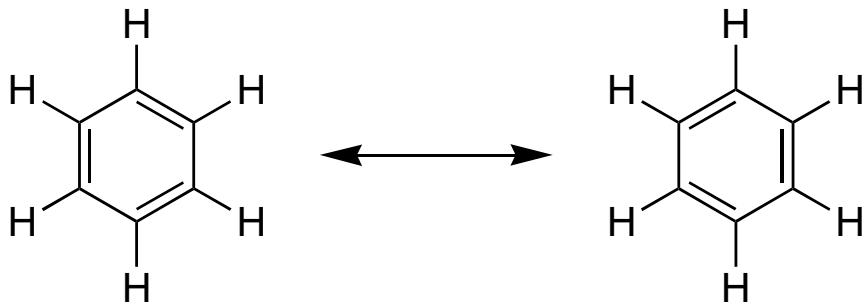


AROMATICITY

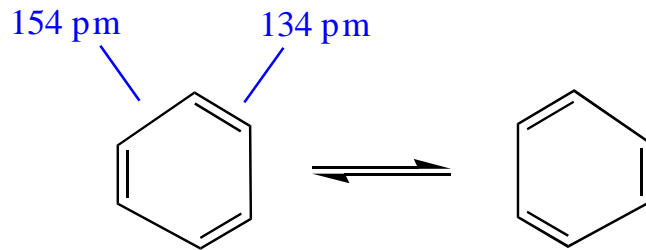
AROMATIC COMPOUNDS

Aromaticity
Benzene - C₆H₆



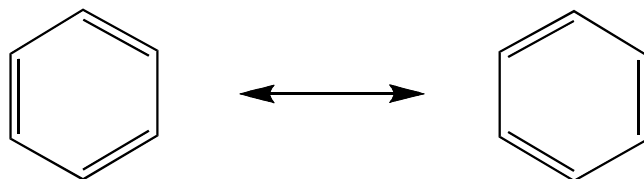
Kekulé and the Structure of Benzene

Kekulé benzene: two forms are in rapid equilibrium

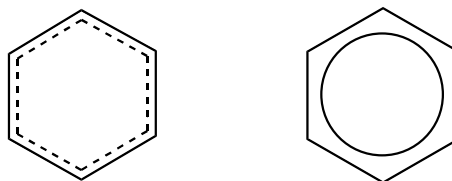


- All bonds are 140 pm (intermediate between C-C and C=C)
- C-C-C bond angles are 120°
- Structure is planar, hexagonal

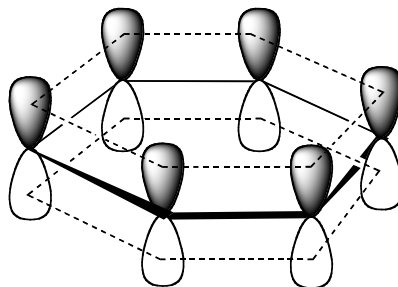
A Resonance Picture of Bonding in Benzene



resonance
hybrid



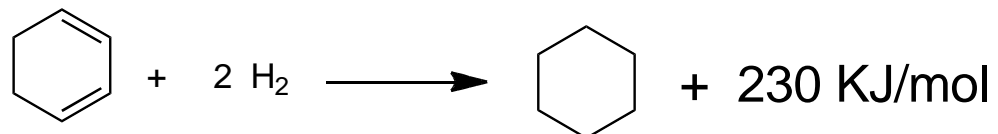
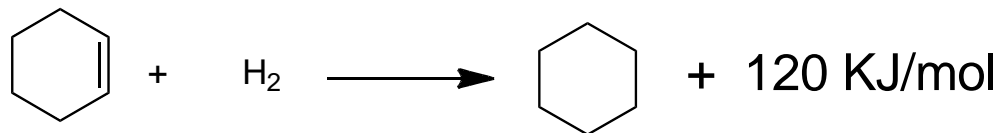
6 π -electron delocalized
over 6 carbon atoms



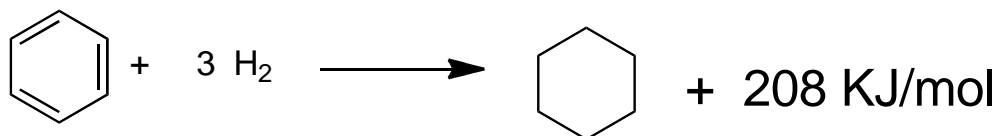
The Stability of Benzene

Aromaticity: cyclic conjugated organic compounds such as benzene, exhibit special stability due to resonance delocalization of π -electrons.

