CHAPTER 16: Aromatic Compounds

We can separate organic compounds into two large categories:
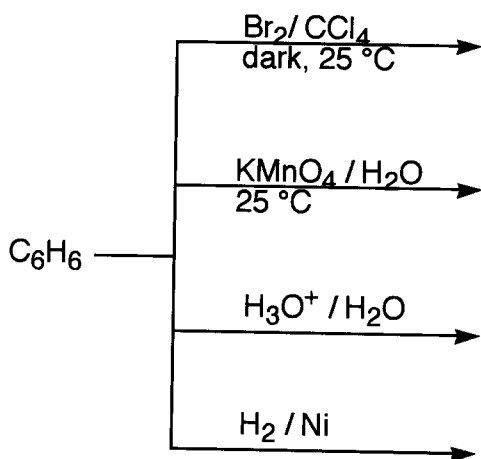
Aliphatic (fatlike)

↓

undergo addition
to π bonds

Aromatic (fragrant)

↓

undergo substitution
at π bonds

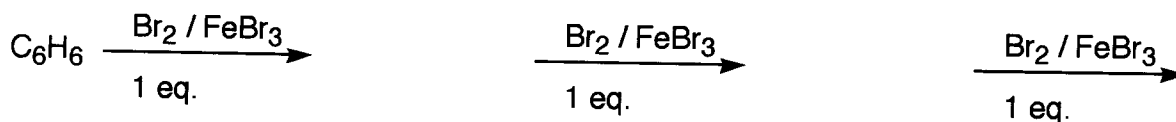**Structure of Benzene** - initially a puzzling compound

1825 - Michael Faraday isolates "benzene" from lampblack (pyrolyzed whale oil)
    - determines empirical formula CH

1834 - Eilhard Mitscherlich synthesizes "benzene" and determines molecular formula C_6H_6

Examine the results of typical reactions of multiple bonds:

$$C_6H_6$$

$$\xrightarrow[\text{dark, 25 °C}]{Br_2/\,CCl_4}$$

$$\xrightarrow[\text{25 °C}]{KMnO_4\,/\,H_2O}$$

$$\xrightarrow{H_3O^+\,/\,H_2O}$$

$$\xrightarrow{H_2\,/\,Ni}$$

Add Lewis acid catalyst during bromination:

$$C_6H_6 \xrightarrow[\text{1 eq.}]{Br_2\,/\,FeBr_3} \qquad \xrightarrow[\text{1 eq.}]{Br_2\,/\,FeBr_3} \qquad \xrightarrow[\text{1 eq.}]{Br_2\,/\,FeBr_3}$$

"Something" gives benzene a special resistance to addition, a special stability:

1866 - Friedrich Kekule proposes cyclic structure of alternating double and single bonds
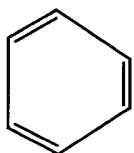
Problem: structure would predict the existence of two 1,2 - dibromobenzene isomers
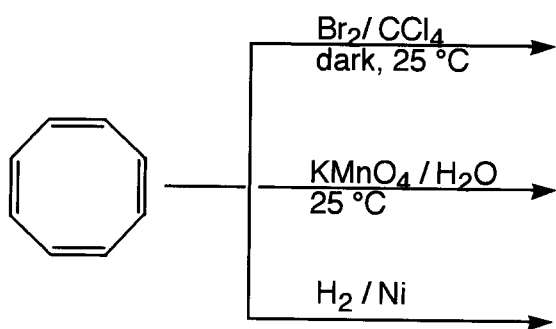
Solution: To explain the observation, Kekule adjusts the proposal:

Problem solved? If the cyclic structure of alternating double and single bonds observed in benzene is the key to aromaticity, should find other evidence.
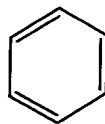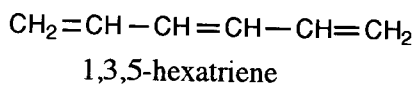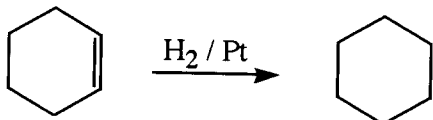
Consider cyclooctatetraene:

Br_2/ CCl_4
dark, 25 °C

$KMnO_4 / H_2O$
25 °C

H_2 / Ni

Kekule's mistake:

The Stability of Benzene

Aromaticity is not the result of conjugation alone OR benzene is not 1,3,5-cyclohexatriene

Bond lengths:

$$CH_2=CH-CH=CH-CH=CH_2$$
1,3,5-hexatriene

Heats of Hydrogenation:

$$\xrightarrow{H_2 \,/\, Pt}$$ $\Delta H_{hydrog} = 28.6$ kcal/mol

$$\xrightarrow{2H_2 \,/\, Pt}$$ Expected:
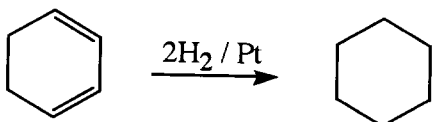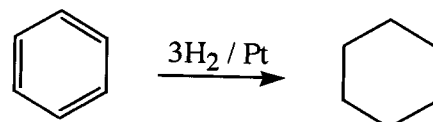
Observed:

$$\xrightarrow{3H_2 \,/\, Pt}$$ Expected:

Observed:

Molecular Orbital Descriptions:
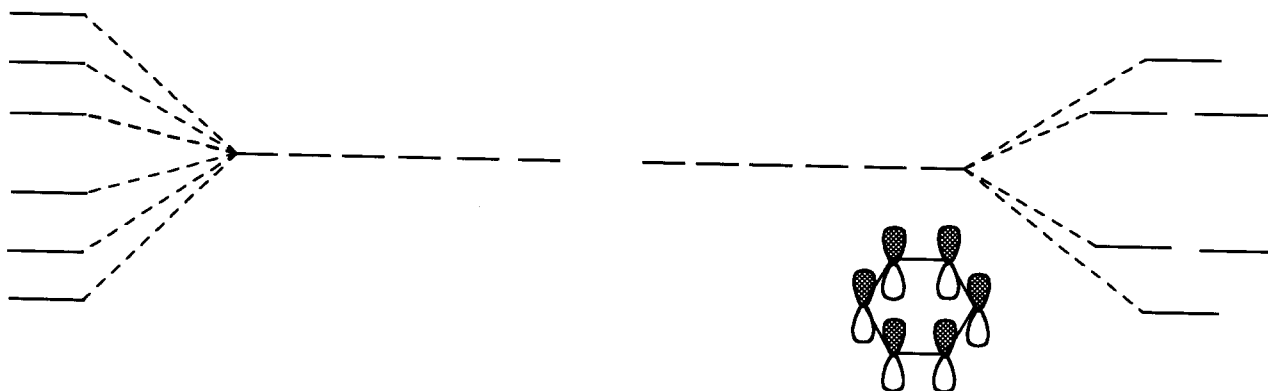
Huckel Rule

The Huckel Rule is applied to molecules that meet the following:

1. Cyclic
2. Planar
3. Each atom in the "cycle" has a p orbital.

If each of the above is true and the cycle has $4n + 2$ π electrons, where $n = 0, 1, 2, 3, \ldots$,the molecule is **aromatic** -
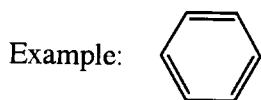
Example:

If each of the above is true and the cycle has $4n$ π electrons, where $n = 0, 1, 2, 3, \ldots$,the molecule is **antiaromatic** -
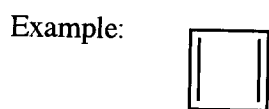
Example:

If one or more of the above is not true, the molecule is **nonaromatic**, regardless of the number π electrons.

