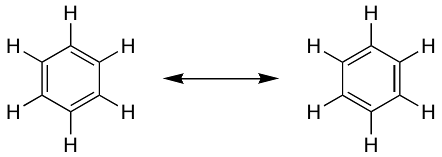
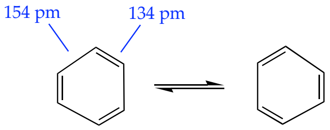
Chapter 11: Arenes and Aromaticity

11.1: Benzene - C_6H_6



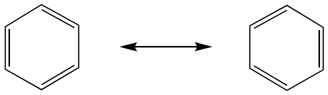
11.2: Kekulé and the Structure of Benzene

Kekule benzene: two forms are in rapid equilibrium

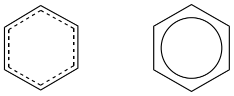


- All bonds are 140 pm (intermediate between C-C and C=C)
- C–C–C bond angles are 120°
- Structure is planar, hexagonal

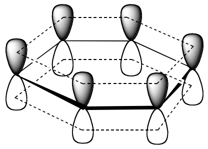
11.3: A Resonance Picture of Bonding in Benzene



resonance
hybrid



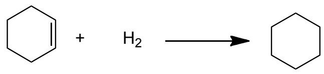
6 π-electron delocalized
over 6 carbon atoms



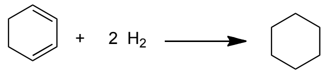
11.4: The Stability of Benzene

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

Heats of hydrogenation (Fig. 11.2, p. 425)

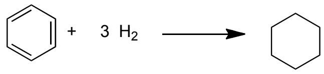


+ 120 KJ/mol



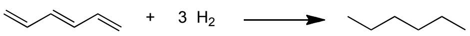
+ 230 KJ/mol calc'd value= 240 KJ/mol

10 KJ/mol added stability



+ 208 KJ/mol calc'd value= 360 KJ/mol

152 KJ/mol added stability



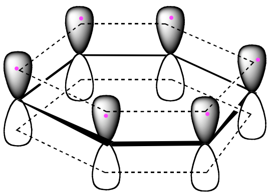
+ 337 KJ/mol

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

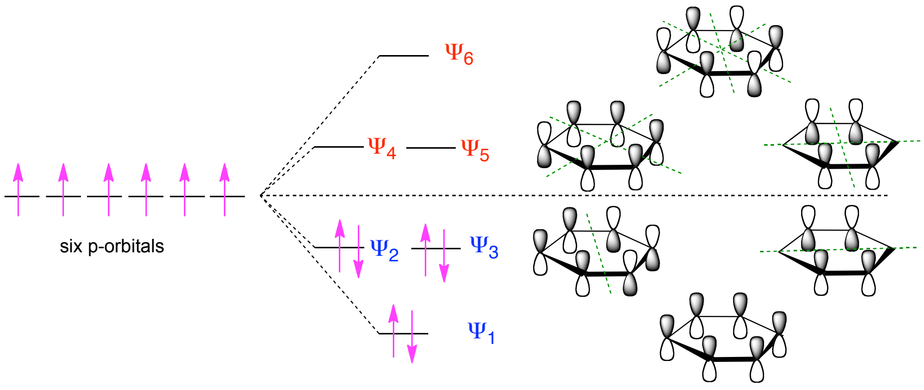
Resonance energy of benzene is 129 - 152 KJ/mol

11.5: An Orbital Hybridization View of Bonding in Benzene

- Benzene is a planar, hexagonal cyclic hydrocarbon
- The C–C–C bond angles are 120° = 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



11.6: 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

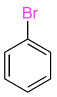
Bonding

Ψ_4 and Ψ_5: two nodes
Ψ_6: three node

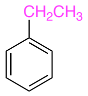
Anti-bonding

11.7: Substituted Derivatives of Benzene and Their Nomenclature

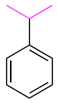
Generally, mono-substituted benzenes are named in a similar manner as hydrocarbons with -benzene as the parent name



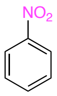
bromobenzene



ethylbenzene

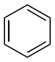


(1-methylethyl)benzene
(isopropylbenzene)

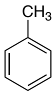


nitrobenzene

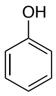
large number of non-systematic names that can serve as the parent name (Table 11.1)



