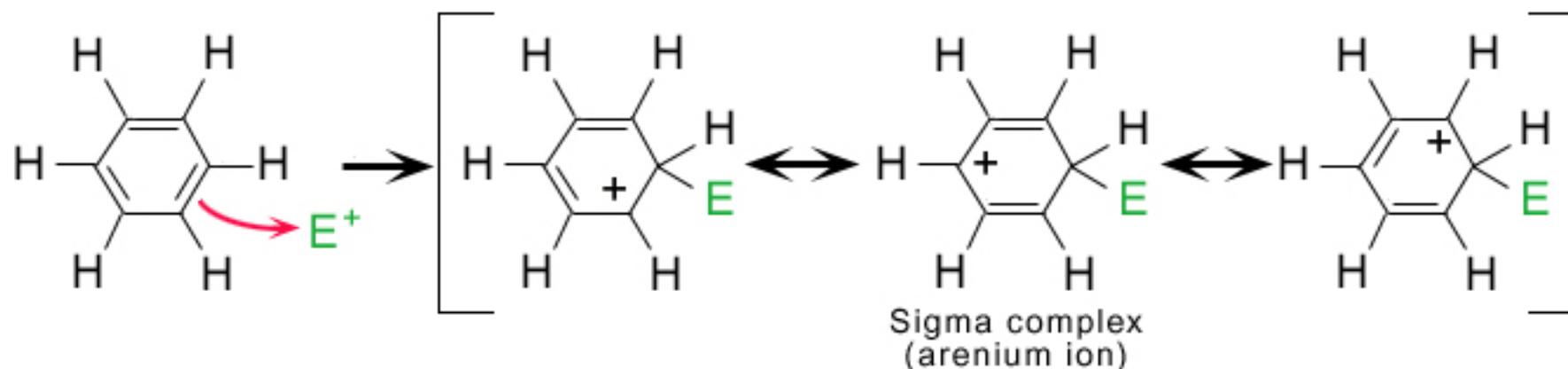


AROMATIC CATIONS AND ANIONS

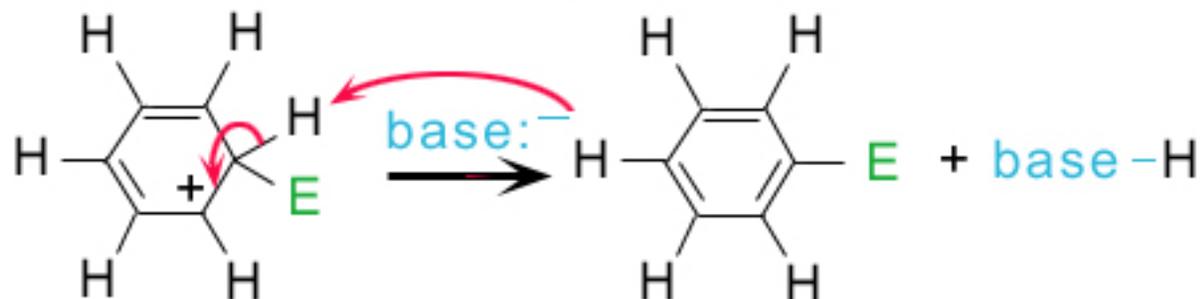


Aromatic Compounds like Benzene Undergo SUBSTITUTION instead of ADDITION

Step 1: Attack on the electrophile forms the sigma complex.