Heats of hydrogenation



calc'd value= 240 KJ/mol
10 KJ/mol added stability



calc'd value= 360 KJ/mol
152 KJ/mol added stability

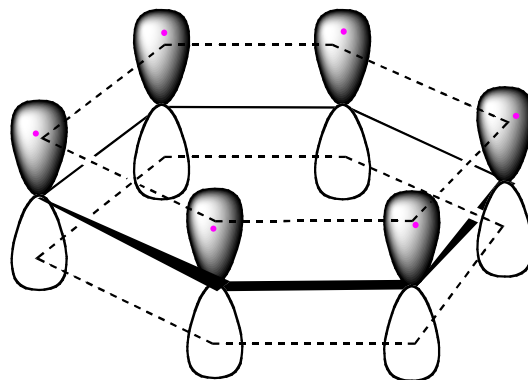


1,3,5-Hexatriene - conjugated but not cyclic

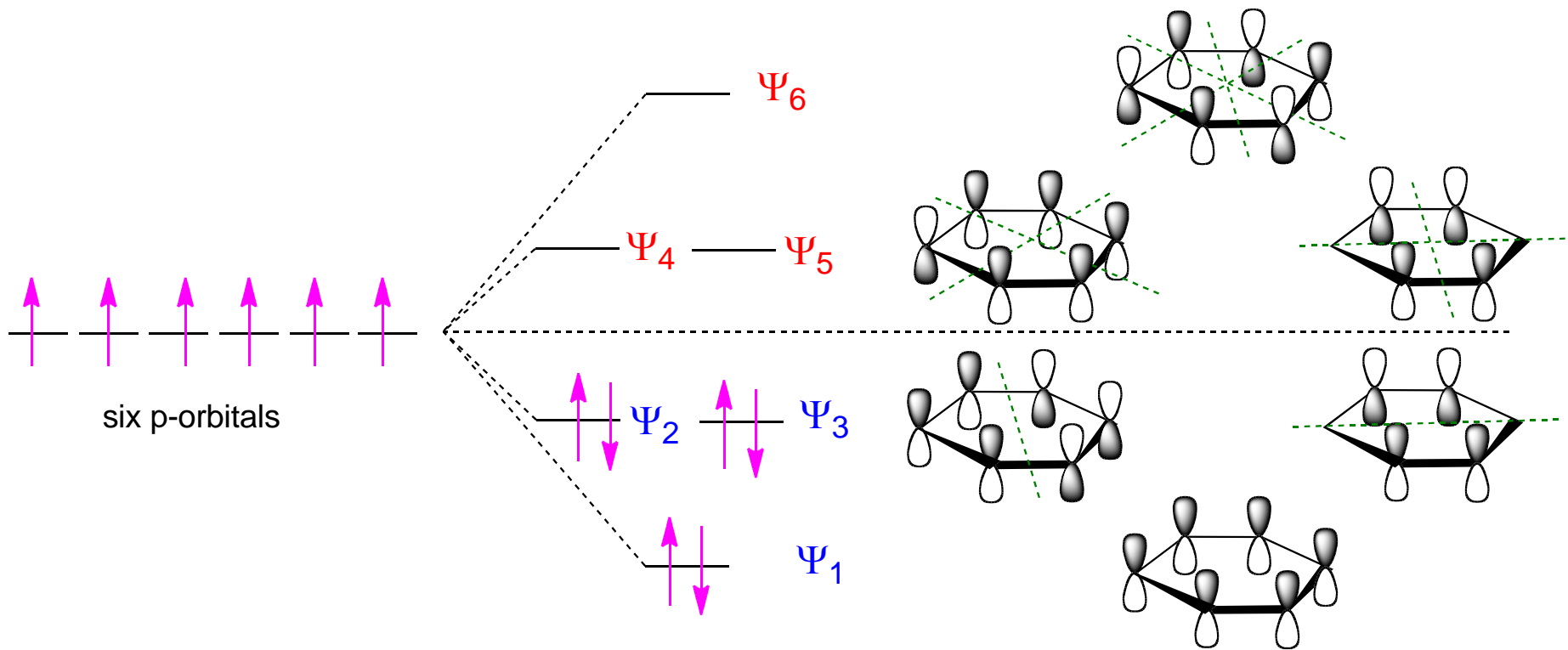
Resonance energy of benzene is 129 - 152 KJ/mol

An Orbital Hybridization View of Bonding in Benzene

- Benzene is a planar, hexagonal cyclic hydrocarbon
- The C–C–C bond angles are $120^\circ = sp^2$ hybridized
- Each carbon possesses an unhybridized p-orbital, which makes up the conjugated π -system.
- The six π -electrons are delocalized through the π -system



The π Molecular Orbitals of Benzene - the aromatic system of benzene consists of six p-orbitals (atomic orbitals). Benzene must have six molecular orbitals.



Degenerate orbitals:
orbitals that have the
same energy

Ψ_1 : zero nodes
 Ψ_2 and Ψ_3 : one node

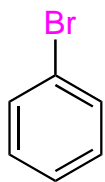
Bonding

Ψ_4 and Ψ_5 : two nodes
 Ψ_6 : three nodes

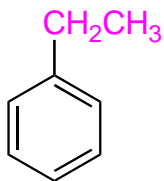
Anti-bonding

Substituted Derivatives of Benzene and Their Nomenclature

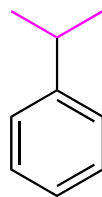
Generally, mono-substituted benzenes are named in a similar manner as hydrocarbons with -benzene as the parent name



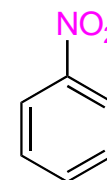
bromobenzene



ethylbenzene

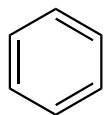


**(1-methylethyl)benzene
(isopropylbenzene)**

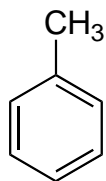


nitrobenzene

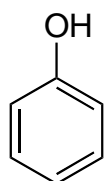
large number of non-systematic names that can serve as the parent name (Table 11.1)



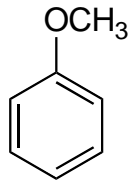
benzene



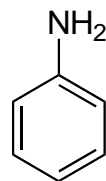
toluene



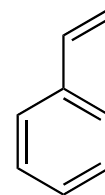
phenol



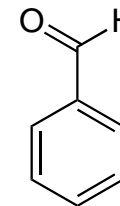
anisole



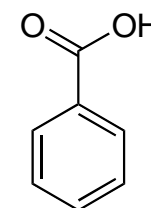
aniline



styrene



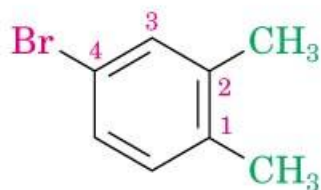
benzaldehyde



benzoic acid

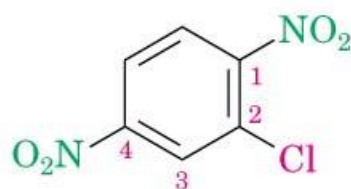
Benzenes with two or more substituents:

- Choose numbers to get lowest possible values
- List substituents alphabetically with hyphenated numbers
- Non-systematic names, such as “toluene” can serve as parent



4-Bromo-1,2-dimethylbenzene

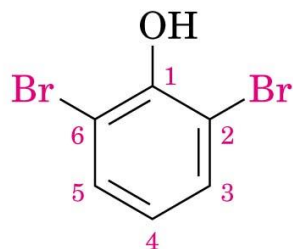
© Thomson - Brooks Cole



2-Chloro-1,4-dinitrobenzene

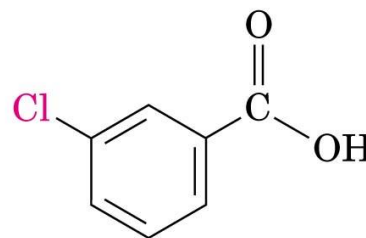


2,4,6-Trinitrotoluene (TNT)