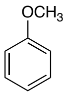
benzene



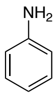
toluene



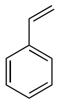
phenol



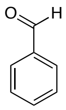
anisole



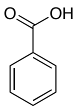
aniline



styrene



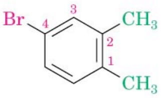
benzaldehyde



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

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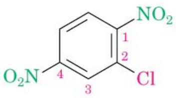
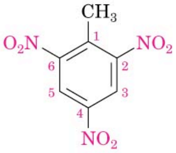
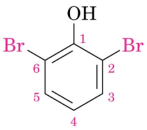


2-Chloro-1,4-dinitrobenzene



2,4,6-Trinitrotoluene (TNT)



2,6-Dibromo*phenol*

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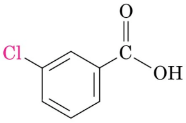
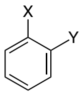
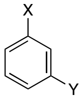


m*-Chloro*benzoic acid

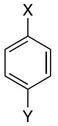
Disubstituted benzene: relative position of the substitutents



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

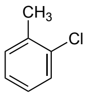


1,3-disubstituted: *meta* (*m*-)

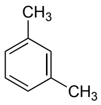


1,4-disubstituted: *para* (*p*-)

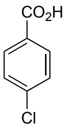
Note: ortho, meta, and para are not used in systematic nomenclature



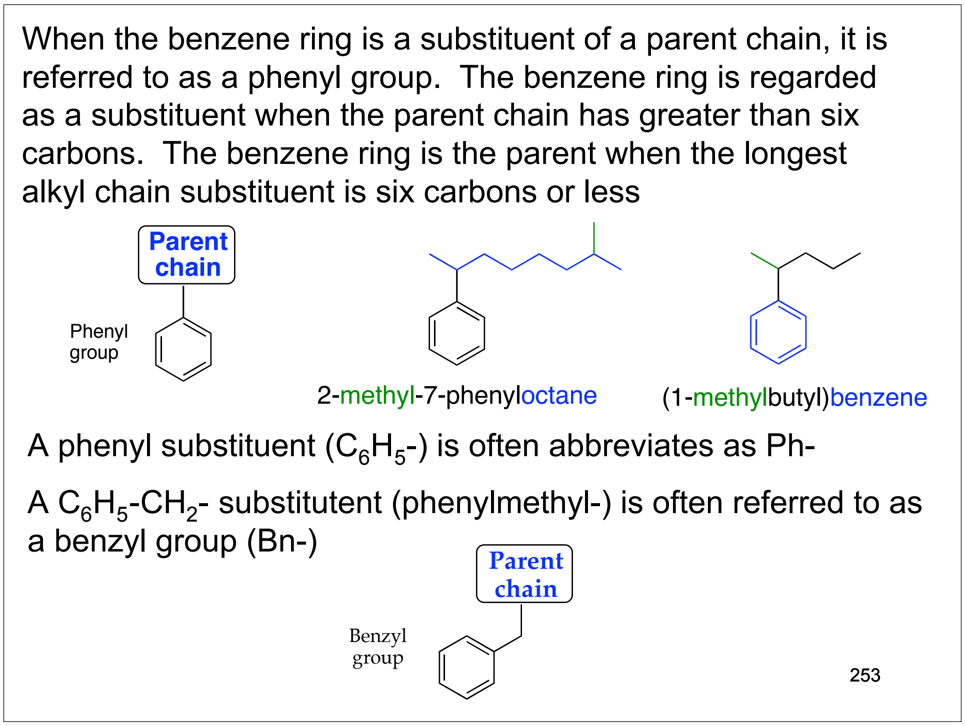
2-chlorotoluene
ortho-chlorotoluene
o-chlorotoluene



