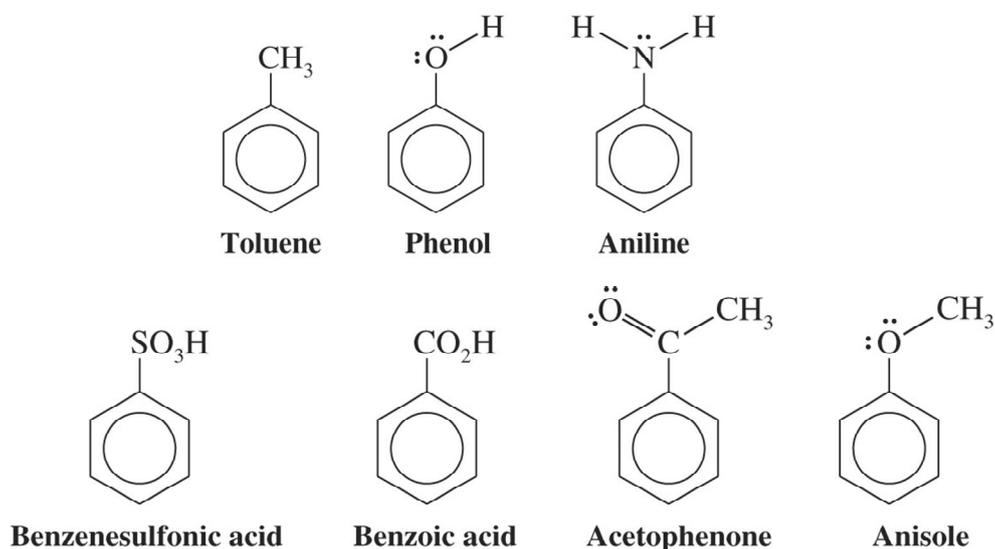


Chapter 14 Aromatic Compounds

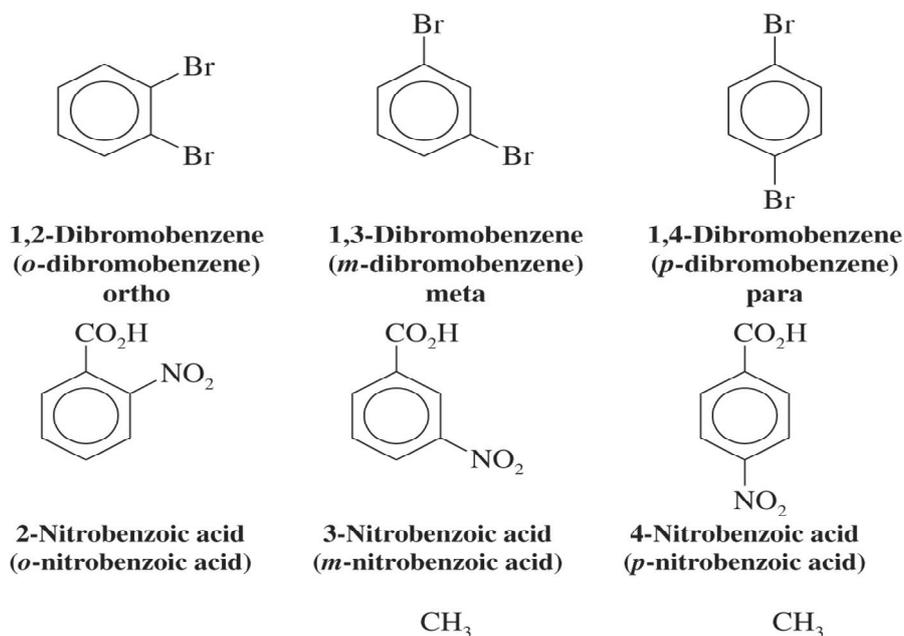
14.2) Nomenclature of Benzene Derivatives:

§ 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



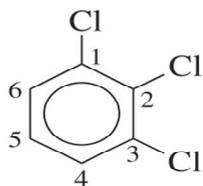
§ When two substituents are present, their position may be indicated by the prefixes *ortho*, *meta*, and *para* (*o*, *m* and *p*) or by the corresponding numerical positions.