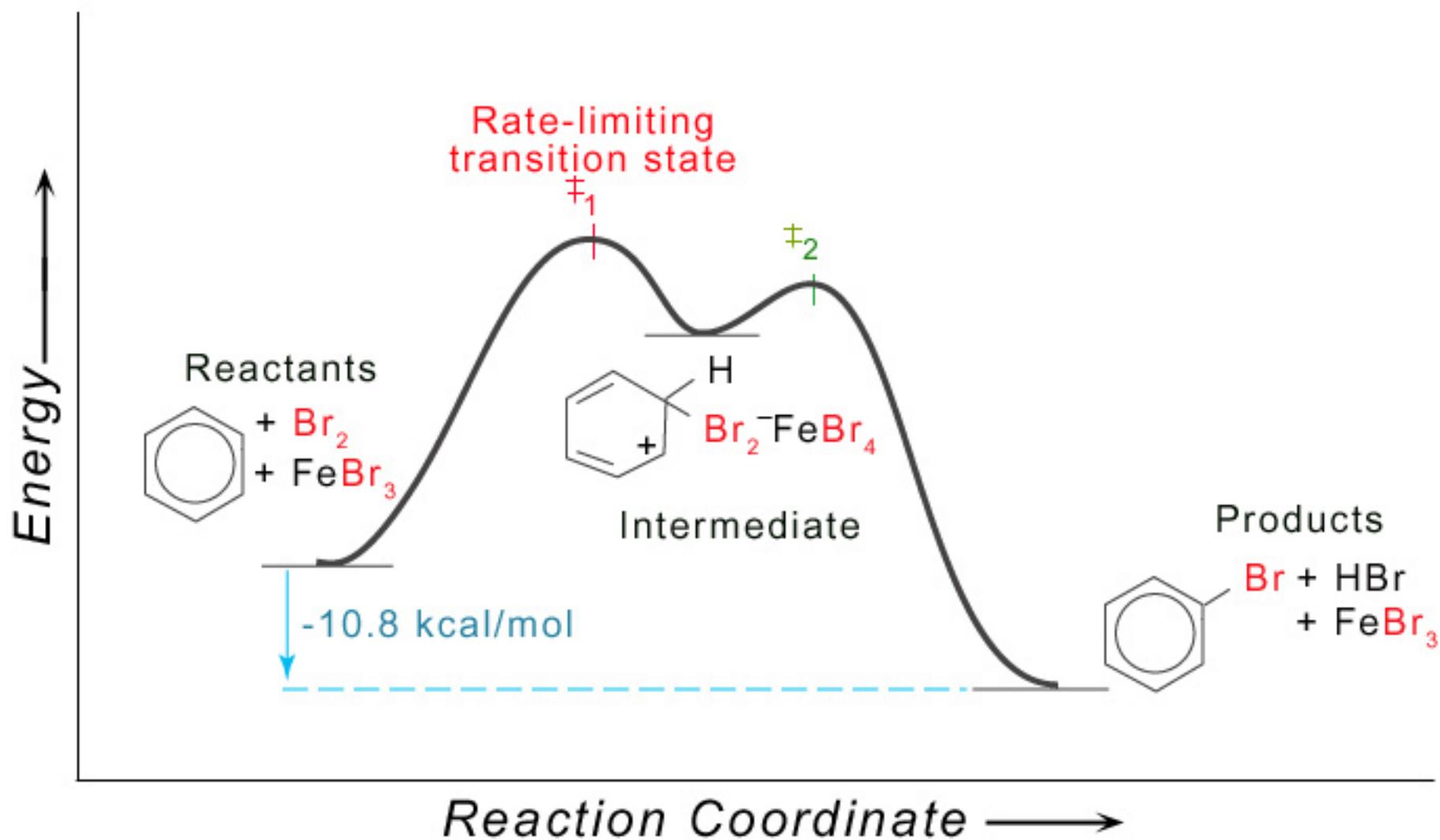


Step 2: Loss of a proton gives the substitution product.