1,3-dimethylbenzene
meta-xylene
m-xylene



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



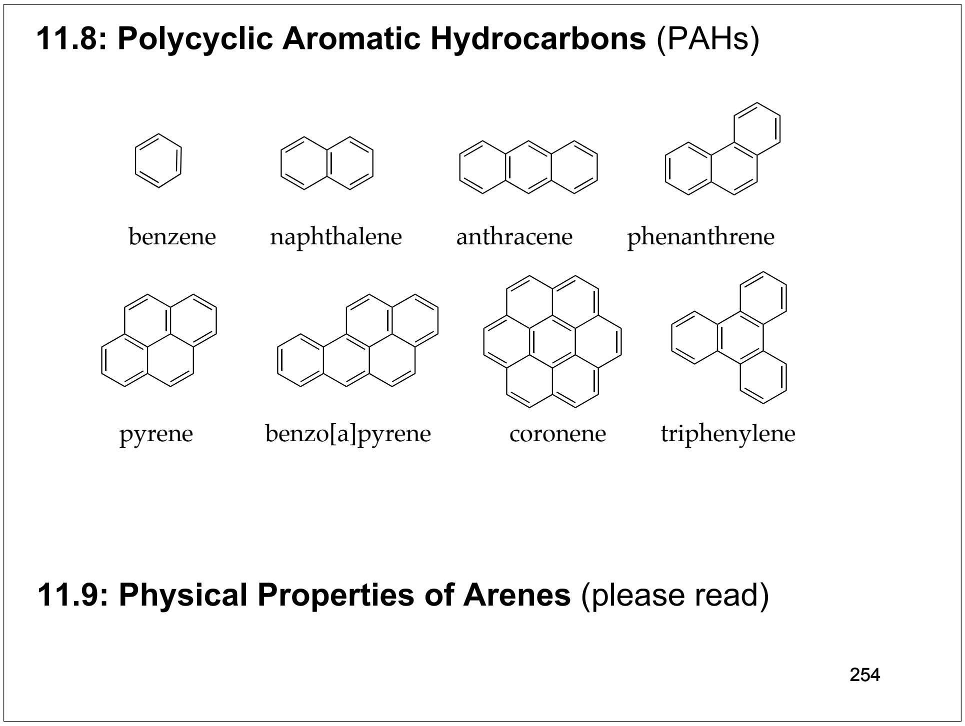
When the benzene ring is a substituent of a parent chain, it is referred to as a phenyl group. The benzene ring is regarded as a substituent when the parent chain has greater than six carbons. The benzene ring is the parent when the longest alkyl chain substituent is six carbons or less

2-methyl-7-phenyloctane

(1-methylbutyl)benzene

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

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



11.8: Polycyclic Aromatic Hydrocarbons (PAHs)

benzene naphthalene anthracene phenanthrene

pyrene benzo[a]pyrene coronene triphenylene

11.9: Physical Properties of Arenes (please read)

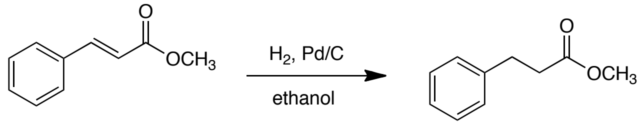
11.10: Reactions of Arenes: A Preview

1. Reactions involving the ring
   A. Reduction
      a. Catalytic hydrogenation (Chapter 11.4)
      b. Birch reduction (Chapter 11.11)
   B. Electrophilic aromatic substitution (Chapter 12)
   C. Nucleophilic aromatic substitution (Chapter 23)

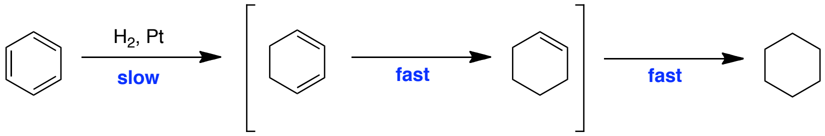
2. The ring as a substituent
   A. Benzylic halogenation (Chapter 11.12)
   B. Benzylic oxidation (Chapter 11.13)
   C. Nucleophilic substitution of benzylic halides (Chapter 11.14-15)

11.11: The Birch Reduction

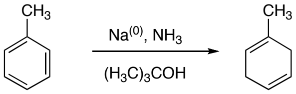
Catalytic Hydrogenation - Aromatic rings are inert to catalytic hydrogenation under conditions that will reduce alkene double bonds. Therefore, an alkene double bond can therefore be selectively reduced in the presence of an aromatic ring



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

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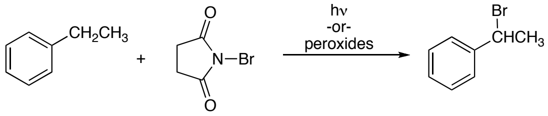
11.12: Free-Radical Halogenation of Alkylbenzenes