Examples:
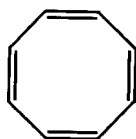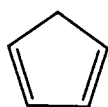
Polygon Rule - inscribe the molecule in a circle with one vertex at the bottom of the circle; each point at which the molecule touches the circle represents the energy level of a molecular orbital
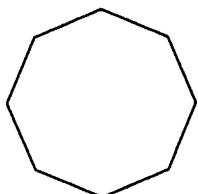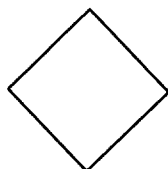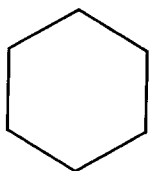
Annulenes - monocyclic compounds with alternating double an single bonds
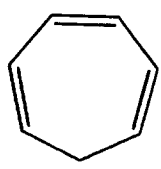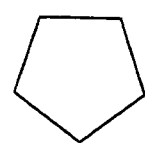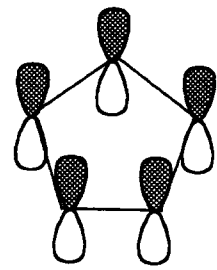- aromatic / antiaromatic / nonaromatic?

Examples:
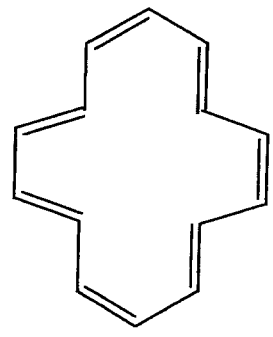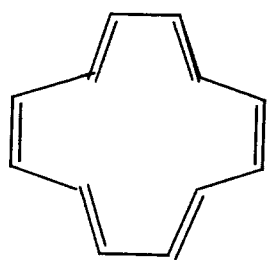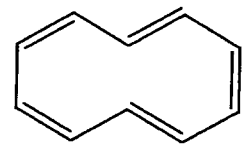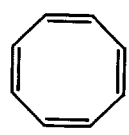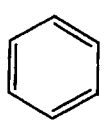
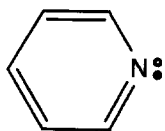nonplanar annulenes:

planar annulenes:

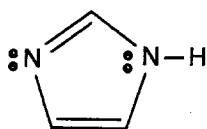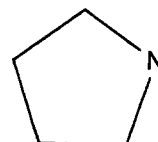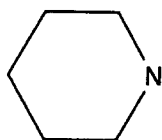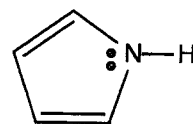**Aromatic Ions**
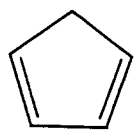
strong base

$\longrightarrow$

$\dfrac{\text{- hydride}}{(- H\colon^-)}$ $\longrightarrow$
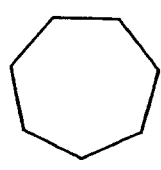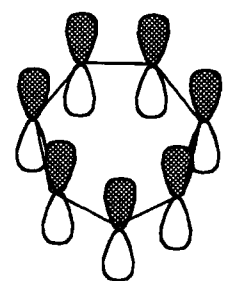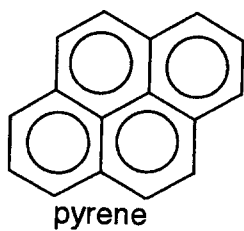
Heterocyclic Aromatic Compounds
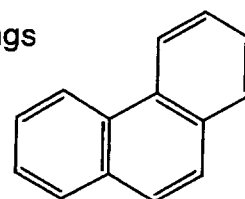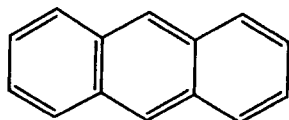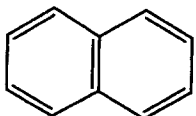
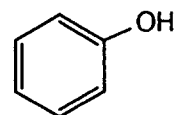Example: aromatic / antiaromatic / nonaromatic? (Do we count the lone pair?)
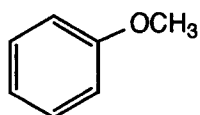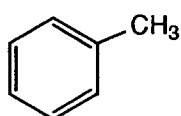
VS