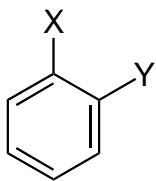
2,6-Dibromophenol

© Thomson - Brooks Cole

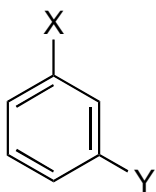


***m*-Chlorobenzoic acid**

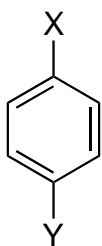
Disubstituted benzene: relative position of the substituents



1,2-disubstituted: *ortho* (*o*-)

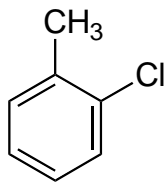


1,3-disubstituted: *meta* (*m*-)

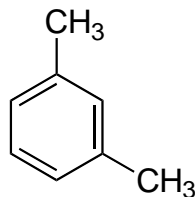


1,4-disubstituted: *para* (*p*-)

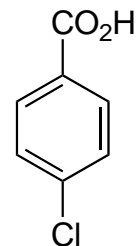
Note: *ortho*, *meta*, and *para* are not used in systematic nomenclature



2-chlorotoluene
ortho-chlorotoluene
o-chlorotoluene

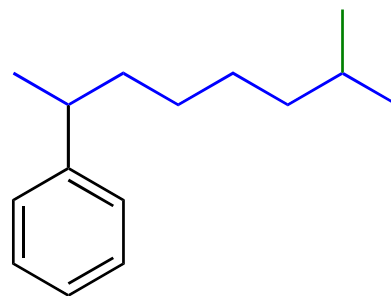
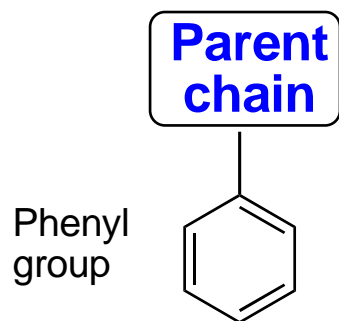


1,3-dimethylbenzene
meta-xylene
m-xylene

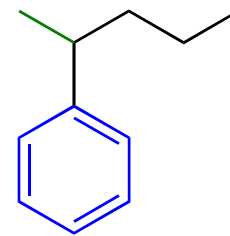


4-chlorobenzoic acid
para-chlorobenzoic acid
p-chlorobenzoic acid

When the benzene ring is a substituent of a parent chain, it is referred to as a phenyl group. The benzene ring is regarded as a substituent when the parent chain has greater than six carbons. The benzene ring is the parent when the longest alkyl chain substituent is six carbons or less



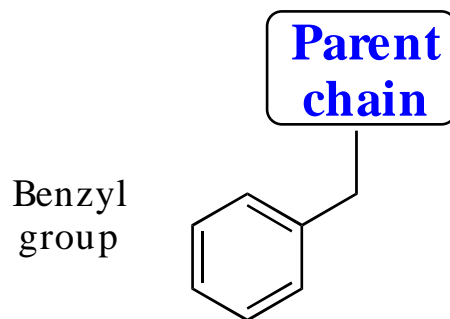
2-methyl-7-phenyloctane



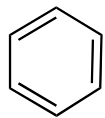
(1-methylbutyl)benzene

A phenyl substituent (C_6H_5-) is often abbreviated as Ph-

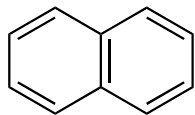
A $C_6H_5-CH_2-$ substituent (phenylmethyl-) is often referred to as a benzyl group (Bn-)



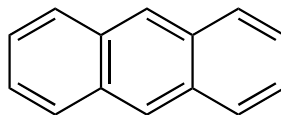
Polycyclic Aromatic Hydrocarbons (PAHs)



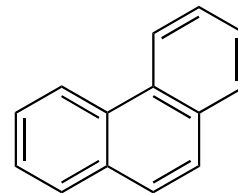
benzene



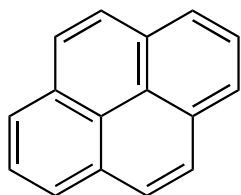
naphthalene



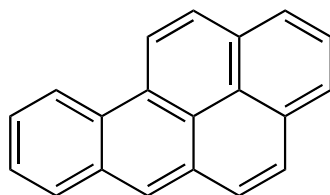
anthracene



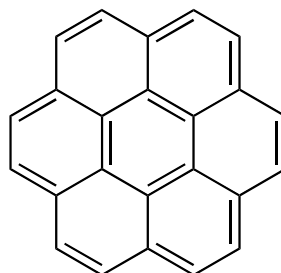
phenanthrene



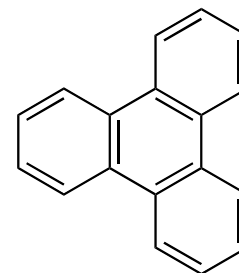
pyrene



benzo[a]pyrene



coronene



triphenylene

11.9: Physical Properties of Arenes (please read)

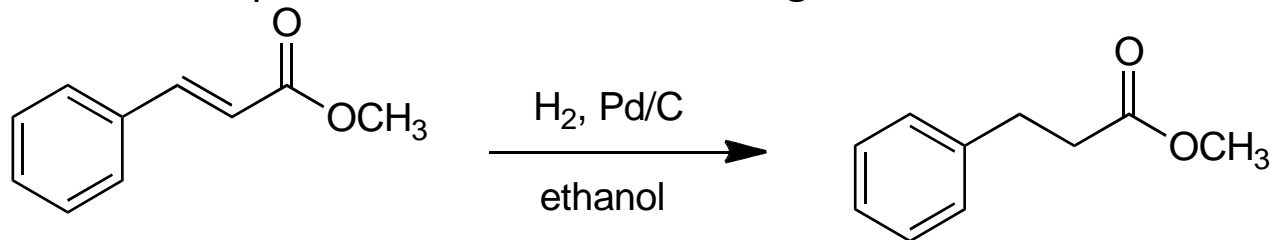
Reactions of Arenes: A Preview

1. Reactions involving the ring
 - A. Reduction
 - a. Catalytic hydrogenation
 - b. Birch reduction
 - B. Electrophilic aromatic substitution
 - C. Nucleophilic aromatic substitution