The benzylic position (the carbon next to a benzene ring) is analogous to the allylic position and can stabilize carbocations, radicals, and anions.

$$(CH_3)_3C{-}H \xrightarrow{380\ \text{kJ/mol}} (CH_3)_3C^{\bullet} + H^{\bullet}$$

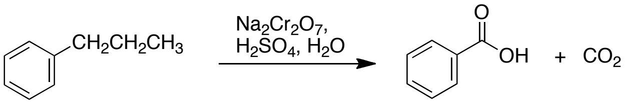
$$H_2C{=}CHCH_2{-}H \xrightarrow{368\ \text{kJ/mol}} H_2C{=}CH\dot{C}H_2 + H^{\bullet}$$

$$C_6H_5CH_2{-}H \xrightarrow{356\ \text{kJ/mol}} C_6H_5\dot{C}H_2 + H^{\bullet}$$

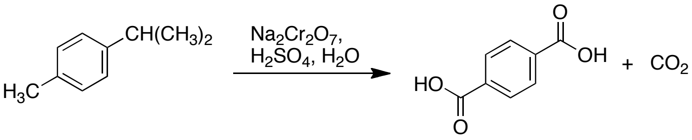


Mechanism is the same as allylic bromination

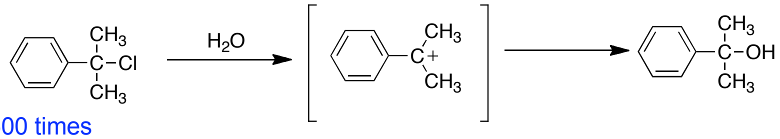
11.13: Oxidation of Alkylbenzenes - Benzene rings do not react with strong oxidants. However, the benzene ring can activate the benzylic position of alkylbenzene toward oxidation with strong oxidants such as $KMnO_4$ and $Na_2Cr_2O_7$ to give benzoic acids.



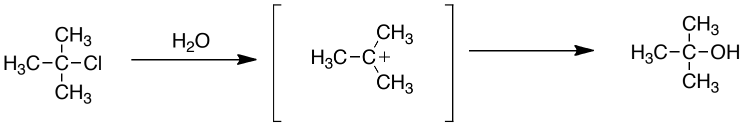
Benzoic acid



11.14: S_N1 Reactions of Benzylic Halides



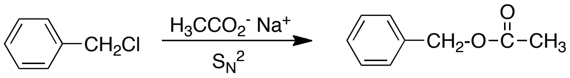
> 600 times
more reactive



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

11.15: S_N2 Reactions of Benzylic Halides -

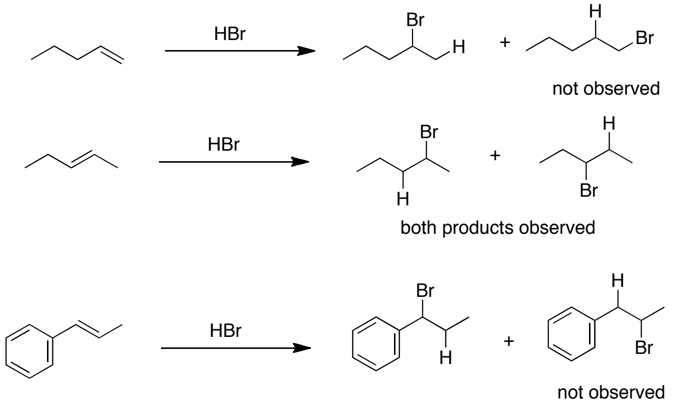
Benzylic halides undergo $S_N{}^2$ reactions faster than a alkyl halides (similar to allylic halides)



11.16: Preparation of Alkenylbenzenes (please read)

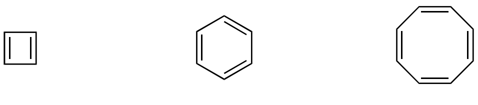
11.17: Addition Reactions of Alkenylbenzenes

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



11.18: Polymerization of Styrene (please read)
11.19: Cyclobutadiene and Cyclooctatetraene

Not all cyclic conjugated systems are aromatic (no special stability)