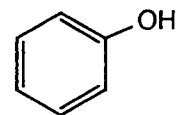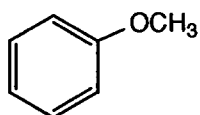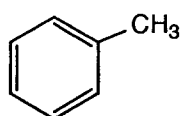# Polynuclear Aromatic Hydrocarbons (PNA's or PAH's) - fused benzene rings

pyrene

dibenzopyrene

benzo[α]pyrene
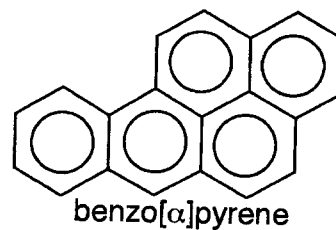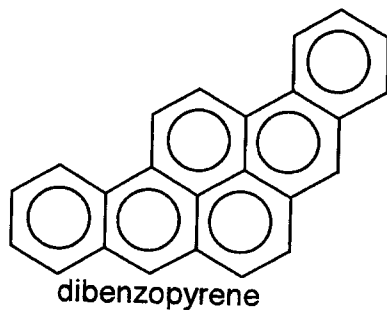
Nomenclature of Benzene Derivatives:

I. Monosubstituted
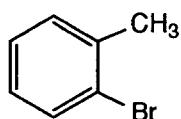### A. IUPAC - named as abenzene derivative

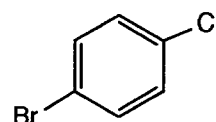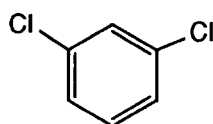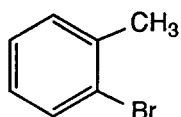## B. Common Names - You MUST know the common names on p. 716 of Wade (p. 736 of 3rd ed)
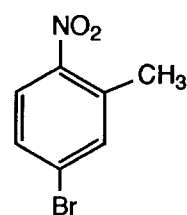

II. Disubstituted
A. Number substituents

B. Ortho, para, meta system

III. Trisubstituted - must use numbers
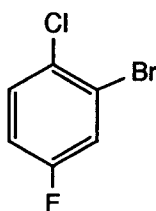
IV. Benzene ring as a substituent : General Guide - larger portion is parent

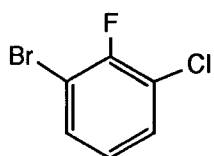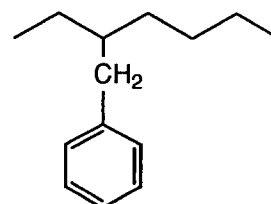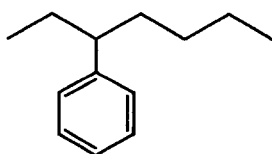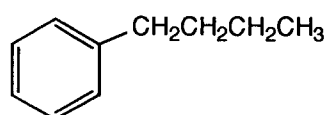**Spectroscopy Summary** (Benzene and Derivatives)

IR:

1. ring "skeletal" vibrations $C\!=\!=\!C$

2 regions: $\left.\begin{array}{l} 1600 - 1585 \text{ cm}^{-1} \\ 1500 - 1400 \text{ cm}^{-1} \end{array}\right\}$ 2 - 4 peaks; peaks at 1500 and 1600 cm^{-1} are usually the most intense; often appear as doublets
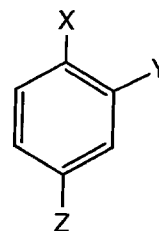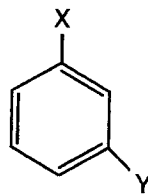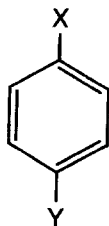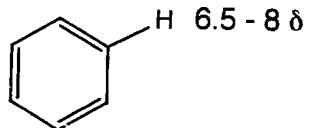
2. CH stretching 3100 - 3000 cm^{-1} : $C\!=\!=\!C\!-\!H$

3. CH out of plane bending 900 - 675 cm^{-1}: $C\!=\!=\!C\!-\!H$

characteristic of ring substitution:

mono: 2 bands, 690 - 710 cm^{-1} and 730 - 770 cm^{-1}

meta: 2 bands, 690 - 710 cm^{-1} and 810 - 850 cm^{-1}

ortho: 1 band, 735 - 770 cm^{-1}

para: 1 band, 810 - 840 cm^{-1}

$\left.\begin{array}{l} \\ \\ \\ \\ \end{array}\right\}$ usually strong

^{1}H NMR:

H 6.5 - 8 δ

^{13}C NMR:

120 - 150 δ