Organic Chemistry II / CHEM 252

Chapter 14 – Aromatic Compounds

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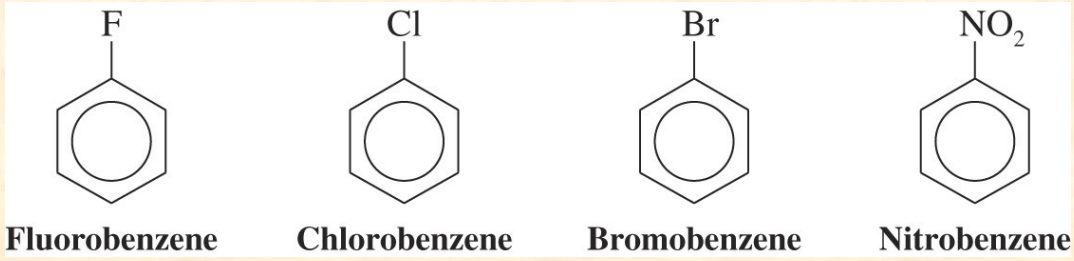
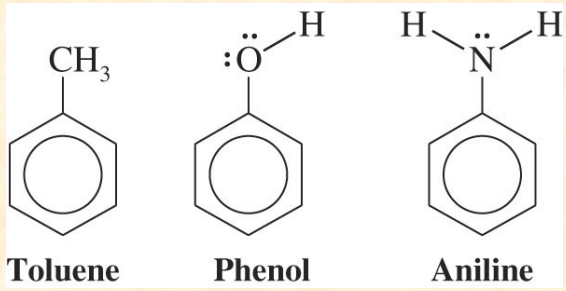
Introduction

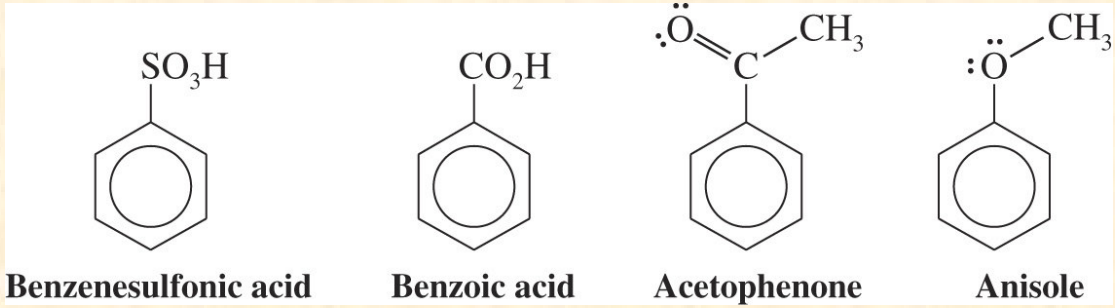
- Historical name, based on smell, no relation to sturcture

- Nomenclature of Benzene Derivatives
  - Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix



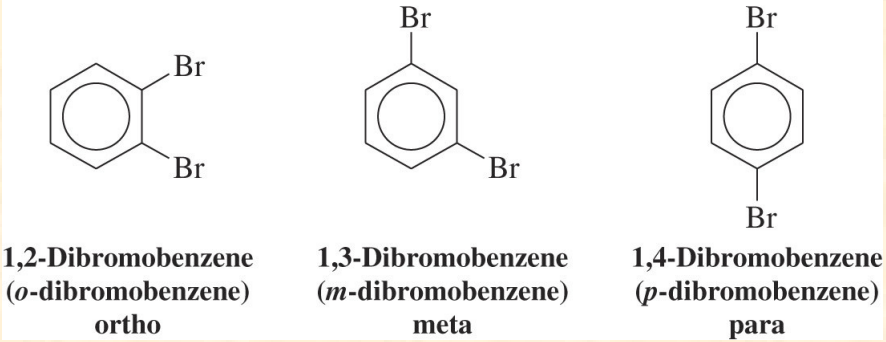
  - For other monosubstituted benzenes, the presence of the substituent results in a new parent name



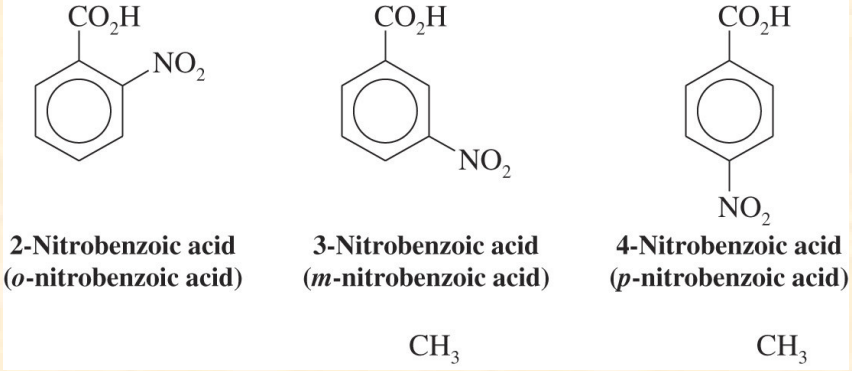


Introduction

- When two substituents are present their position may be indicated by the prefixes *ortho*, *meta,* and *para* (*o*, *m* and *p*) or by the corresponding numerical positions

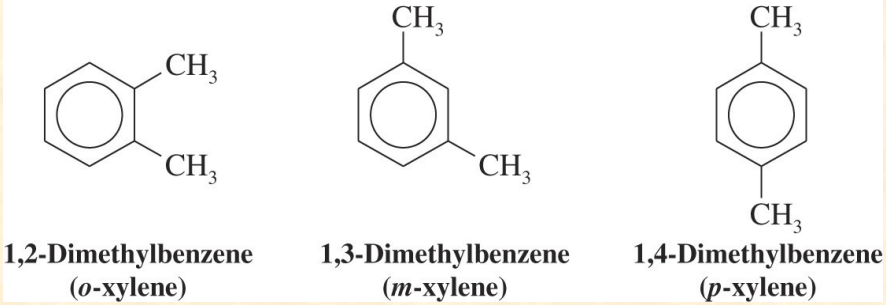


1,2-Dibromobenzene (*o*-dibromobenzene) ortho | **1,3-Dibromobenzene (*m*-dibromobenzene) meta** | **1,4-Dibromobenzene (*p*-dibromobenzene) para**



2-Nitrobenzoic acid (*o*-nitrobenzoic acid) | **3-Nitrobenzoic acid (*m*-nitrobenzoic acid)** | **4-Nitrobenzoic acid (*p*-nitrobenzoic acid)**

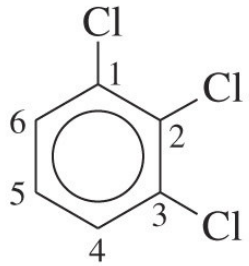
- Dimethyl substituted benzenes are called xylenes



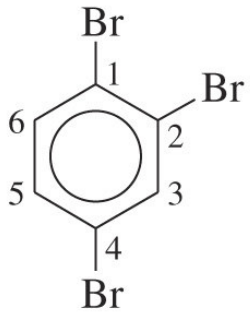
1,2-Dimethylbenzene (*o*-xylene) | **1,3-Dimethylbenzene (*m*-xylene)** | **1,4-Dimethylbenzene (*p*-xylene)**

Introduction

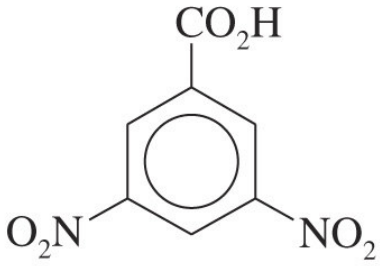
- Numbers must be used as locants when more than two substituents are present
  - The lowest possible set of numbers should be given to the substituents
  - The substituents should be listed in alphabetical order
  - If one of the substituents defines a parent other than benzene, this substituent defines the parent name and should be designated position 1