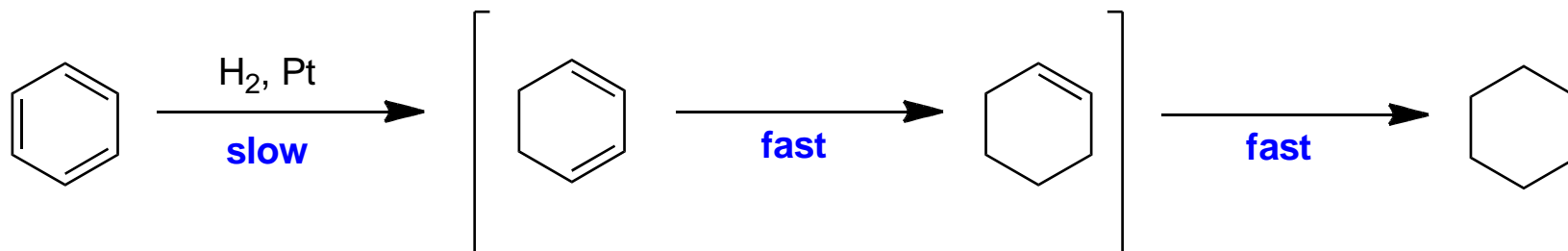
2. The ring as a substituent
 - A. Benzylic halogenation
 - B. Benzylic oxidation
 - C. Nucleophilic substitution of benzylic halides

The Birch Reduction

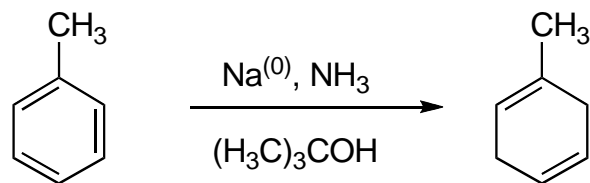
Catalytic Hydrogenation - Aromatic rings are inert to catalytic hydrogenation under conditions that will reduce alkene double bonds. Therefore, an alkene double bond can therefore be selectively reduced in the presence of an aromatic ring



Reduction of an aromatic ring requires forcing reducing conditions (high pressure and/or highly active catalysts)

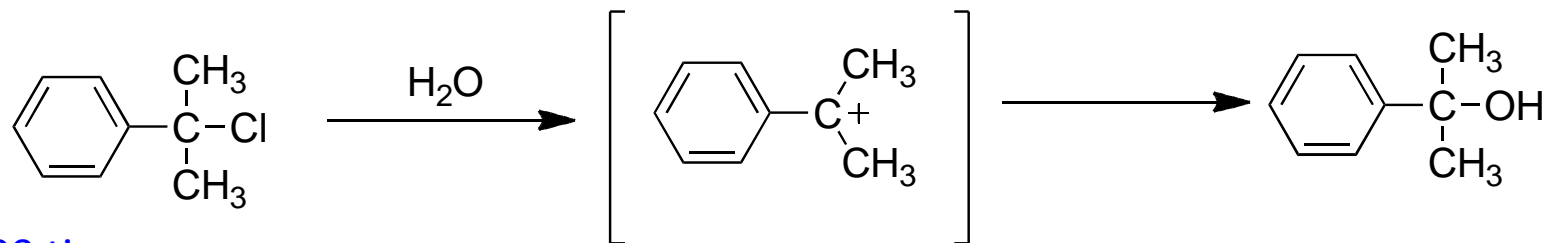


Birch Reduction – dissolving metal reduction of an aromatic ring
Li, Na or K metal in liquid ammonia.