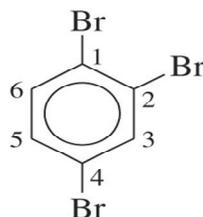
§ **Dimethyl substituted benzenes are called xylenes**

§ **Numbers must be used as locants when more than two substituents are present**

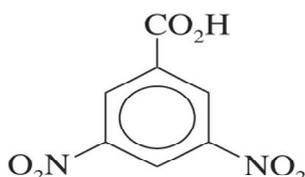
- **The lowest possible set of numbers should be given to the substituents**
- **The substituents should be listed in alphabetical order**
- **If one of the substituents defines a parent other than benzene, this substituent defines the parent name and should be designated position 1**



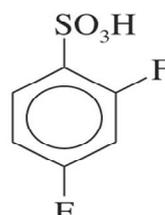
1,2,3-Trichlorobenzene



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



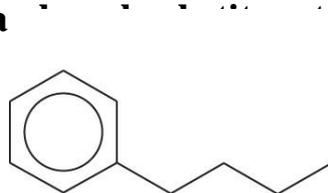
3,5-Dinitrobenzoic acid



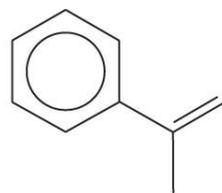
2,4-Difluorobenzenesulfonic acid

§ The C_6H_5 - group is called phenyl when it is a substituent:

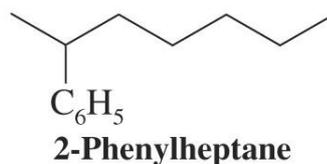
- Phenyl is abbreviated Ph or Φ
- A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent
- If the chain is unsaturated then it must be the parent and the benzene is then a substituent



Butylbenzene

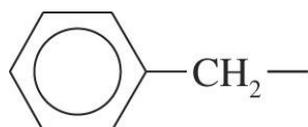


(Z)-2-Phenyl-2-butene

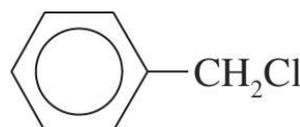


C_6H_5
2-Phenylheptane

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



The benzyl group
(the phenylmethyl group)



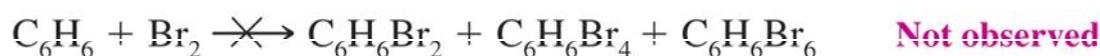
Benzyl chloride
(phenylmethyl chloride or BzCl)

14.3) Reactions of Benzene:

§ Benzene is highly unsaturated, but it does not undergo any of the regular reactions of alkenes such as addition or oxidation

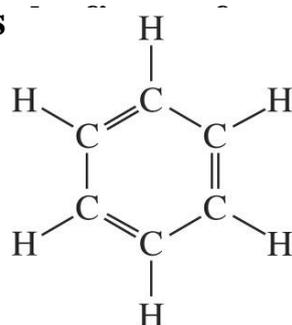
§ Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition

- Benzene produces only one monobrominated compound, which indicates that all 6 carbon-hydrogen bonds are equivalent in benzene



14.4) The Kekule Structure for Benzene:

§ Kekule was the first to propose a structural representation of benzene



or



The Kekulé formula for benzene

§ The Kekule structure suggests alternating double and single carbon-carbon bonds

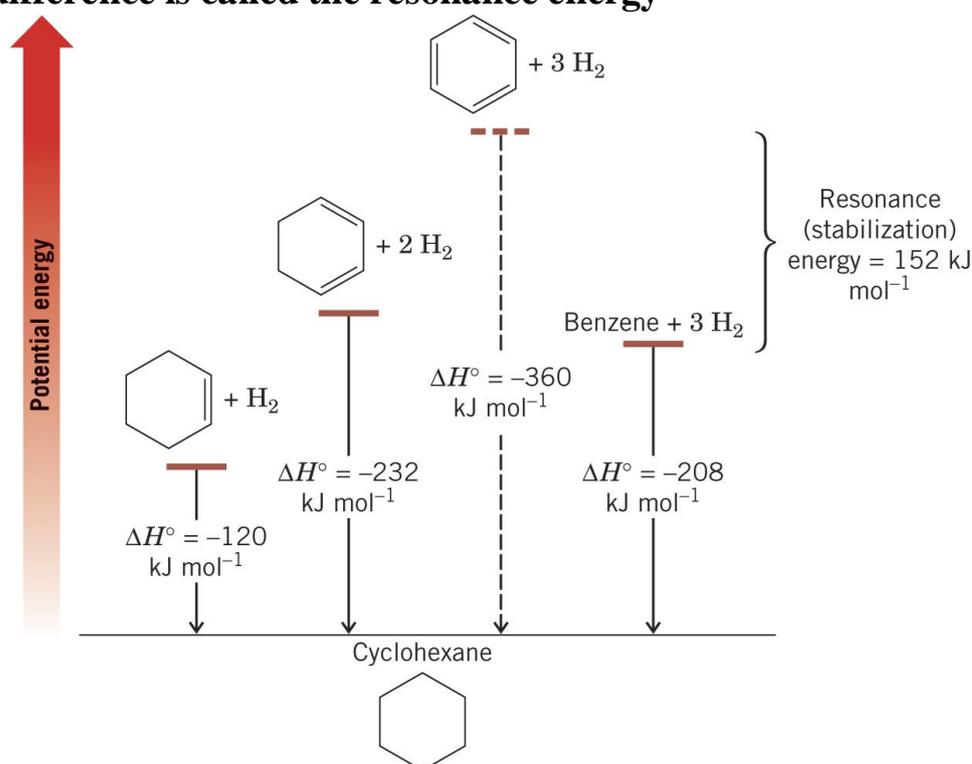
- Based on the Kekule structure one would expect there to be two different 1,2-dibromobenzenes but there is only one
- Kekule suggested an equilibrium between these compounds to explain this observation but it is now known no such equilibrium exists



14.5) The Stability of Benzene:

§ Benzene is much more stable than would be expected based on calculations for “cyclohexatriene”.