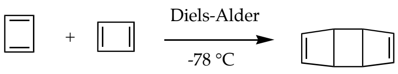


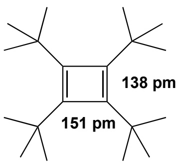
cyclobutadiene
4 π-electrons

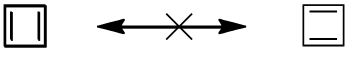
benzene
6 π-electrons

cyclooctatetraene
8 π-electrons

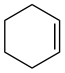
Cyclobutadiene: highly reactive
two different C-C bonds

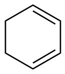


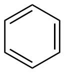


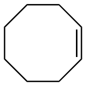


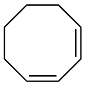
Cyclooctatetraene:
Heats of hydrogenation - No special stability for cyclooctatetraene

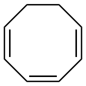

120 KJ/mol

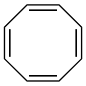

230 KJ/mol

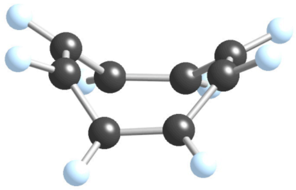

208 KJ/mol


97 KJ/mol


205 KJ/mol


303 KJ/mol

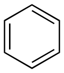

410 KJ/mol

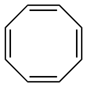


reactivity similar to normal C=C

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.

11.20: 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:

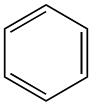
cyclic, conjugated, planar molecules that contain 4n π-electrons (where n is an integer).

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

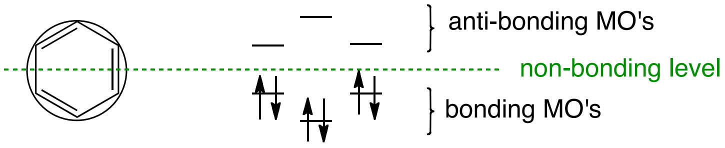
Frost Circles: relative energies of the molecular orbitals of cyclic, conjugated systems

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:

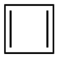


Benzene
6 π-electrons

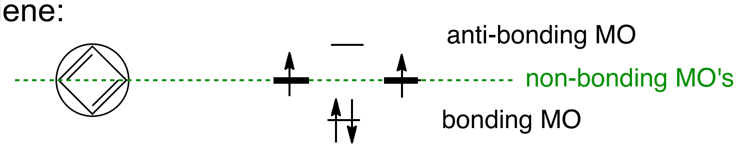


The bonding MO's will be filled for aromatic compounds, such as benzene.

Cyclobutadiene:

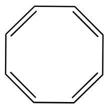


Cyclobutadiene
4 π-electrons

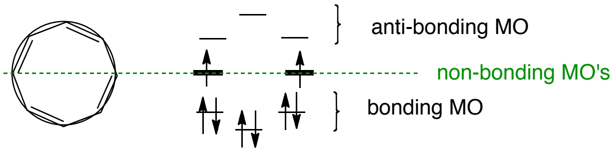


For anti- aromatic compounds, such as cyclobutadiene and cyclooctatetraene, there will be unpaired electrons in bonding, non-bonding or antibonding MO's.

Cyclooctatetraene:

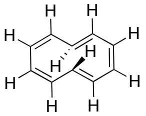


Cyclooctatetraene
8 π-electrons



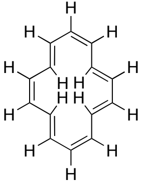
11.21: Annulenes - monocyclic, conjugated, planar polyenes that conform to Hückel's rule.

[10]annulene



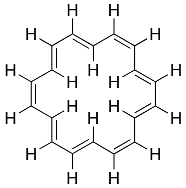
10 π-electrons
4n+2 = 10, n=2.

[14]annulene

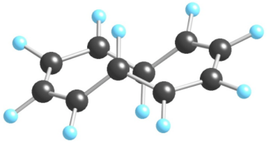


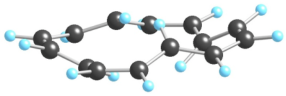
14 π-electrons
4n+2=14, n=3

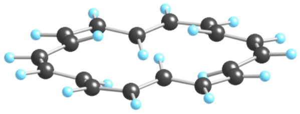
[18]annulene

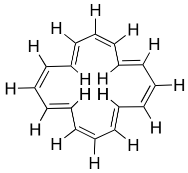


18 π-electrons
4n+2=18, n=4



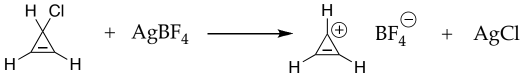


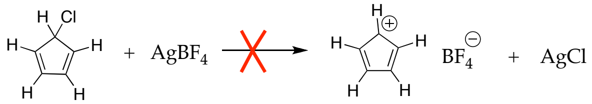


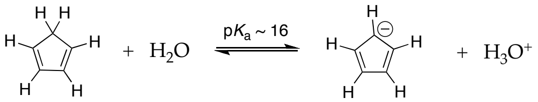


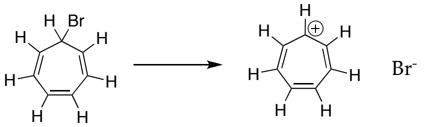
[16]annulene
16 π-electrons
4n=16, n=4

11.22: Aromatic Ions

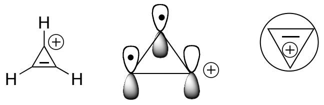




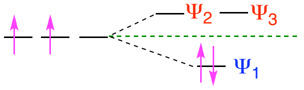




Cyclopropenyl cation

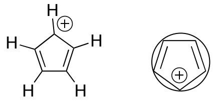


cyclopropenyl cation
2 π-electrons

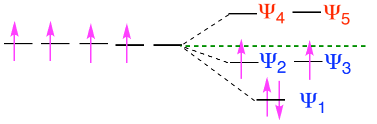


4*n*+2=2
n=0
aromatic

Cyclopentadienyl cation

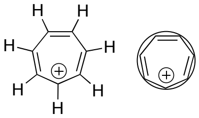


cyclopentadienyl cation
4 π-electrons

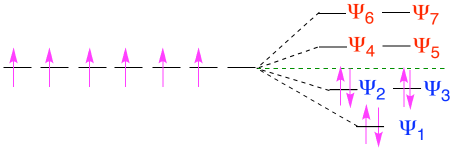


4*n*=4
n=1
anti-aromatic

Cycloheptatrienyl cation

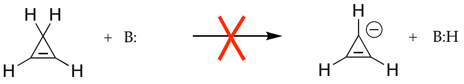


cycloheptatrienyl cation
6 π-electrons



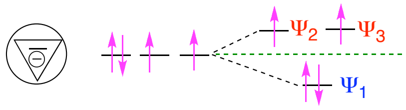
4n+2=6
n=1
aromatic

Cyclopropenyl anion

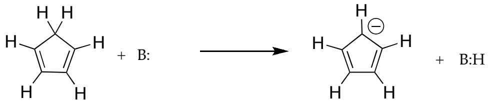


cyclopropenyl anion
4 π-electrons

4*n*=4
n=1
anti-aromatic



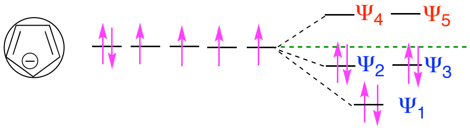
Cyclopentadienyl anion



pK_a ~ 16

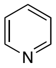
cyclopentadienyl anion
6 π-electrons

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

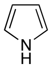


11.23: Heterocyclic Aromatic Compounds (please read)

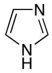
Heterocycle: any cyclic compound that contains ring atom(s) other than carbon (N, O, S, P). Cyclic compounds that contain only carbon are called carbocycles



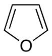
pyridine



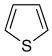
pyrrole



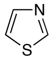
imidazole



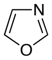
furan



thiophene



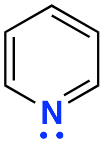
thiazole



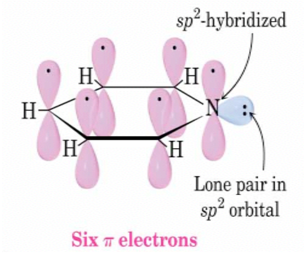
oxazole

11.24: Heterocyclic Aromatic Compounds and Hückel's Rule

Pyridine: π-electron structure resembles benzene (6 π-electrons) The nitrogen lone pair electrons are <u>not</u> part of the aromatic system.



pyridine



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