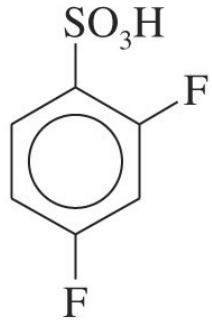
1,2,3-Trichlorobenzene



1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)



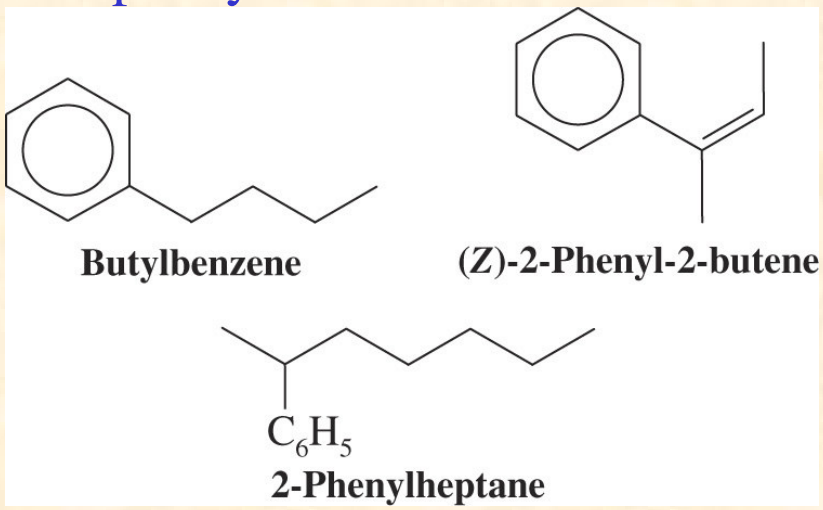
3,5-Dinitrobenzoic acid



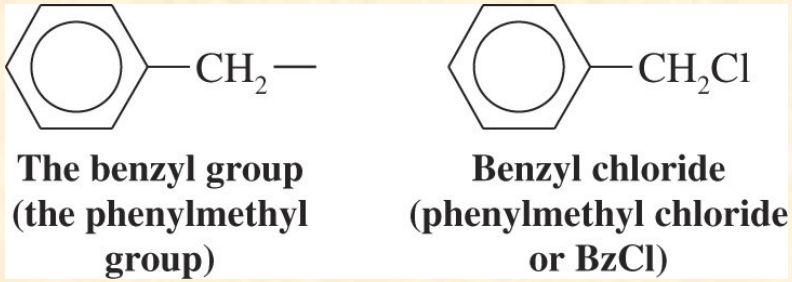
2,4-Difluorobenzenesulfonic acid

Introduction

- The C_6H_5- group is called phenyl when it is a substituent
  - Phenyl is abbreviated Ph or Φ
  - A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent
  - If the chain is unsaturated then it must be the parent and the benzene is then a phenyl substituent

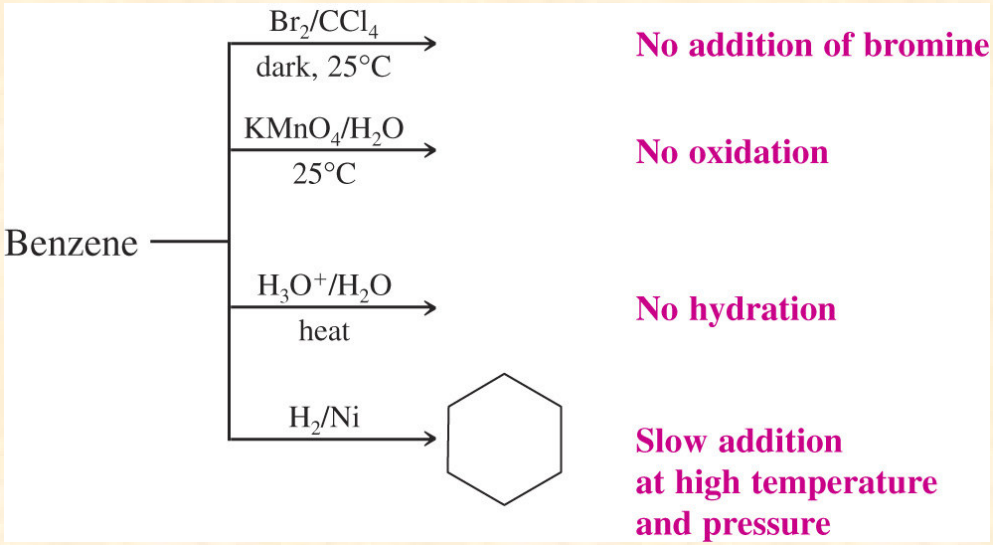


- The phenylmethyl group is called a benzyl (abbreviated Bz)



Reactions of Benzenes

- Reactions of Benzene
  - Even though benzene is highly unsaturated it does not undergo any of the regular reactions of alkenes such as addition or oxidation



  - Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition
    - Benzene produces only one monobrominated compound, which indicates that all 6 carbon-hydrogen bonds are equivalent

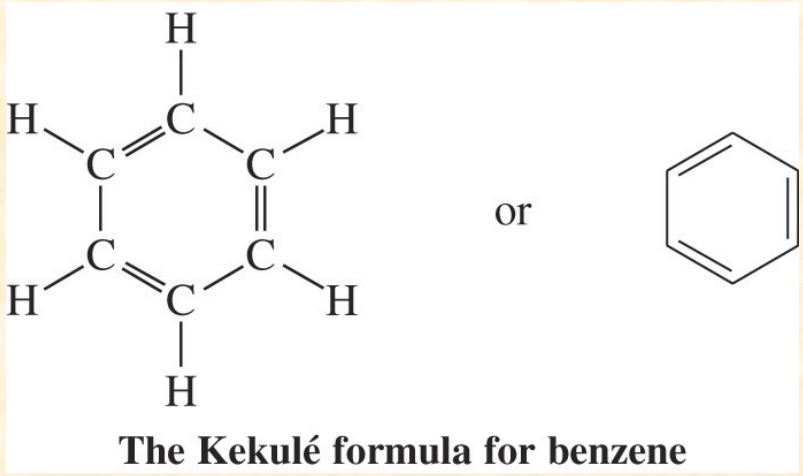
$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr \qquad \text{Observed}$$

$$C_6H_6 + Br_2 \not\longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6 \qquad \text{Not observed}$$

Structure of Benzene

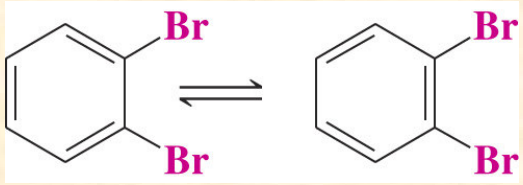
- The Kekule Structure for Benzene
  - Kekule was the first to formulate a reasonable representation of benzene