- The prediction for the heat of hydrogenation of hypothetical cyclohexatriene is -360 kJ mol^{-1} (3 times that of cyclohexene, -120 kJ mol^{-1})
- The experimentally heat of hydrogenation for benzene is -208 kJ mol^{-1} , 152 kJ mol^{-1} more stable than hypothetical cyclohexatriene. This difference is called the resonance energy

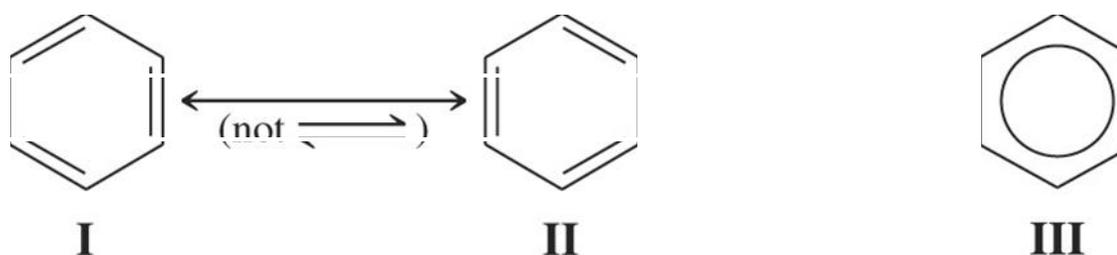


14.6) Modern Theories of the Structure of Benzene:

I The Resonance Explanation of the Structure of Benzene:

§ Structures I and II are equal resonance contributors to the real structure of benzene

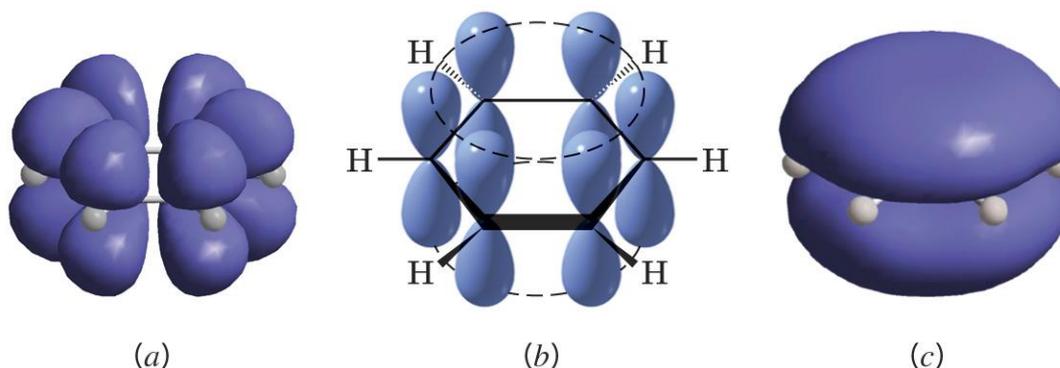
- Benzene is stable because it has two equivalent and important resonance structures
- Each carbon-carbon bond is 1.39 \AA , which is between the length of a carbon-carbon single bond between sp^2 carbons (1.47 \AA) and a carbon-carbon double bond (1.33 \AA)
- Often the hybrid is represented by a circle in a hexagon (III)



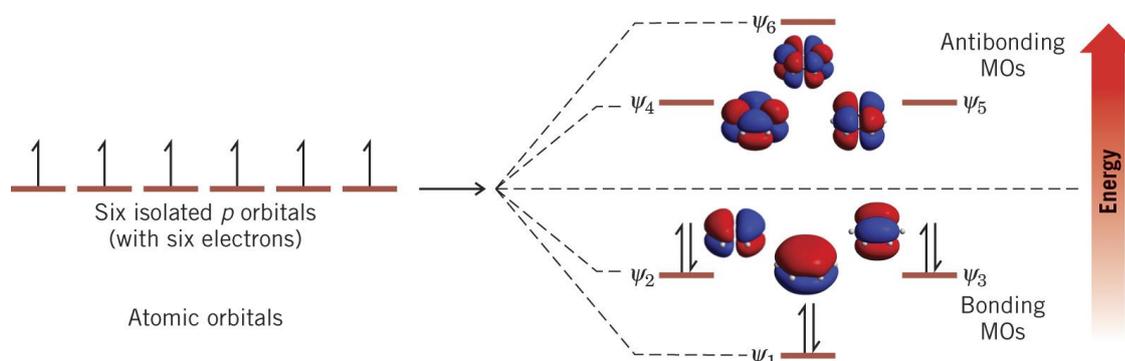
I The Molecular Orbital Explanation of the Structure of Benzene:

§ 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.