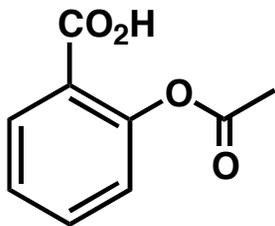


For Bromination $E^+ = Br-Br + FeBr_3$

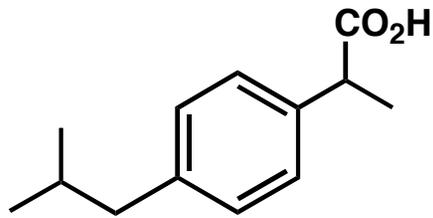
Energy Diagram for Bromination



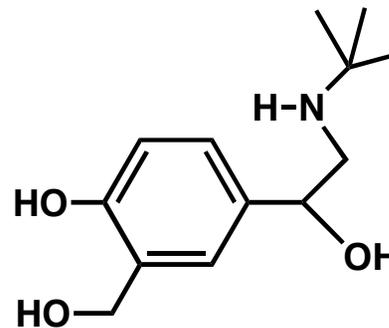
MANY BENZENE AND NAPHTHALENE DERIVATIVES ARE USEFUL DRUGS



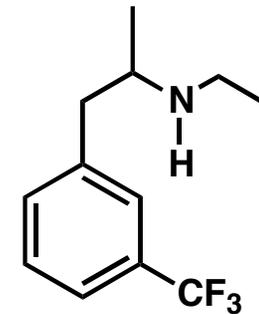
acetyl salicylic acid
ASPIRIN



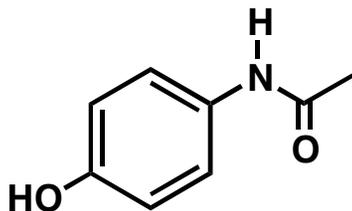
ibuprofen
ADVIL



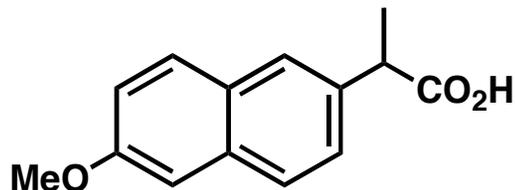
ALBUTEROL
bronchodilator



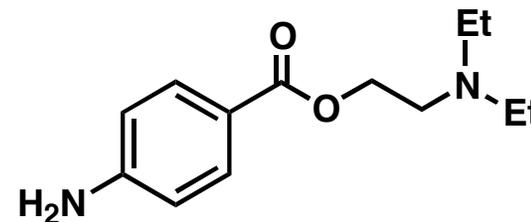
FENFLURAMINE
appetite suppressant



acetaminophen
TYLENOL



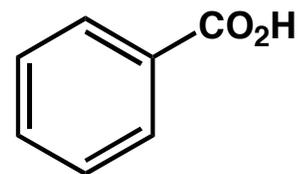
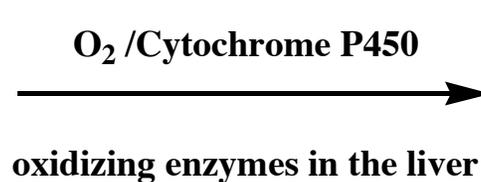
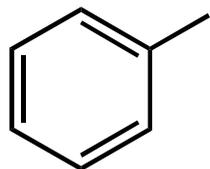
naproxen
ALEVE



procaine
NOVOCAINE
local anaesthetic

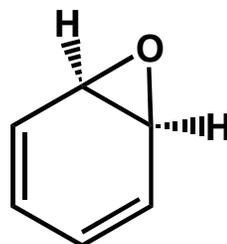
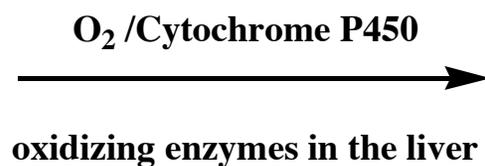
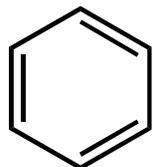
CARCINOGENICITY OF AROMATIC COMPOUNDS

TOLUENE

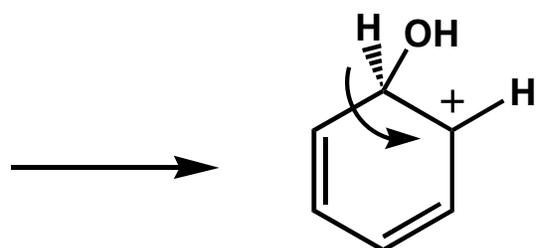
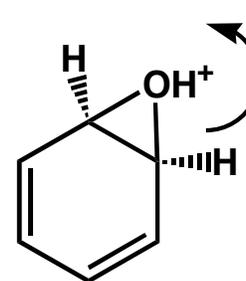


Reactive intermediate for
attack by nucleophile

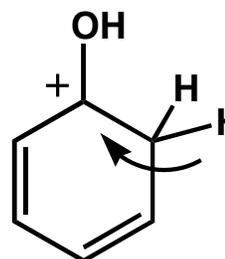
BENZENE



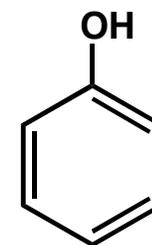
arene oxide



1,2-hydride shift

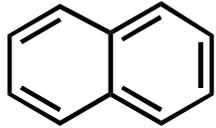


Base

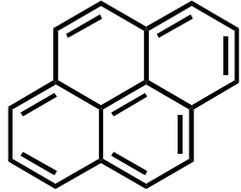


PHENOL

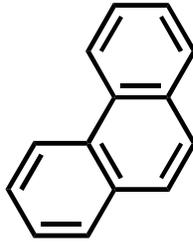
POLYNUCLEAR AROMATIC HYDROCARBONS



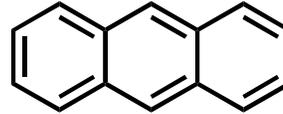
NAPHTHALENE



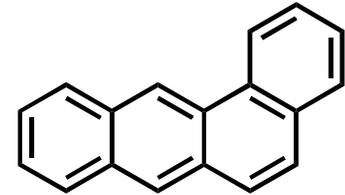
PYRENE



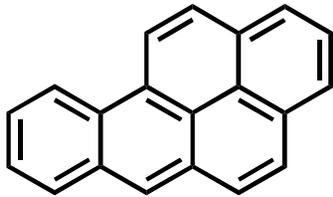
PHENANTHRENE



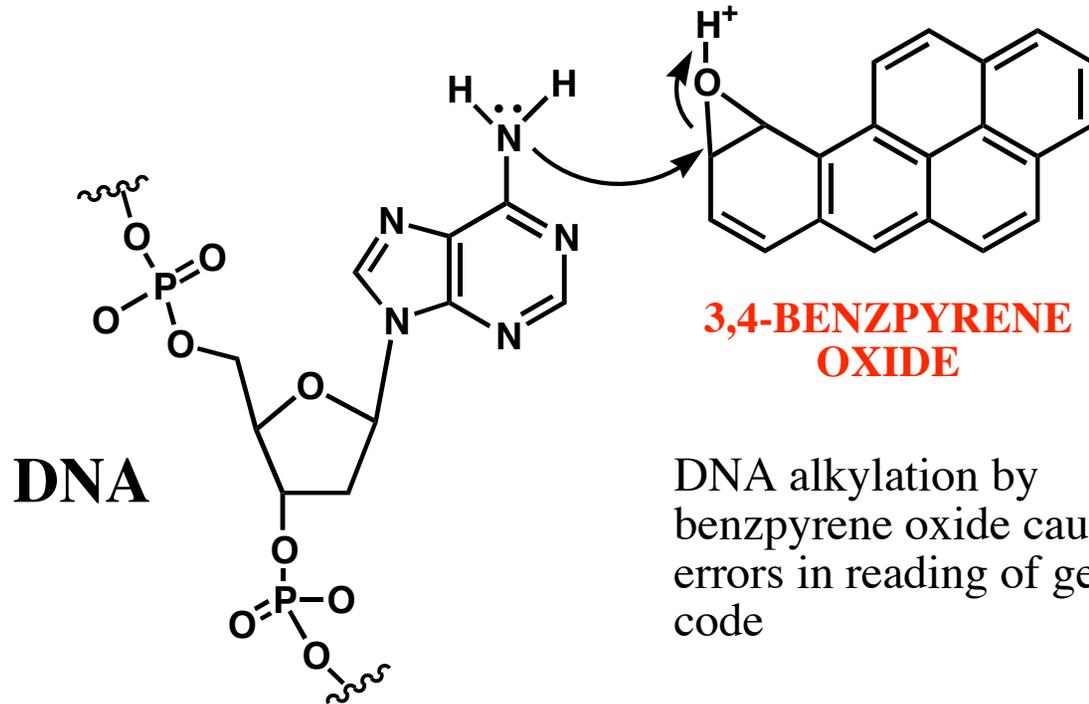
ANTHRACENE



BENZ[a]ANTHRACENE



3,4-BENZPYRENE



DNA alkylation by benzpyrene oxide causes errors in reading of genetic code

DNA → **mRNA** → **PROTEINS**