Friedrich August Kekule von Stradonitz



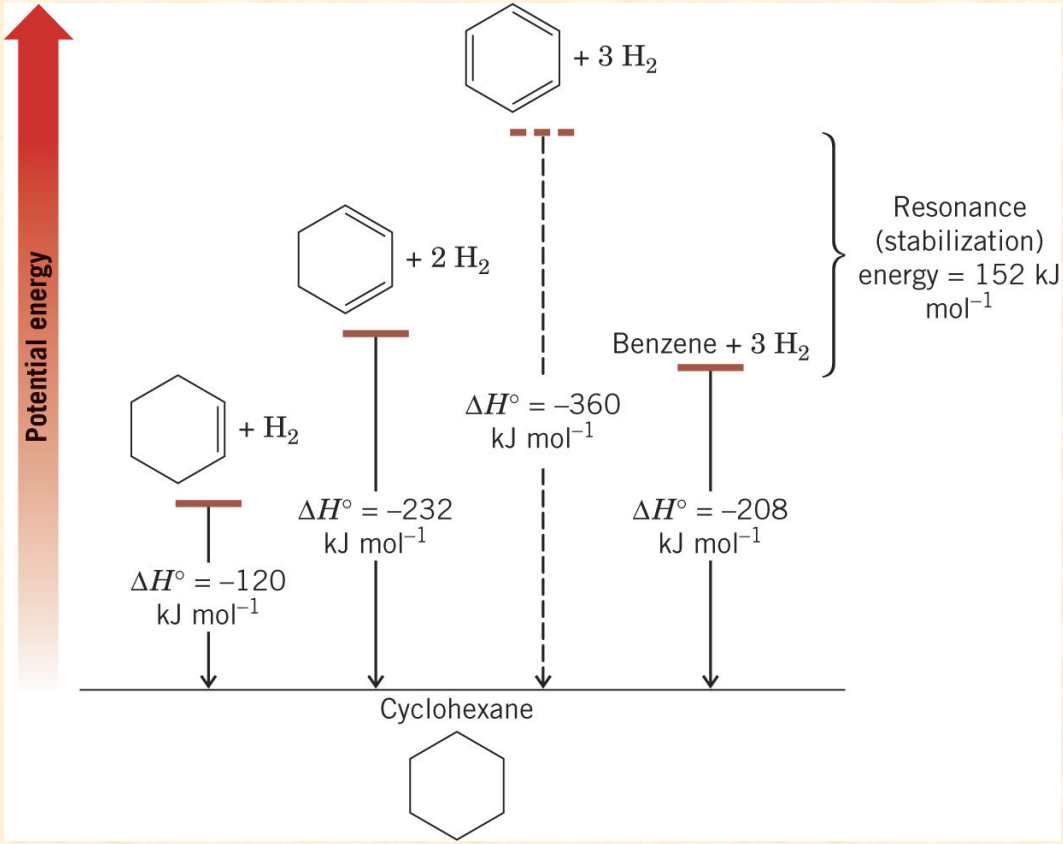
The Kekulé formula for benzene

  - The Kekule structure suggests alternating double and single bonds
    - Based on the Kekule structure one would expect there to be two different 1,2-dibromobenzenes but there is only one
    - Kekule suggested an equilibrium between these compounds to explain this observation but it is now known no such equilibrium exists



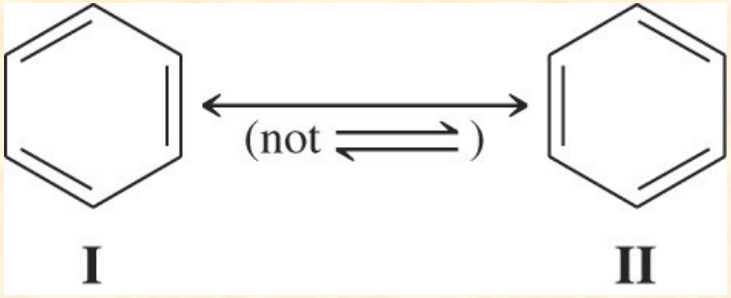
Structure of Benzene

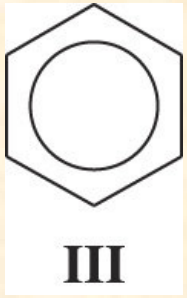
- The Stability of Benzene
  - Benzene is much more stable than the cyclohexatriene
    - A reasonable prediction for the heat of hydrogenation of hypothetical cyclohexatriene is -360 kJ mol^{-1} (3 x cyclohexene, -120 kJ mol^{-1})
    - The heat of hydrogenation for benzene is -280 mol^{-1}, 152 kJ mol^{-1} more stable than hypothetical cyclohexatriene
    - This difference is called the resonance energy



Structure of Benzene

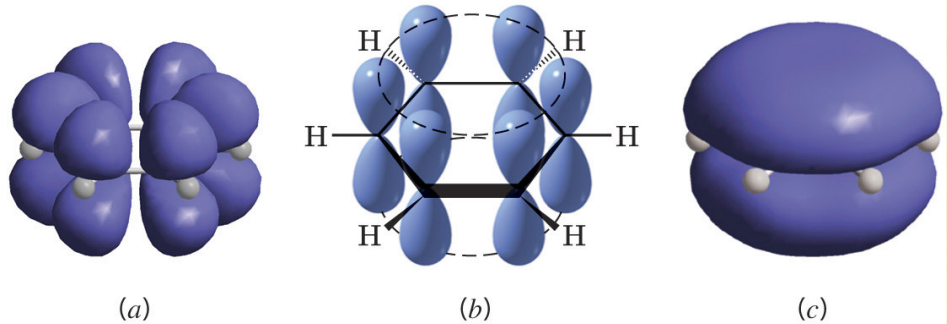
- Modern Theories of the Structure of Benzene
  - The Resonance Explanation of the Structure of Benzene
    - Structures I and II are equal resonance contributors to the real structure of benzene
      - Benzene is particularly stable because it has two equivalent and important resonance structures
      - Each carbon-carbon bond is 1.39 Å, which is between the length of a carbon-carbon single bond between sp^2 carbons (1.47Å) and a carbon-carbon double bond (1.33 Å)
      - Often the hybrid is represented by a circle in a hexagon (III)



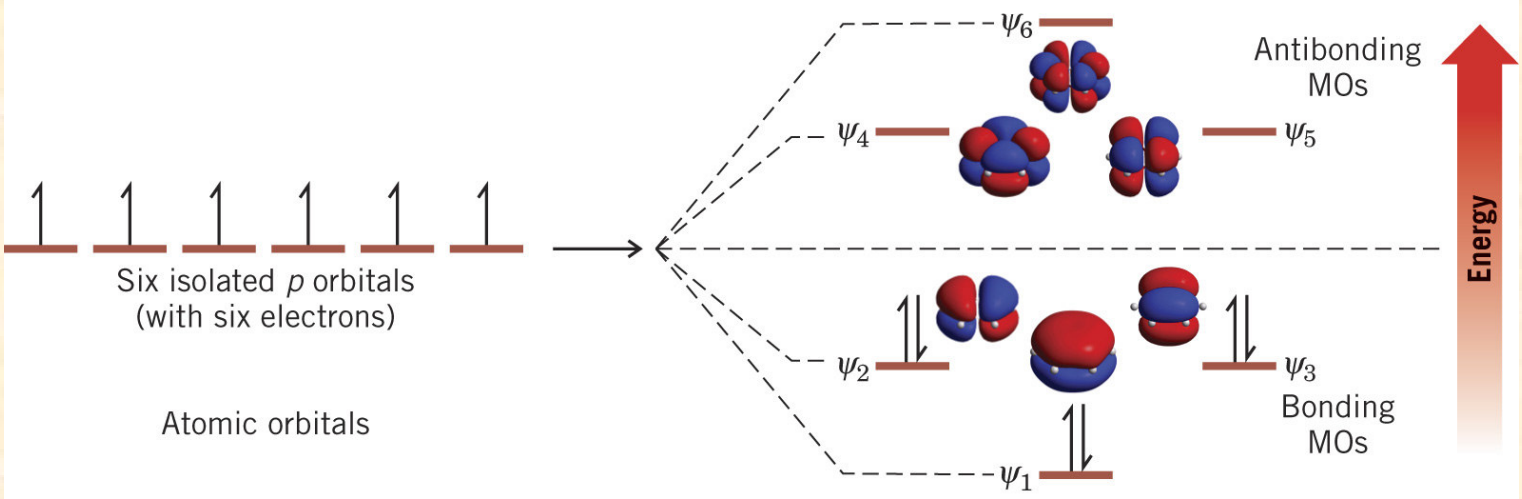


Structure of Benzene

- The Molecular Orbital Explanation of the Structure of Benzene
  - The carbons in benzene are sp^2 hybridized with *p* orbitals on all 6 carbons (a)
    - The *p* orbitals overlap around the ring (b) to form a bonding molecular orbital with electron density above and below the plane of the ring (c)



  - There are six π molecular orbitals for benzene



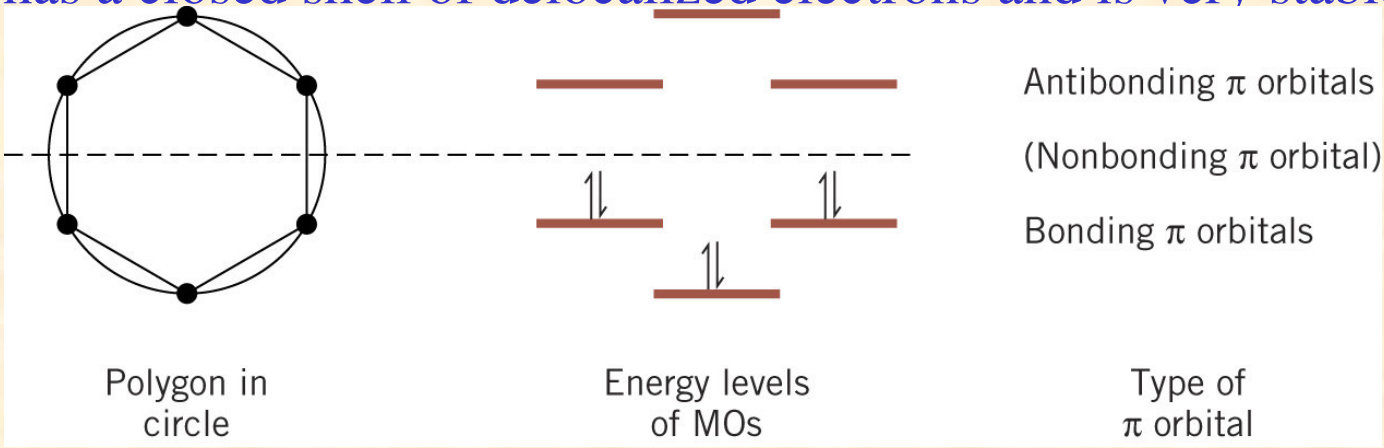
Structure of Benzene

- Huckel's Rule: The 4n+2π Electron Rule
  - Planar monocyclic rings with a continuous system of *p* orbitals and 4n + 2π electrons are aromatic (n = 0, 1, 2, 3 etc)
    - Aromatic compounds have substantial resonance stabilization
    - Benzene is aromatic: it is planar, cyclic, has a *p* orbital at every carbon, and 6 π electrons (n=1)
  - There is a *polygon-and-circle method* for deriving the relative energies of orbitals of a system with a cyclic continuous array of *p* orbitals
    - A polygon corresponding to the ring is inscribed in a circle with one point of the polygon pointing directly down
    - A horizontal line is drawn where vertices of the polygon touch the circle - each line corresponds to the energy level of the π MOs at those atoms
    - A dashed horizontal line half way up the circle indicates the separation of bonding and antibonding orbitals

Structure of Benzene

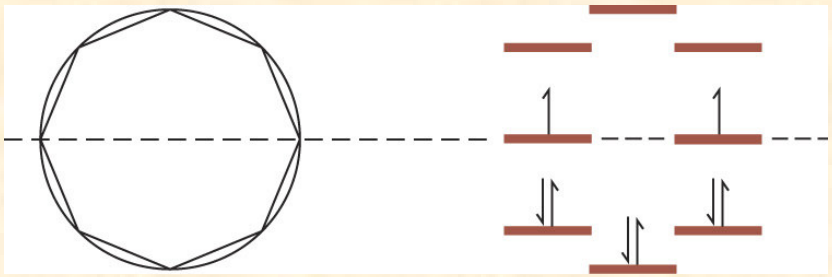
Benzene has 3 bonding and 3 antibonding orbitals

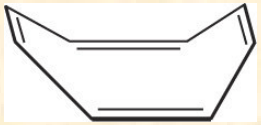
All the bonding orbitals are full and there are no electrons in antibonding orbitals; benzene has a closed shell of delocalized electrons and is very stable



Cyclooctatetraene has two nonbonding orbitals each with one electron

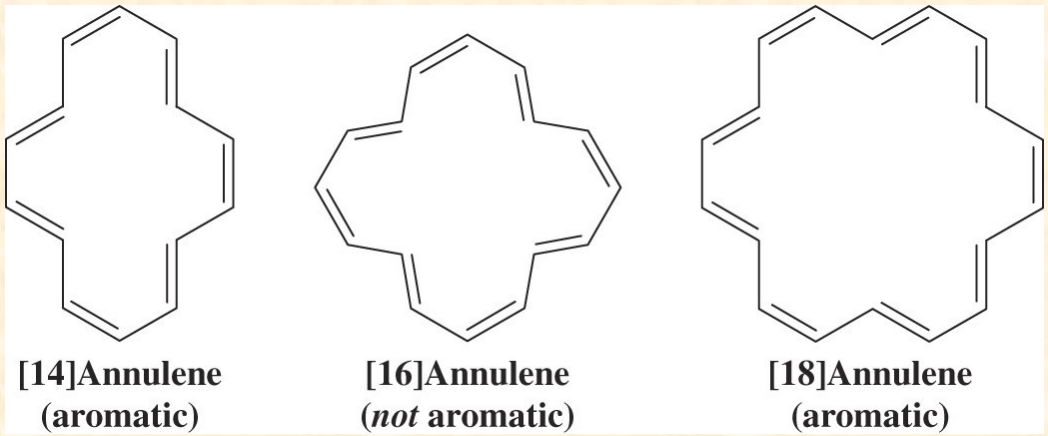
This is an unstable configuration; cyclooctatetraene adopts a nonplanar conformation with localized p bonds to avoid this instability





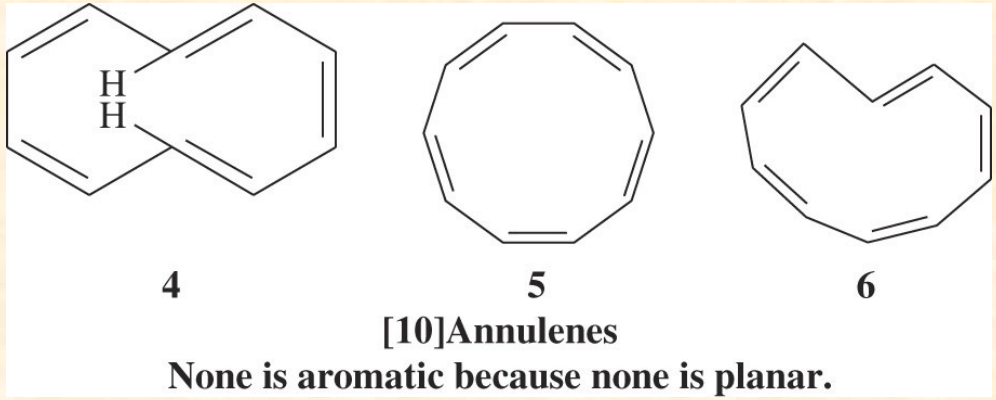
Annulenes

- The Annulenes
  - Annulenes are monocyclic compounds with alternating double and single bonds
    - Annulenes are named using a number in brackets that indicates the ring size
    - Benzene is [6]annulene and cyclooctatetraene is [8]annulene
    - An annulene is aromatic if it has $4n+2\pi$ electrons and a planar carbon skeleton
  - The [14]and [18]annulenes are aromatic (4n+2, where n= 3,4)
    - The [16] annulene is not aromatic



Annulenes

- The [10]annulenes below should be aromatic but none of them can be planar
  - 4 is not planar because of steric interaction of the indicated hydrogens
  - 5 and 6 are not be planar because of large angle strain in the flat molecules



4 **5** **6**

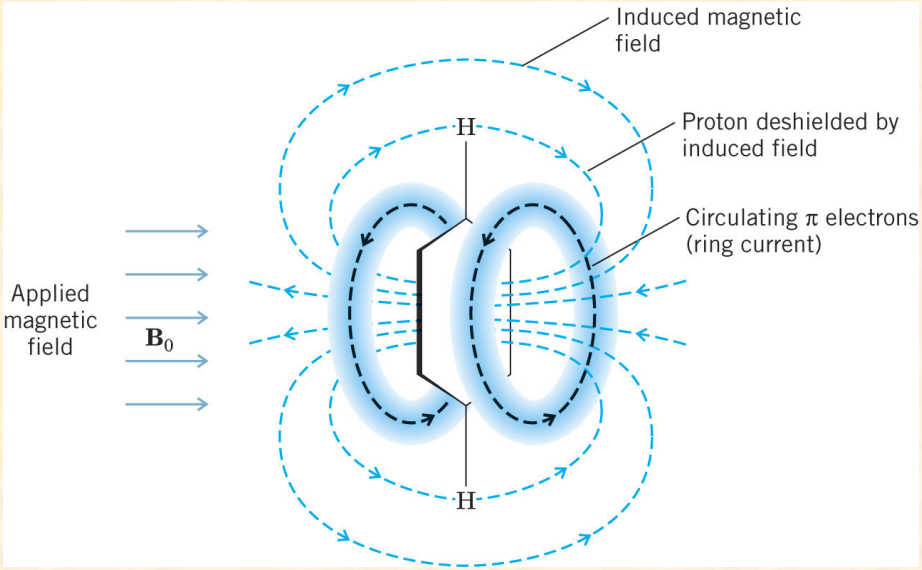
[10]Annulenes
None is aromatic because none is planar.

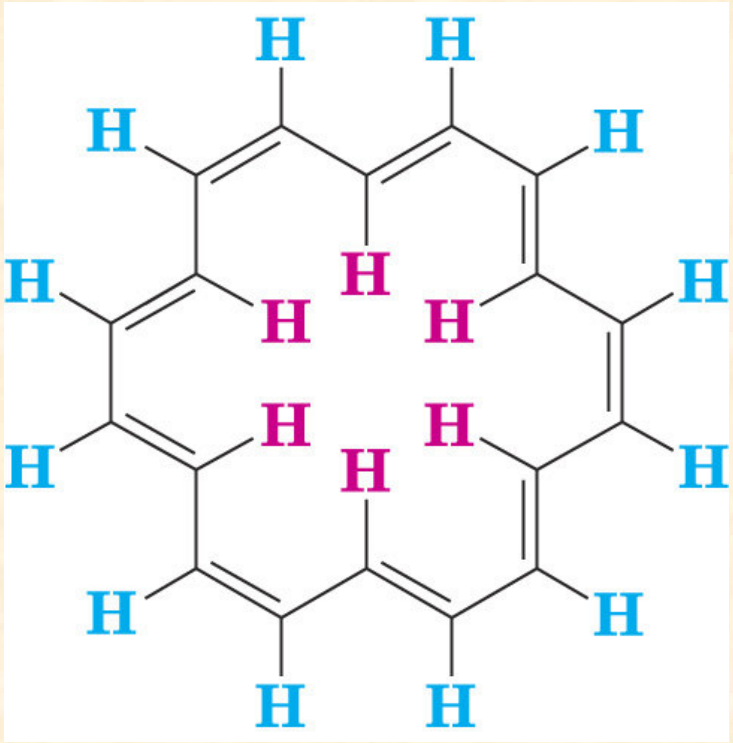
  - Cyclobutadiene is a [4]annulene and is not aromatic
  - It does not follow the 4n+ 2 rule and is highly unstable

Cyclobutadiene
or [4]annulene
(*not* aromatic)

Evidence of Electron Delocalization

NMR Spectroscopy: Evidence for Electron Delocalization in Aromatic Compounds

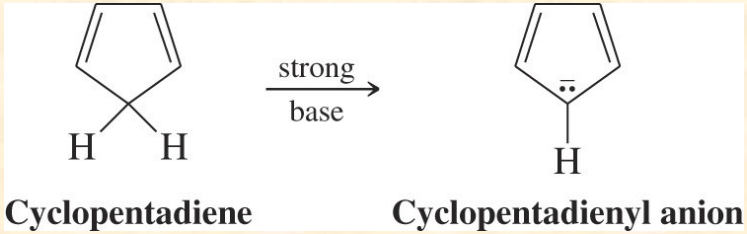


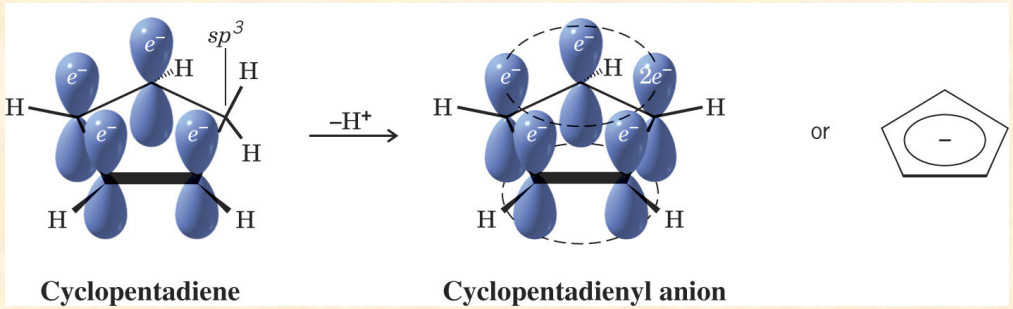


UV-Vis Spectroscopy

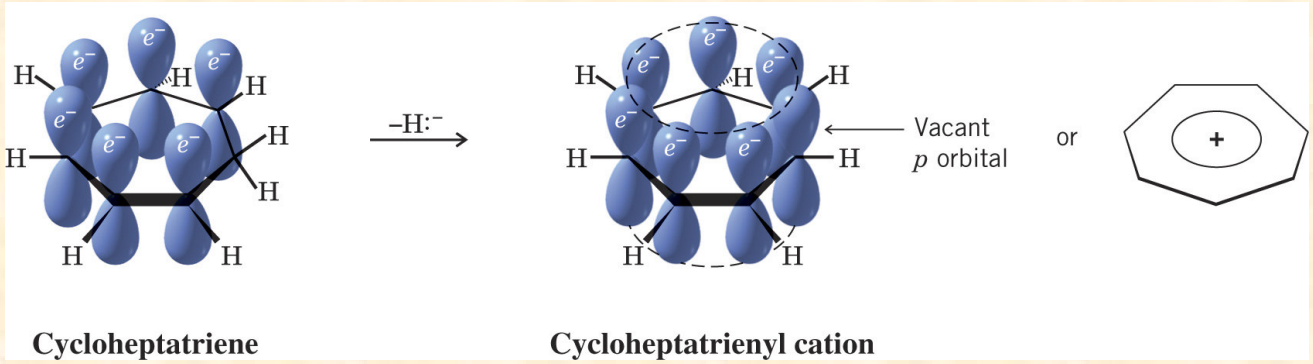
Aromatic Ions

- Cyclopentadiene is unusually acidic ($_pK_a$ = 16) because it becomes the aromatic cyclopentadienyl anion when a proton is removed
  - Cyclopentadienyl anion has 6 π electrons in a cyclic, continuous π-electron system, and hence follows the 4n + 2 rule for aromaticity





- Cycloheptatriene is not aromatic because its π electrons are not delocalized around the ring (the sp^3-hybrid CH_2 group is an "insulator")
  - Lose of hydride produces the aromatic cycloheptatrienyl cation (tropylium cation)



Aromatic Ions

PROBLEM 2

a. Draw arrows to show the movement of electrons in going from one resonance contributor to the next in the cyclopentadienyl anion.

b. How many ring atoms share the negative charge?