14.7) Huckel's Rule: The $4n+2\pi$ Electron Rule:

Planar monocyclic rings with a continuous system of p orbitals and $4n + 2\pi$ electrons are aromatic ($n = 0, 1, 2, 3$ etc)

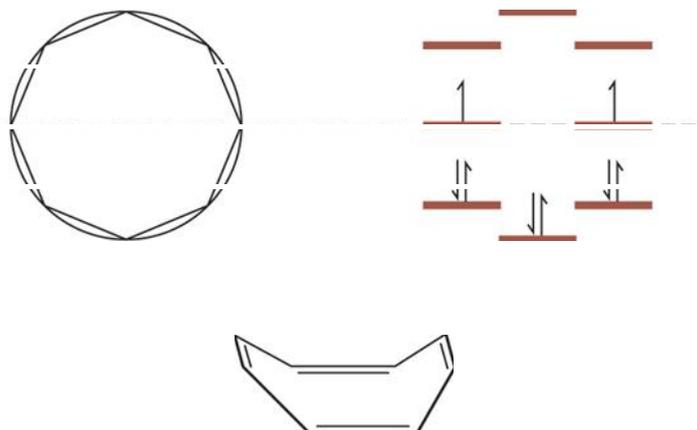
- Aromatic compounds have substantial resonance stabilization
- Benzene is aromatic: it is planar, cyclic, has a p orbital at every carbon, and 6 p electrons ($n=1$).

§ 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.

§ 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

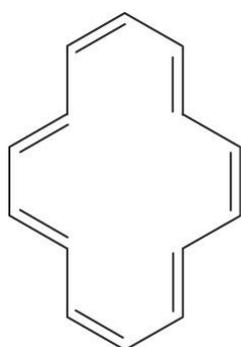
§ Cyclooctatetraene has two nonbonding orbitals each with one electron. This is an unstable configuration; cyclooctatetraene adopts a nonplanar conformation with localized π bonds to avoid this instability



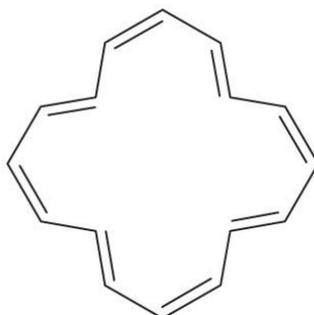
| The Annulenes:

§ Annulenes are monocyclic compounds with alternating double and single bonds

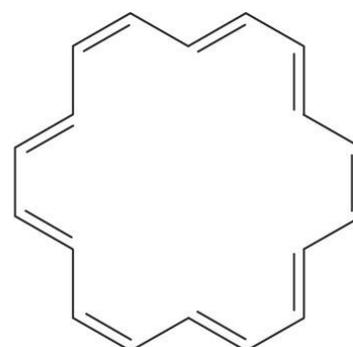
- Annulenes are named using a number in brackets that indicates the ring size
Ex. Benzene is [6]annulene and cyclooctatetraene is [8]annulene
- An annulene is aromatic if it has $4n+2\pi$ electrons and a planar carbon skeleton.



[14]Annulene
(aromatic)



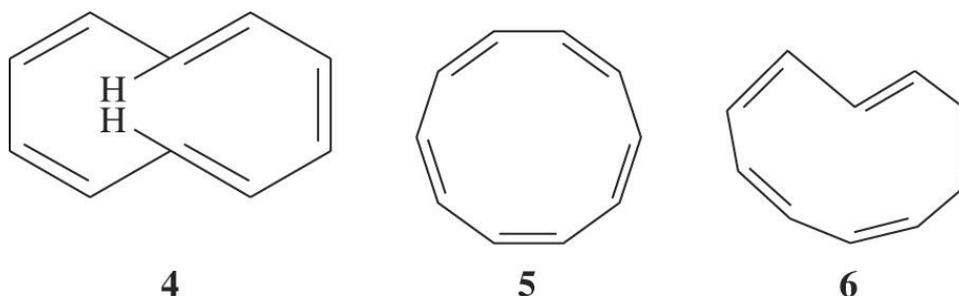
[16]Annulene
(not aromatic)



[18]Annulene
(aromatic)

§ 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



[10]Annulenes

None is aromatic because none is planar.

§ Cyclobutadiene is a [4]annulene and is not aromatic.