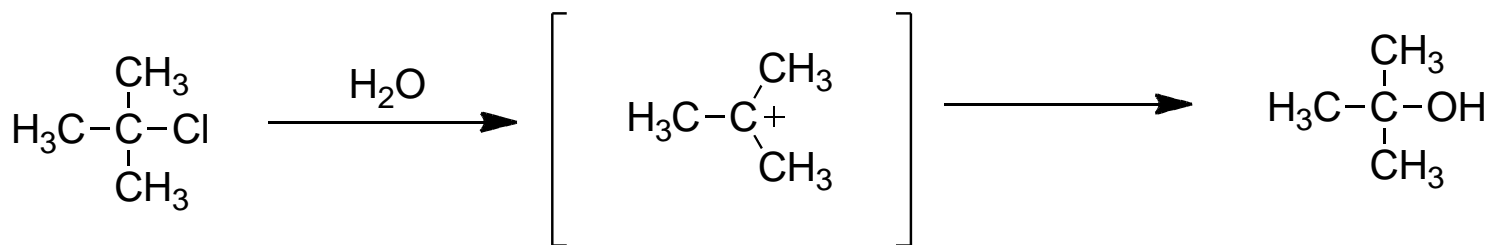


Mechanism is related to the reduction of C≡C to
trans-alkenes

S_N1 Reactions of Benzylic Halides



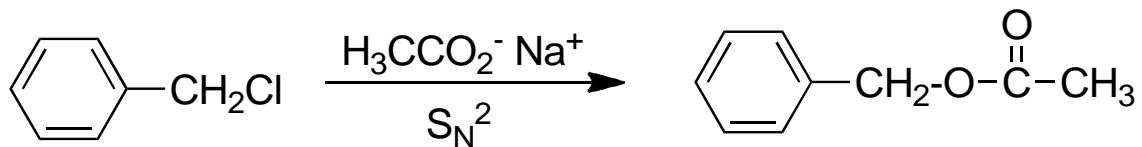
> 600 times
more reactive



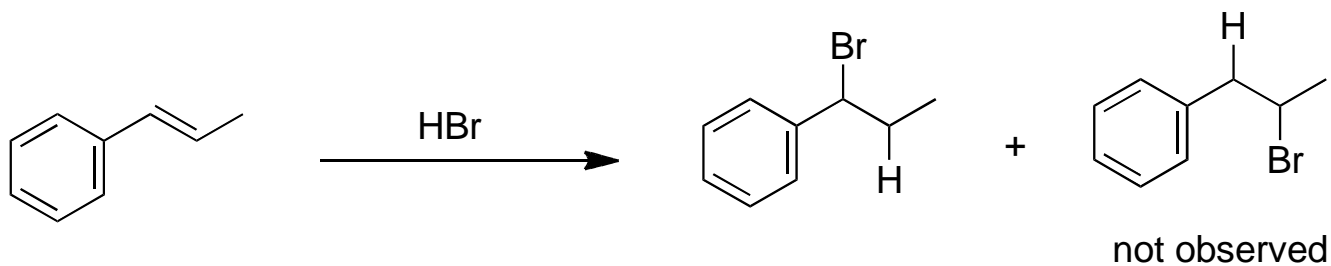
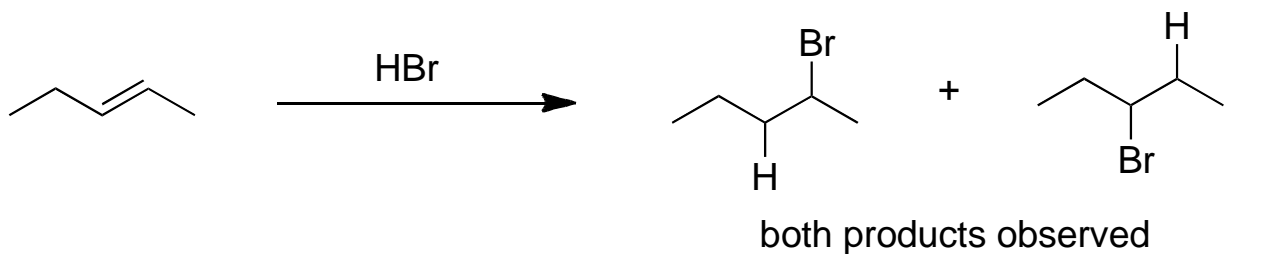
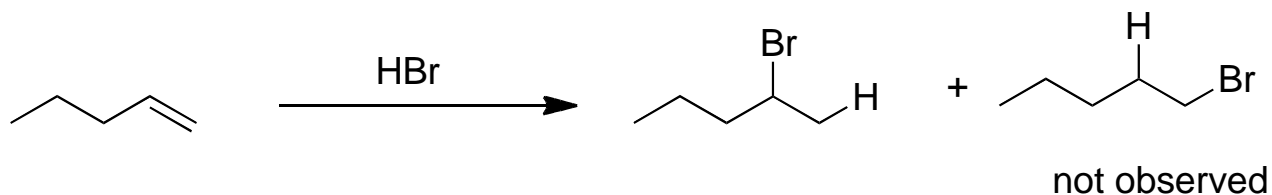
Reactivity is reflective of the greater stability of the benzylic carbocation intermediate

S_N2 Reactions of Benzylic Halides -

Benzylic halides undergo S_N2 reactions faster than alkyl halides (similar to allylic halides)

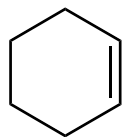


Addition Reactions of Alkenylbenzenes - alkenyl substituents on a benzene ring undergo reactions typical of an alkene. The benzene ring can influence the reactivity.

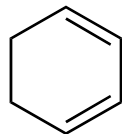


Cyclooctatetraene:

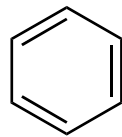
Heats of hydrogenation - No special stability for cyclooctatetraene



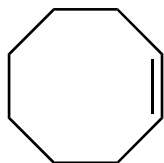
120 KJ/mol



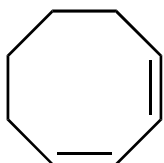
230 KJ/mol



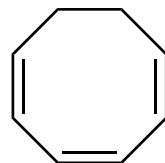
208 KJ/mol



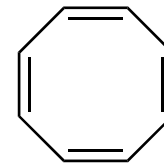
97 KJ/mol



205 KJ/mol



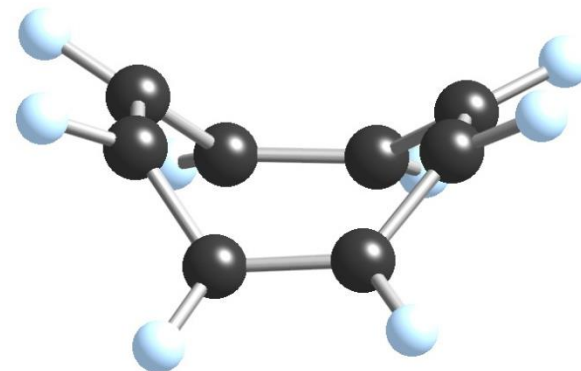
303 KJ/mol



410 KJ/mol

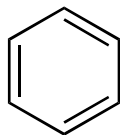
reactivity similar to normal C=C

Exists in a boat-like conformation:
little overlap between double bonds

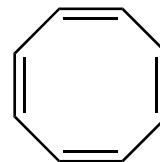




not aromatic



aromatic



not aromatic

Cyclic conjugation is necessary, but not sufficient criteria for aromaticity.

Hückel's Rule:

Aromatic:

Cyclic

Conjugated: "alternating single and double bonds"

Planar: maximum overlap between conjugated π -bonds

Must contain $4n+2$ π -electrons, where n is an integer
(Hückel's rule)

Anti-aromatic:

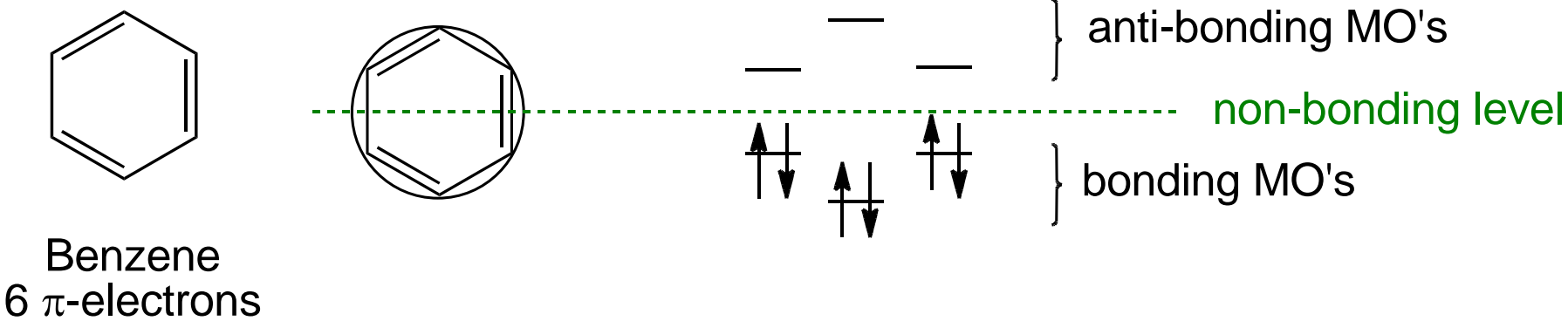
cyclic, conjugated, planar molecules that contain $4n$ π -electrons (where n is an integer).

Destabilized (highly reactive) relative to the corresponding open-chain conjugated system

Frost Circles: relative energies of the molecular orbitals of cyclic, conjugated systems

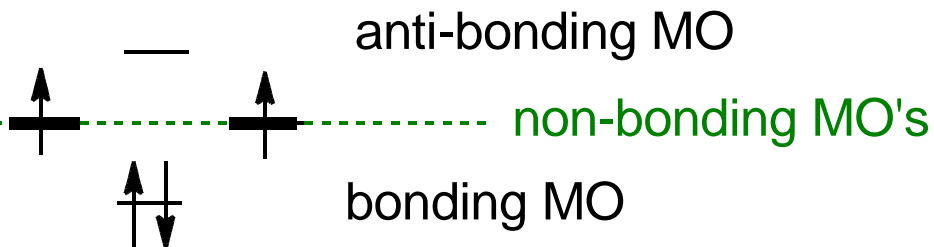
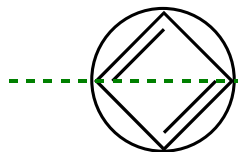
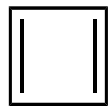
Inscribe the cyclic, conjugated molecule into a circle so that a vertex is at the bottom. The relative energies of the MO's are where the ring atoms intersect the circle

benzene:



The bonding MO's will be filled for aromatic compounds, such as benzene.

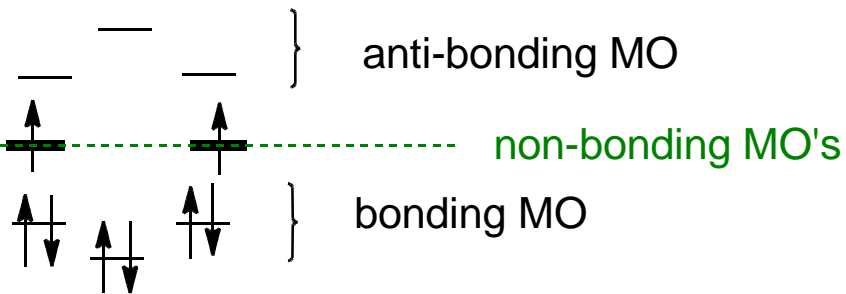
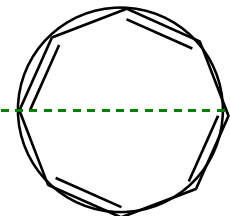
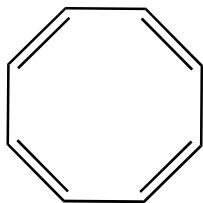
Cyclobutadiene:



Cyclobutadiene
4 π -electrons

For anti-aromatic compounds, such as cyclobutadiene and cyclooctatetraene, there will be unpaired electrons in bonding, non-bonding or antibonding MO's.

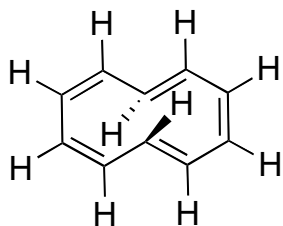
Cyclooctatetraene:



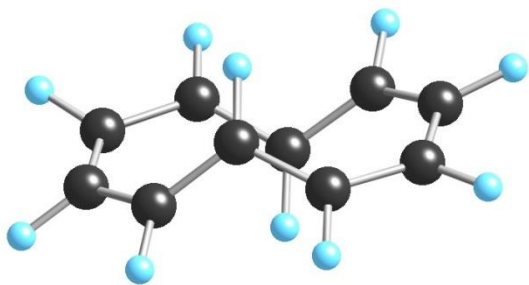
Cyclooctatetraene
8 π -electrons

Annulenes - monocyclic, conjugated, planar polyenes that conform to Hückel's rule.

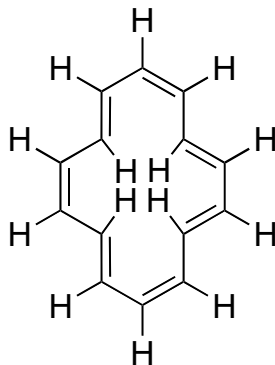
[10]annulene



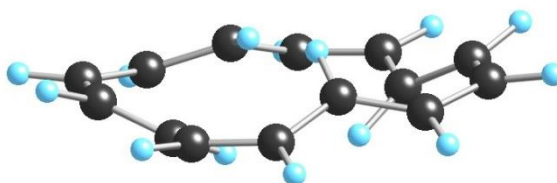
10 π -electrons
 $4n+2 = 10, n=2$.



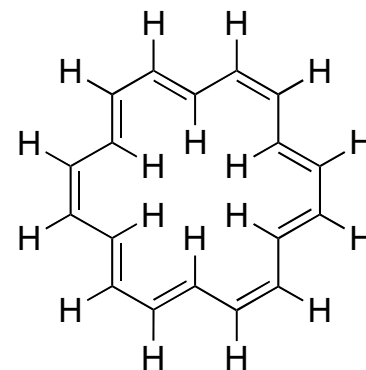
[14]annulene



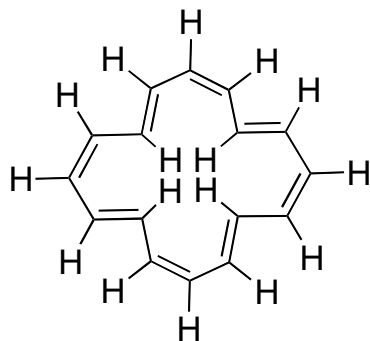
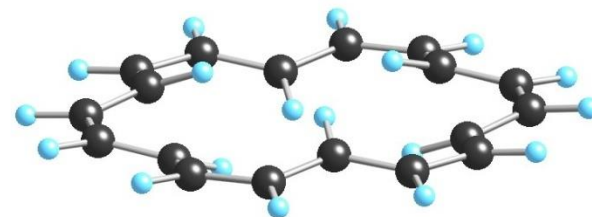
14 π -electrons
 $4n+2=14, n=3$



[18]annulene

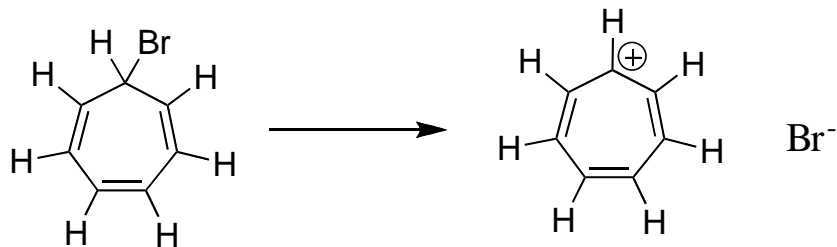
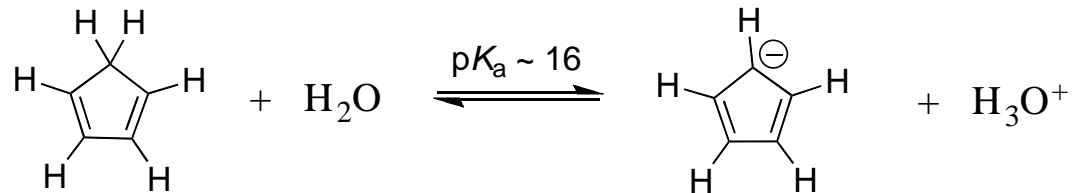
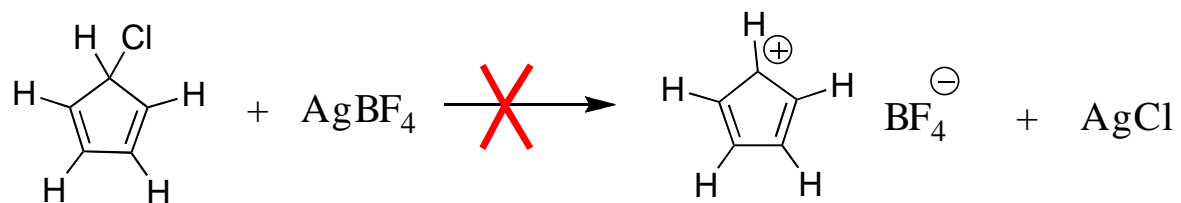
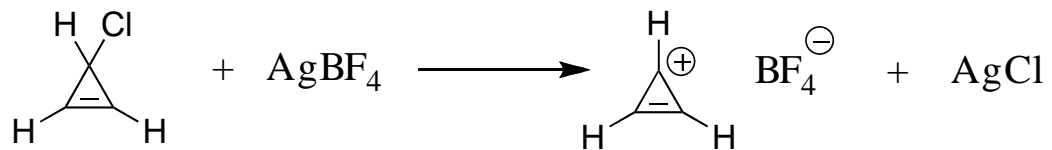


18 π -electrons
 $4n+2=18, n=4$

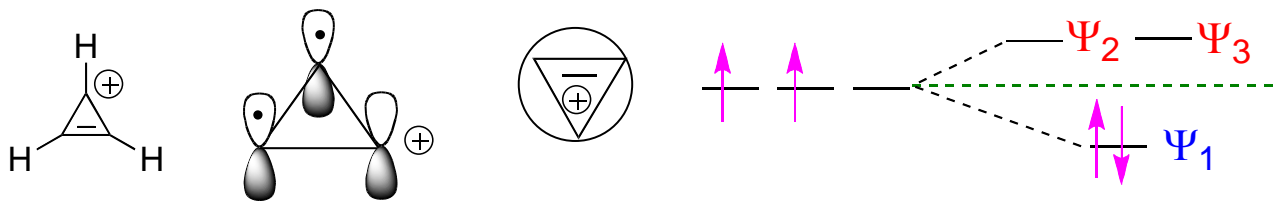


[16]annulene
16 π -electrons
 $4n=16, n=4$

Aromatic Ions



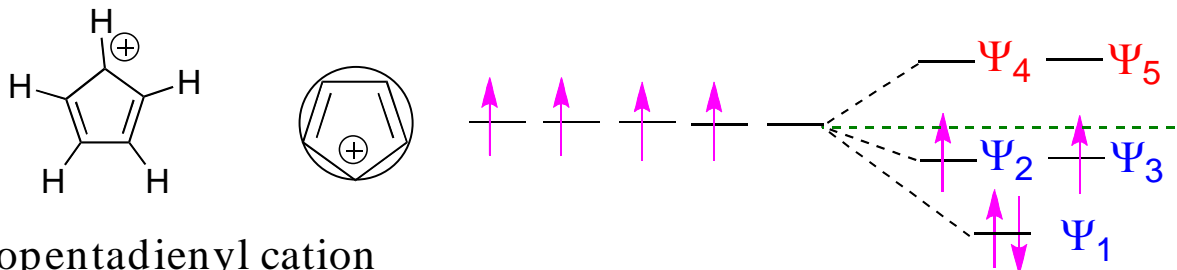
Cyclopropenyl cation



cyclopropenyl cation
2 π -electrons

$4n+2=2$
 $n=0$
aromatic

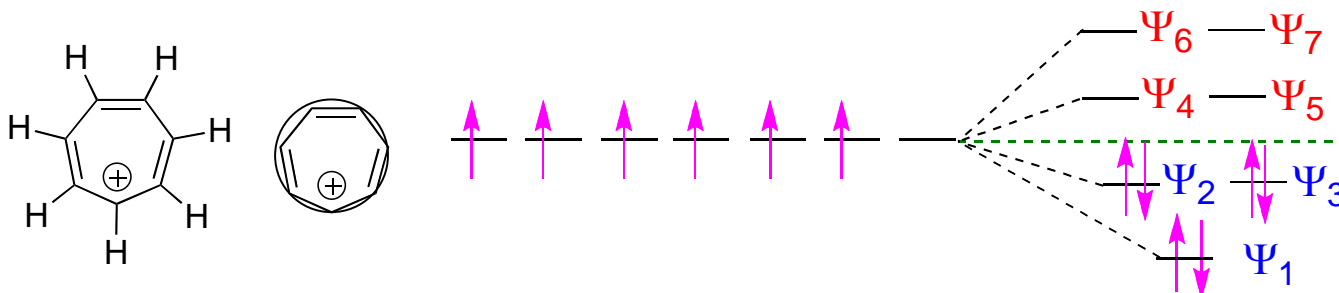
Cyclopentadienyl cation



cyclopentadienyl cation
4 π -electrons

$4n=4$
 $n=1$
anti-aromatic

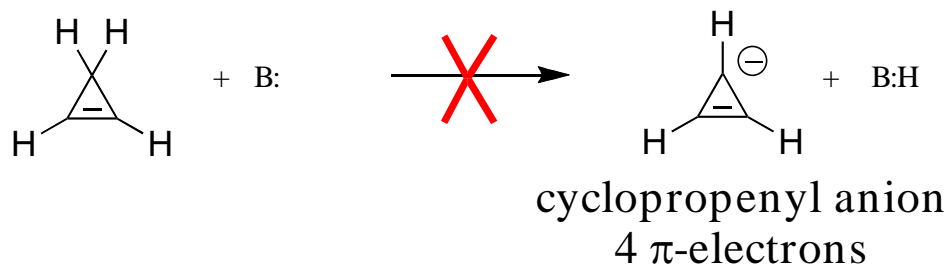
Cycloheptatrienyl cation



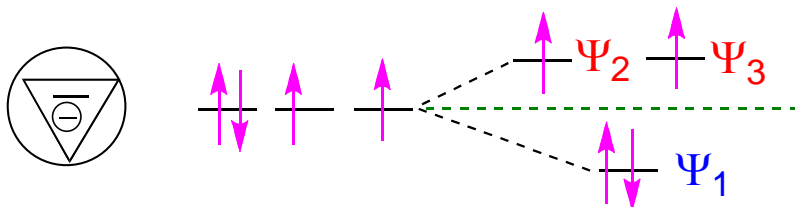
cycloheptatrienyl cation
6 π -electrons

$4n+2=6$
 $n=1$
aromatic

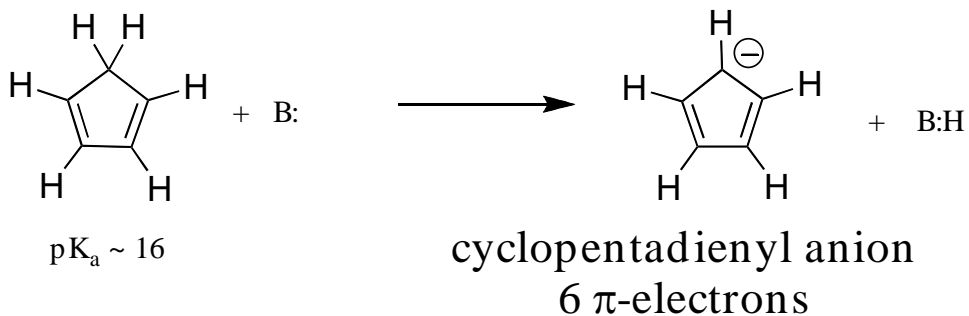
Cyclopropenyl anion



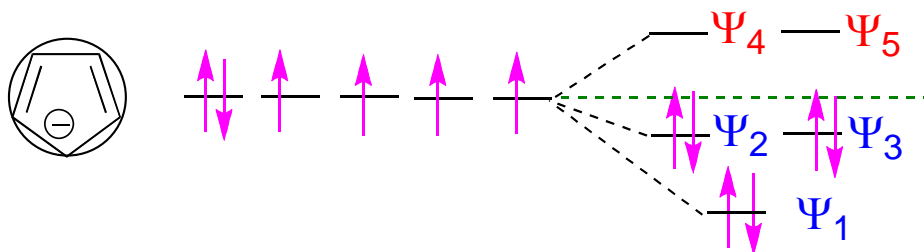
$4n=4$
 $n=1$
anti-aromatic



Cyclopentadienyl anion

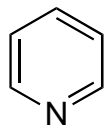


$4n+2=6$
 $n=1$
aromatic

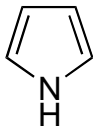


Heterocyclic Aromatic Compounds (please read)

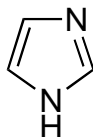
Heterocycle: any cyclic compound that contains ring atom(s) other than carbon (N, O, S, P). Cyclic compounds that contain only carbon are called carbocycles



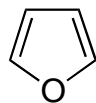
pyridine



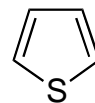
pyrrole



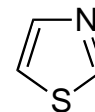
imidazole



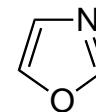
furan



thiophene



thiazole

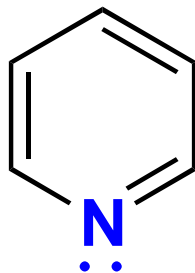


oxazole

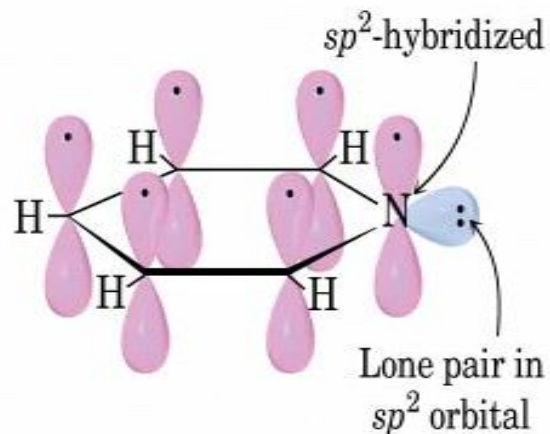
Heterocyclic Aromatic Compounds and Hückel's Rule

Pyridine: π -electron structure resembles benzene (6 π -electrons)

The nitrogen lone pair electrons are not part of the aromatic system.



pyridine



Six π electrons

Pyrrole: 6 π -electron system similar to that of cyclopentadienyl anion. There are four sp^2 -hybridized carbons with 4 p orbitals perpendicular to the ring and 4 π -electrons and a lone pair of electrons in an unhybridized p^2 orbital that is part of the aromatic sextet