Aromatic Ions

PROBLEM 3◆

Which compound in each set is aromatic? Explain your choice.

a.

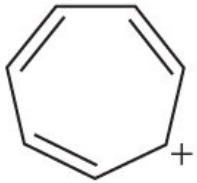
cyclopropene

cyclopropenyl cation

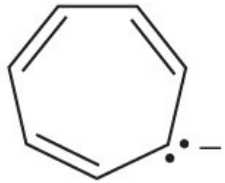
cyclopropenyl anion

b.

cycloheptatriene



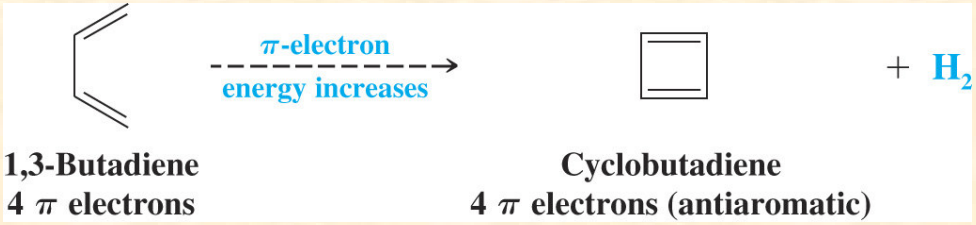
cycloheptatrienyl cation

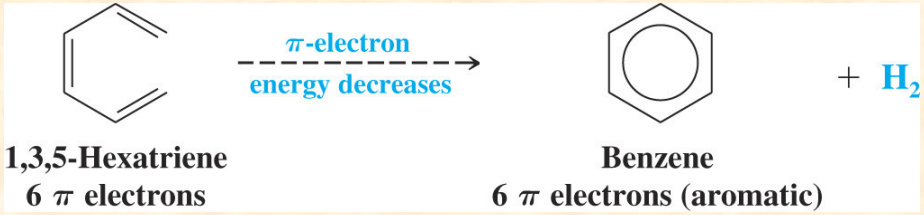


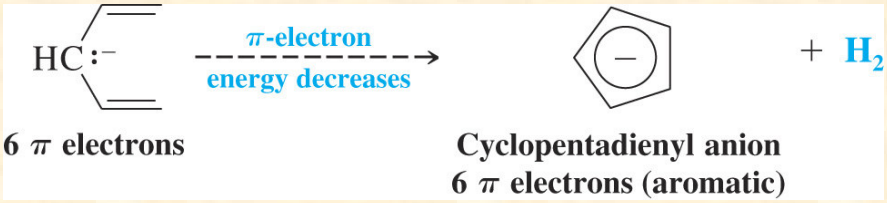
cycloheptatrienyl anion

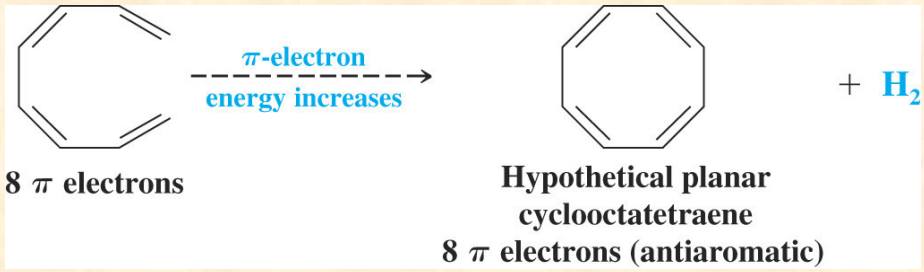
Anti- and Nonaromatic Compounds

- Aromatic, Antiaromatic, and Nonaromatic Compounds
  - A comparison of cyclic annulenes with their acyclic counterparts provides a measures of the stability conferred by aromaticity
    - ring has lower π-electron energy than the open chain: aromatic
    - ring has the same π-electron energy as the open chain: nonaromatic
    - ring has higher π-electron energy than the open chain: antiaromatic
  - Benzene and cylcopentadientl anion are aromatic
  - Cyclobutadiene is antiaromatic
    - Cyclooctatetraene, if it were planar, would be antiaromatic