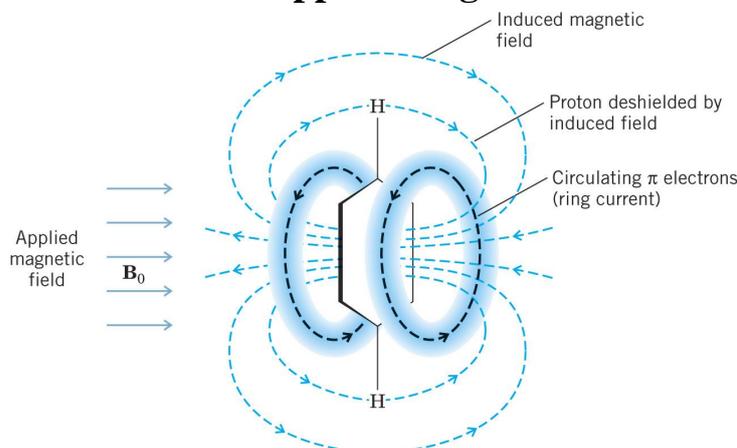
Cyclobutadiene
or [4]annulene
(not aromatic)

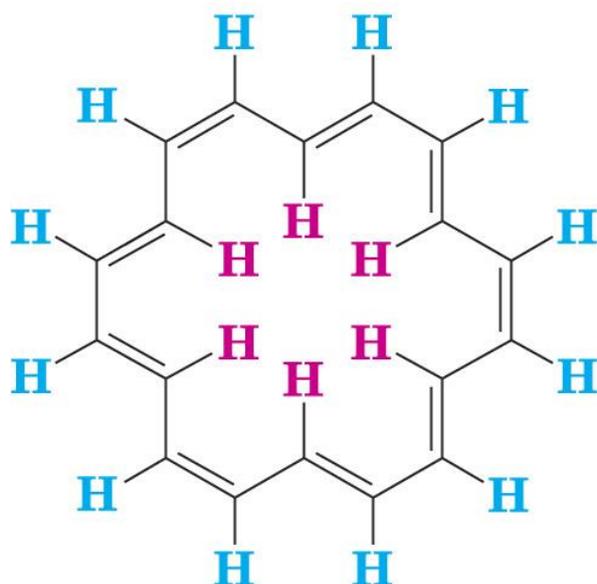
It does not follow the $4n+2$ rule and is highly unstable

NMR Spectroscopy: Evidence for Electron Delocalization in Aromatic Compounds:

§ When benzene is placed in a strong magnetic field a π -electron ring current is induced which reinforces the applied magnetic field at the location of the protons

The net effect is that the protons of benzene are highly deshielded (their signal is a singlet at δ 7.27) and this is evidence for aromaticity.





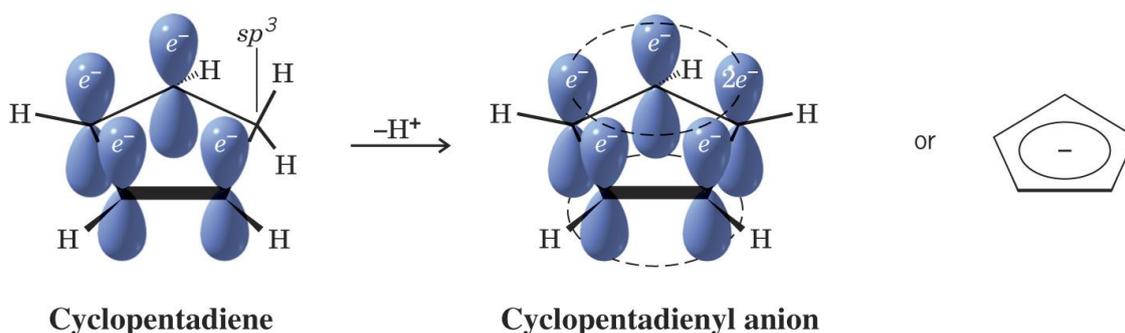
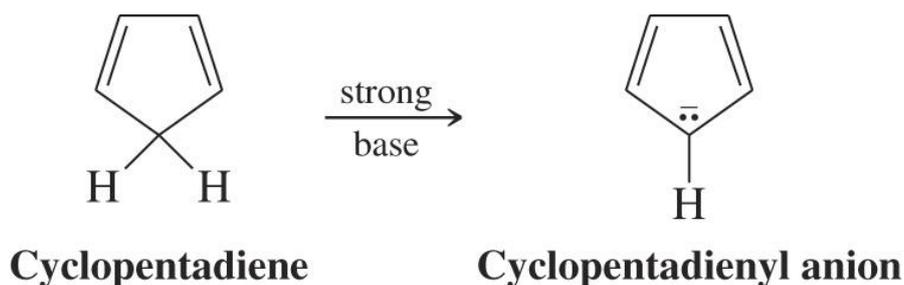
stems also provides regions of great

In large annulenes the internal protons tend to be highly shielded. For example, In [18]annulenes the protons along the outside of the ring (blue) appear at δ 9.3 whereas those on the inside of the ring (pink) appear at δ -3.0 (very highly shielded)

| Aromatic Ions:

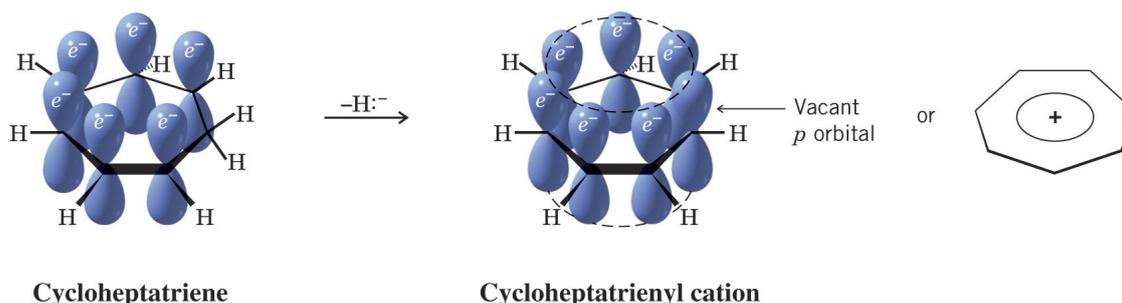
§ Cyclopentadiene is unusually acidic ($pK_a = 16$) because it becomes the aromatic cyclopentadienyl anion when a proton is removed

- Cyclopentadienyl anion has 6 p electrons in a cyclic, continuous p-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 -hybridized CH_2 group is an “insulator”)

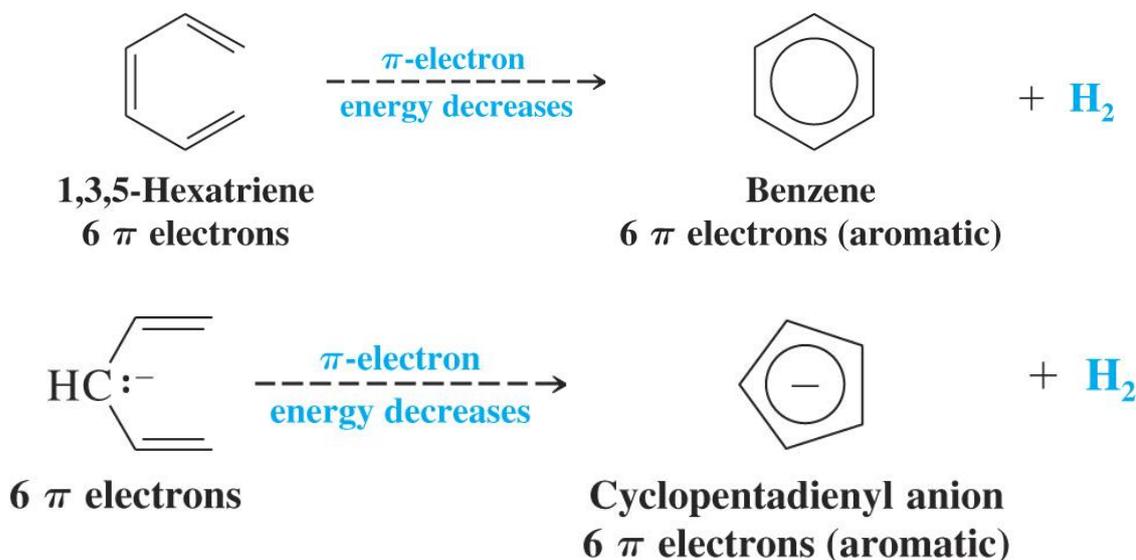
- Lose of hydride produces the aromatic cycloheptatrienyl cation (tropylium cation)