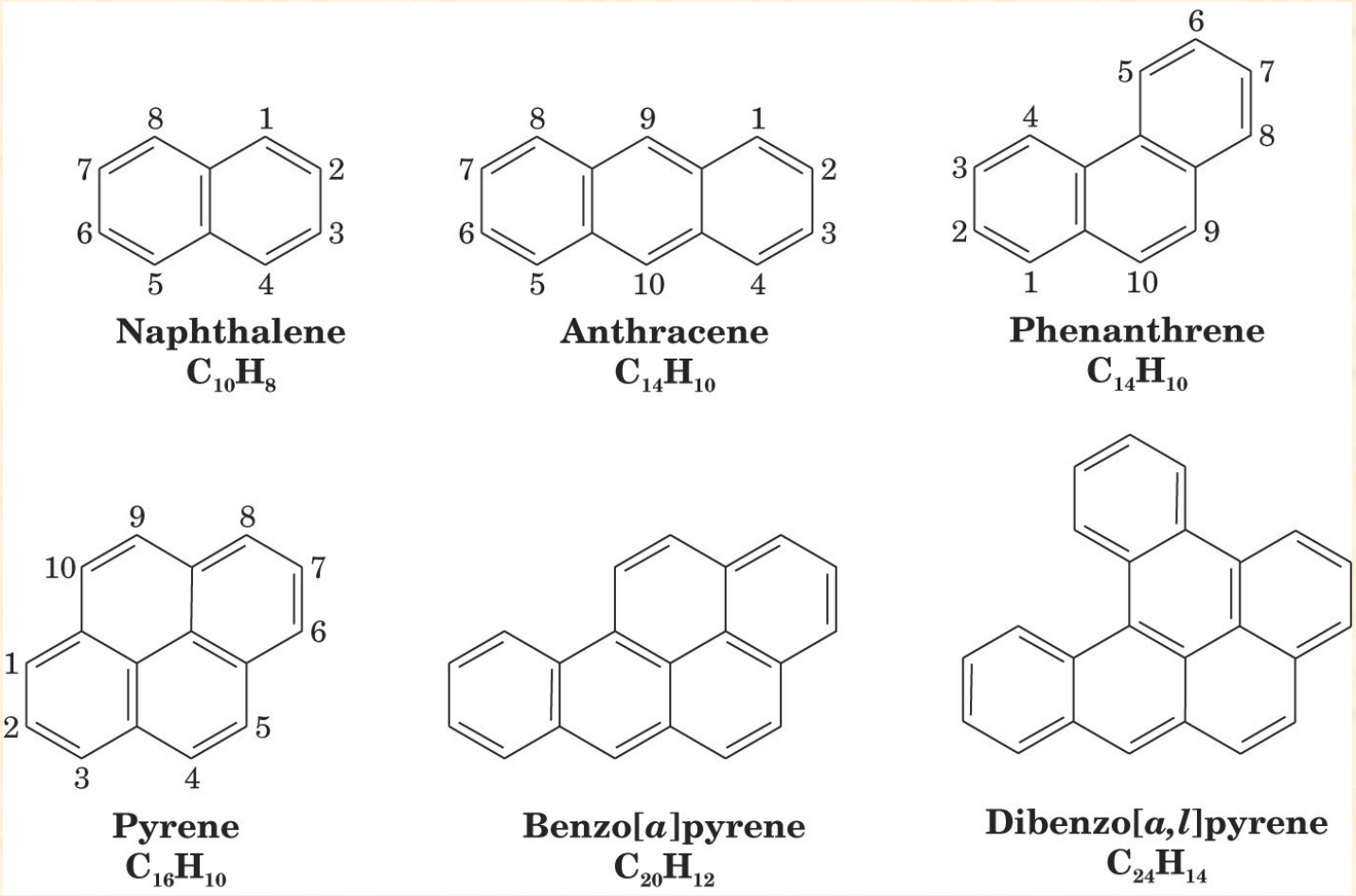






Other Aromatic Compounds

- Other Aromatic Compounds
  - Benzenoid Aromatic Compounds
    - Polycyclic benzenoid aromatic compounds have two or more benzene rings fused together



Other Aromatic Compounds

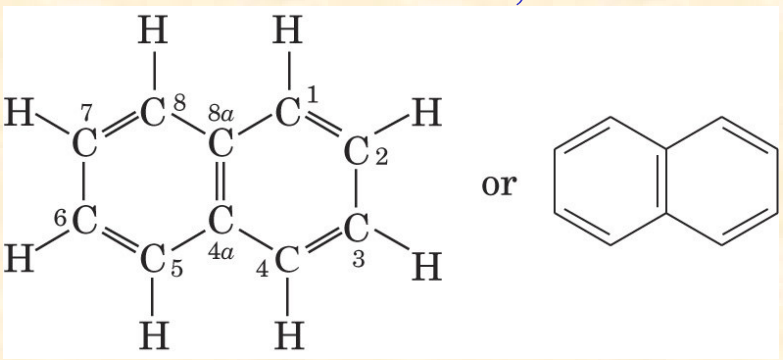
PROBLEM 5◆ *SOLVED*

a. How many monobromonaphthalenes are there?

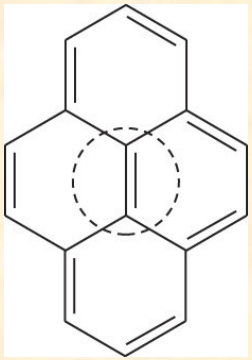
b. How many monobromophenanthrenes are there?

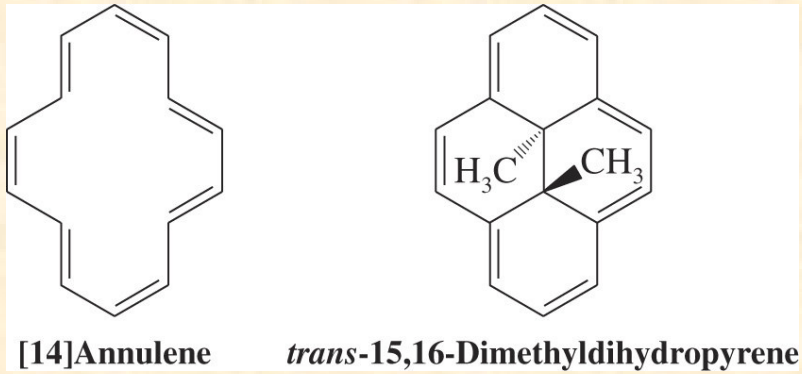
Alkadienes and Polyunsaturated Hydrocarbons

- Naphthalene can be represented by three resonance structures
  - The most important resonance structure is shown below
  - the 10 π electrons are delocalized; it has substantial resonance energy



- Pyrene has 16 π electrons, a non-Huckel number, yet is known to be aromatic
  - Ignoring the central double bond, the periphery of pyrene has 14 π electrons, a Huckel number, and on this basis it resembles the aromatic [14]annulene

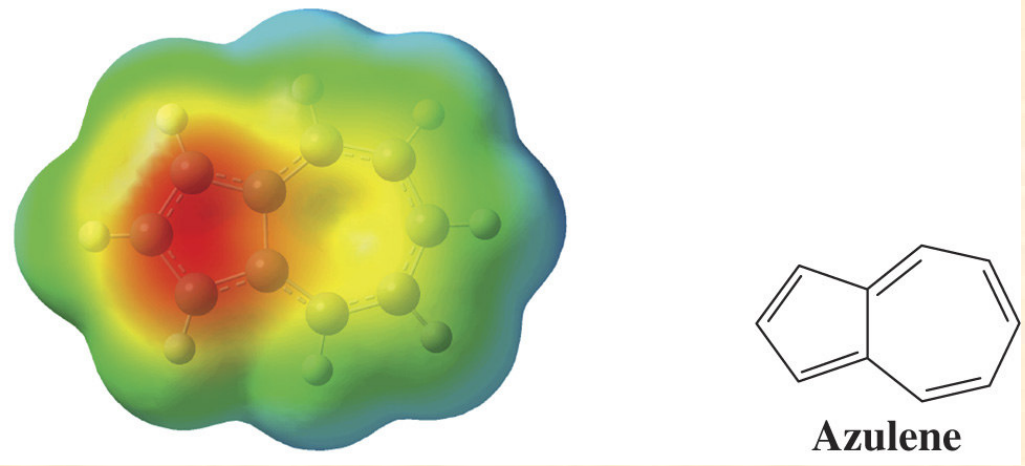




[14]Annulene **_trans_-15,16-Dimethyldihydropyrene**

Nonbenzenoid Aromatic Compounds

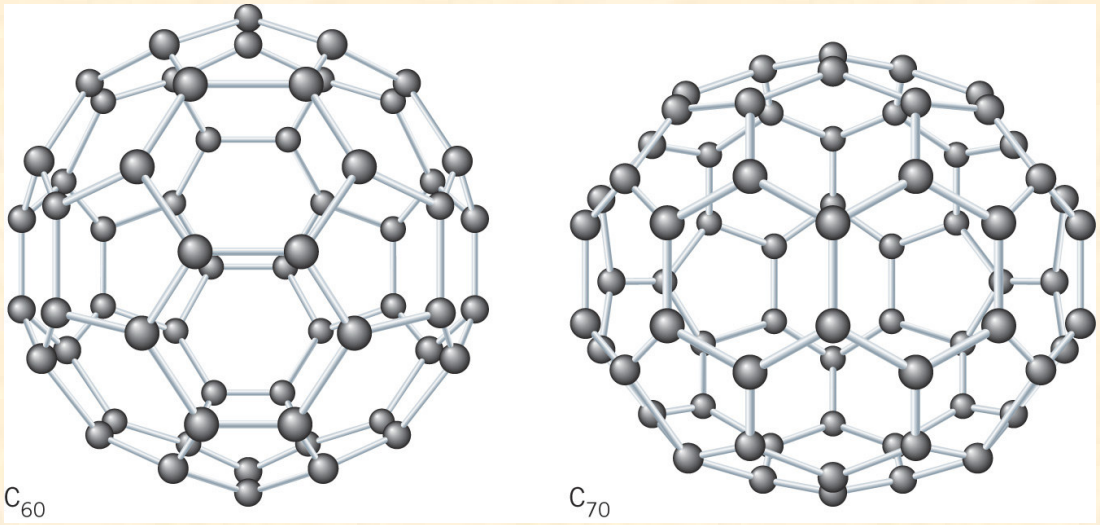
- Nonbenzenoid aromatic compounds do not contain benzene rings
  - Examples are cyclopentadienyl anion and the aromatic annulenes (except [6] annulene)
- Azulene has substantial resonance energy and also substantial separation of charge, as shown in the electrostatic potential map



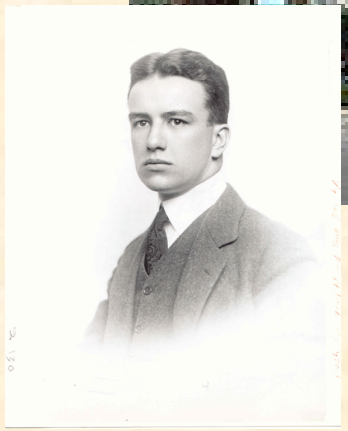
Azulene

Fullerenes

- Fullerenes
  - Buckminsterfullerene is a C_{60} compound shaped like a soccer ball with interconnecting pentagons and hexagons
    - Each carbon is sp^2 hybridized and has bonds to 3 other carbons
    - Buckminsterfullerene is aromatic
  - Analogs of "Buckyballs" have been synthesized (*e.g.* C_{70})



Bioshpere



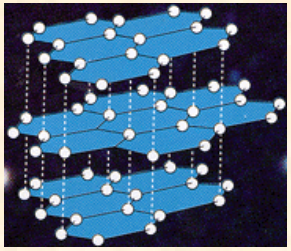
Richard Buckminster Fuller

Carbon Forms

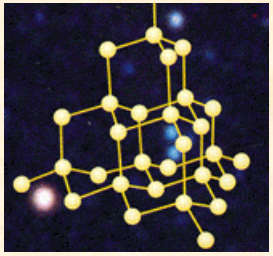
- Forms of Carbon

Charcoal

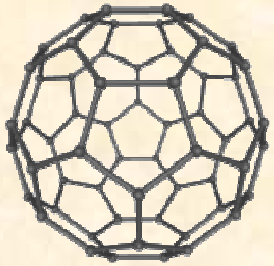
Graphite

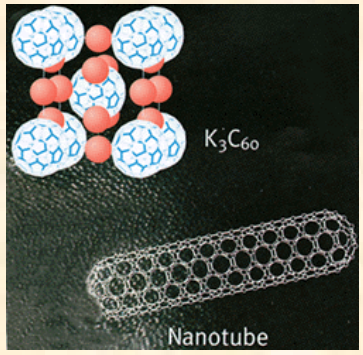


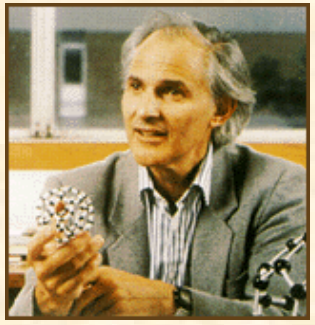
Diamond



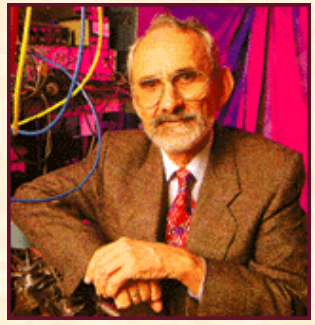
- Fullerenes







Sir Harold W. Kroto



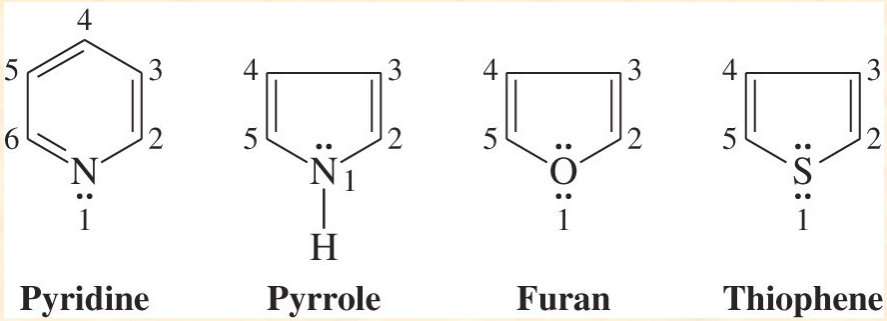
Robert F. Curl Jr

Nobel Prize in Chemistry
1996

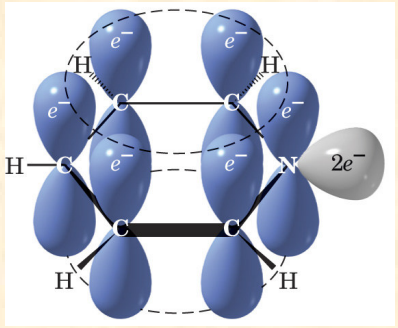
Richard E. Smalley

Heterocyclic Aromatic Compounds

- Heterocyclic compounds have an element other than carbon in the ring
- Example of aromatic heterocyclic compounds are shown below
  - Numbering always starts at the heteroatom

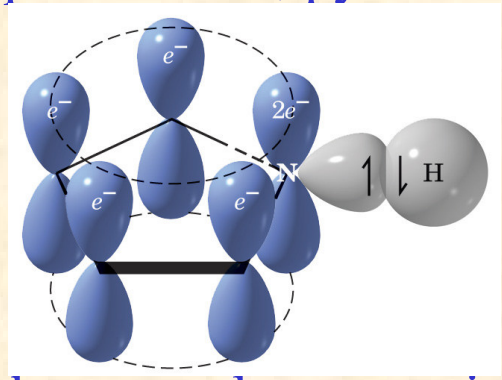


- **Pyridine** has an sp^2 hybridized nitrogen
  - The *p* orbital on nitrogen is part of the aromatic π system of the ring
  - The nitrogen lone pair is not part of the aromatic system
  - The lone pair on nitrogen is available to react so pyridine is basic

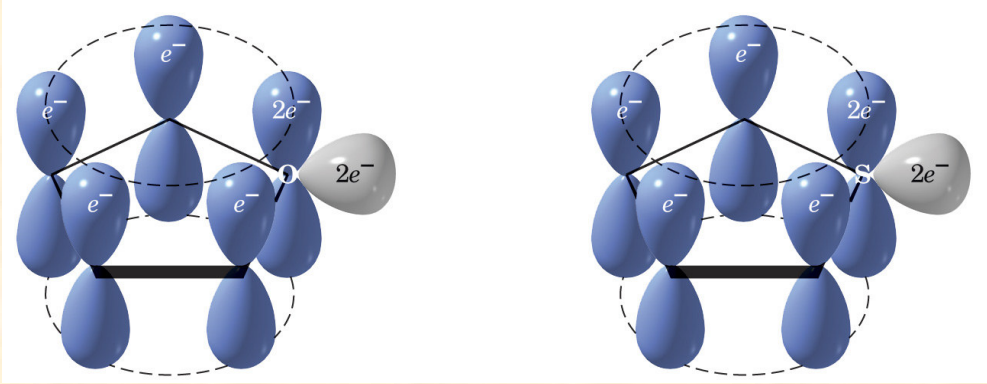


Heterocyclic Aromatic Compounds

- The nitrogen in pyrrole is sp^2 hybridized and the lone pair is in the p orbital
  - This p orbital contains two electrons and is in the aromatic system
  - The lone pair of pyrrole is part of the aromatic system and not available for protonation; pyrrole is therefore not basic



- In furan and thiophene an electron pair on the heteroatom is also in a *p* orbital which is part of the aromatic system



Heterocyclic Aromatic Compounds

PROBLEM 7

a. Draw arrows to show the movement of electrons in going from one resonance contributor to the next in pyrrole.

b. How many ring atoms share the negative charge?