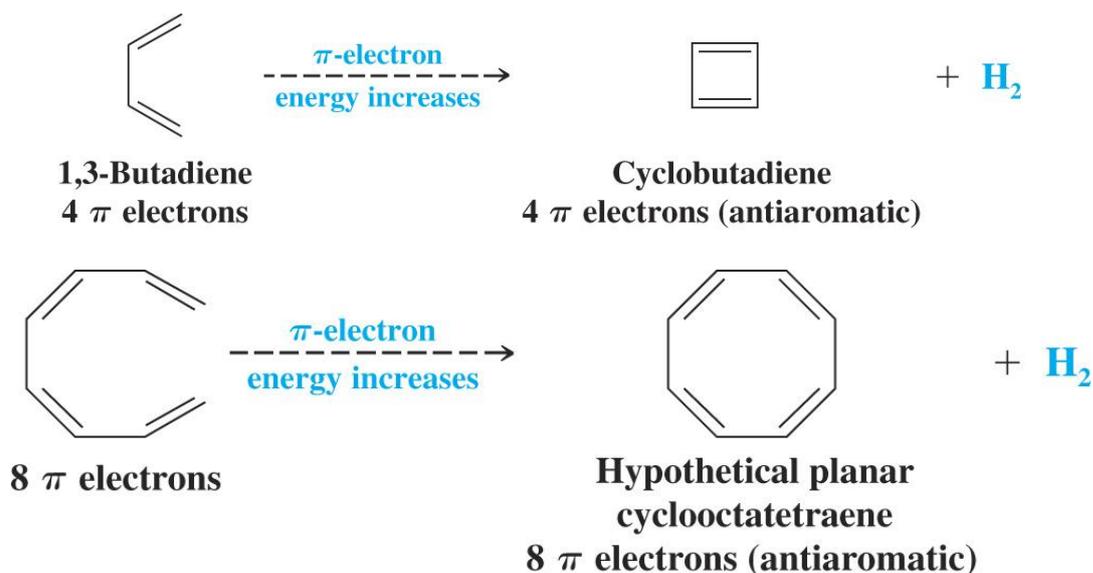


| Aromatic, Antiaromatic, and Nonaromatic Compounds:

§ A comparison of cyclic annulenes with their acyclic counterparts provides a measure of the stability conferred by aromaticity.

- If the ring has lower π -electron energy than the open chain, then it is aromatic
- If the ring has the same π -electron energy as the open chain, then it is nonaromatic
- If the ring has higher π -electron energy than the open chain, then it is antiaromatic



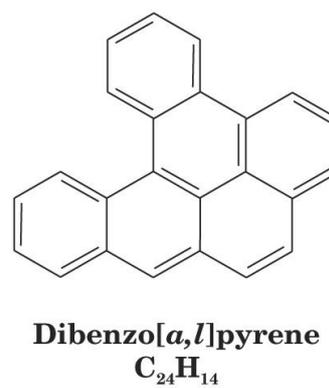
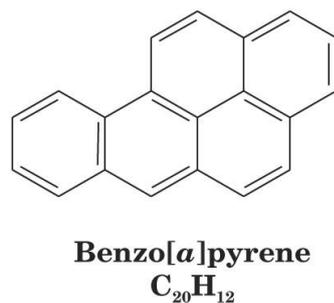
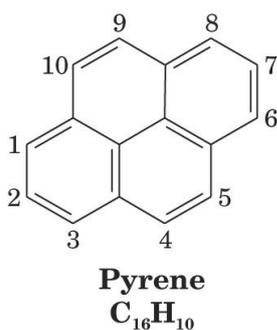
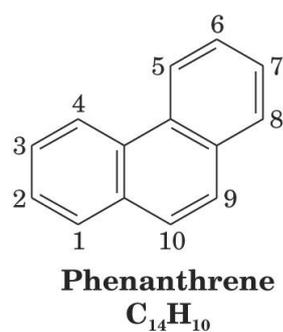
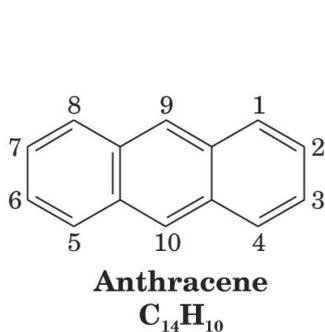
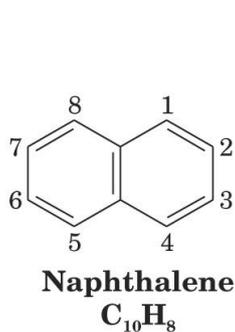


**Cyclooctatetraene is not planar and
 behave as a simple cyclic polyene.
 would be antiaromatic**

14.8) Other Aromatic Compounds:

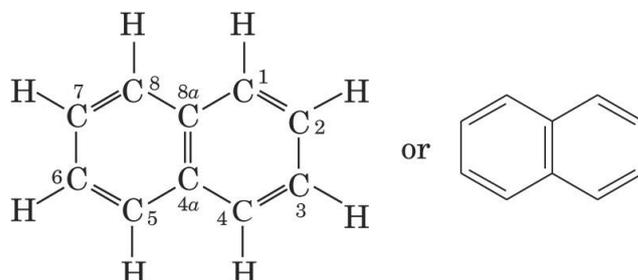
| Benzenoid Aromatic Compounds

- è Polycyclic benzenoid aromatic compounds have two or more benzene rings fused together



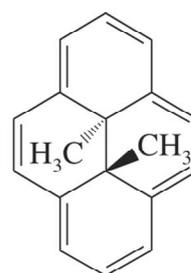
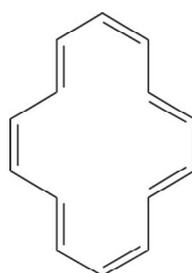
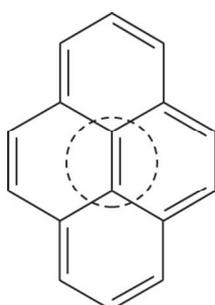
§ Naphthalene can be represented by three resonance structures:

- The most important resonance structure is



§ Pyrene has 16 p 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

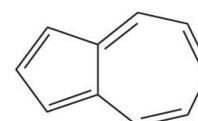
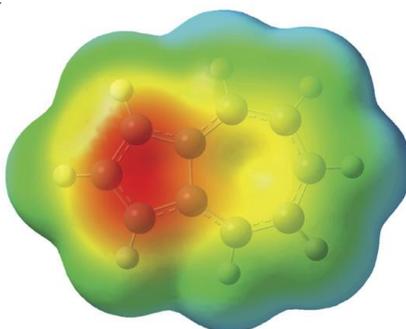
trans-15,16-Dimethyldihydropyrene

I Nonbenzenoid Aromatic Compounds:

§ Nonbenzenoid aromatic compounds do not contain benzene rings.

- Examples are cyclopentadienyl anion and the aromatic annulenes (except [6] annulene).

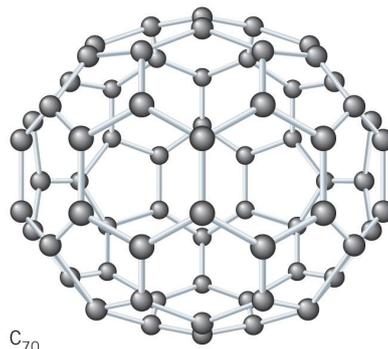
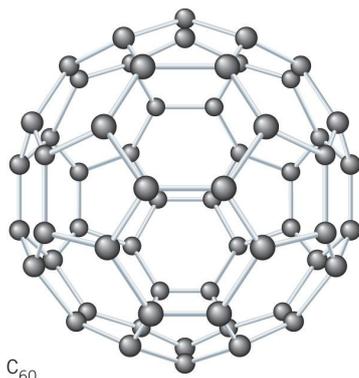
Azulene has substantial resonance energy and also substantial separation of charge, as shown in the electrostatic potential map



Azulene

| Fullerenes:

§ Buckminsterfullerene is a C₆₀ compound shaped like a soccer ball with interconnecting pentagons and hexagons, and each carbon is *sp*² hybridized and bonds to 3 other carbons. It is aromatic.



Buckyballs” have been synthesized (e.g. C₇₀)

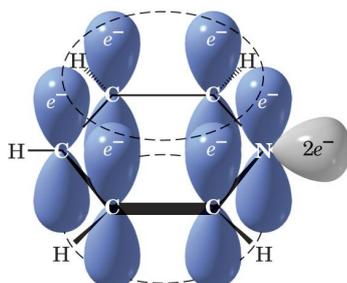
14.9) Heterocyclic Aromatic Compounds:

§ Heterocyclic compounds have an element other than carbon as a member of the ring

§ Example of aromatic heterocyclic compounds are shown below:

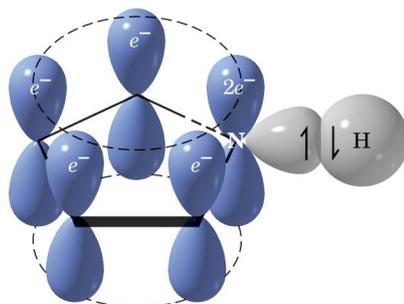
§ Pyridine has an sp^2 hybridized nitrogen:

- The p orbital on nitrogen is part of the aromatic π system of the ring
- The nitrogen lone pair is in an sp^2 orbital orthogonal to the p orbitals of the ring; these electrons are not part of the aromatic system
- The lone pair on nitrogen is available to react with protons and so pyridine is basic

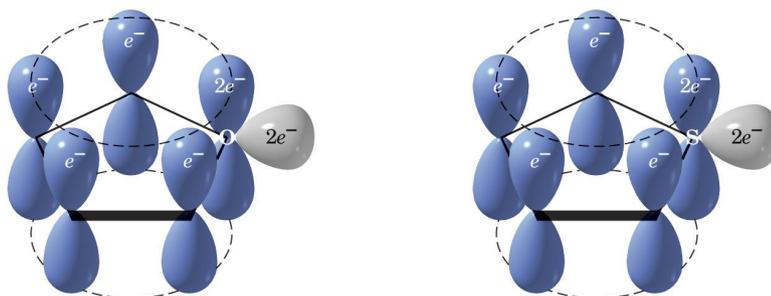


§ The nitrogen in pyrrole is sp^2 hybridized and the lone pair resides in the p orbital

- This p orbital contains two electrons and participates 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



14.11) Spectroscopy of Aromatic Compounds:

| ^1H NMR Spectra:

Protons of benzene: appear in the region δ 6.0 to δ 9.5.

| ^{13}C NMR Spectra:

Aromatic carbons: generally appear in the δ 100-170 region

Example: the spectrum of 4-*N,N*-diethylaminobenzaldehyde:

