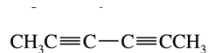


Chapter 14 Aromatic Compounds

Benzene – a remarkable compound

- ◆ Discovered by Faraday 1825
- ◆ Formula C_6H_6
- ◆ Highly unsaturated, but remarkably stable
- ◆ Whole new class of benzene derivatives – called aromatic compounds

Some proposed structures for C_6H_6

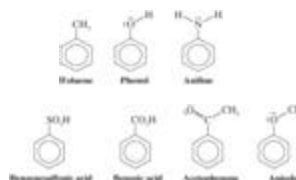


Nomenclature of Benzene Derivatives

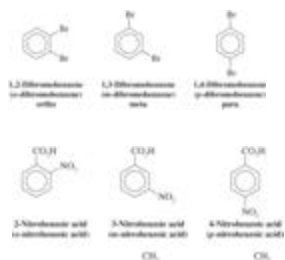
Benzene is the parent name for some monosubstituted benzenes



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



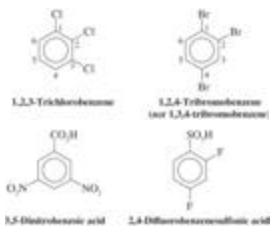
Dimethyl substituted benzenes are called xylenes



ortho = " at right angles"
para = " across"
(meta = above, behind, beyond = middle)

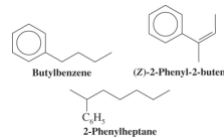
Numbers must be used when more than two substituents

1. Assign the lowest possible set of numbers
2. Substituents are in alphabetical order
3. If one of the substituents defines the parent name, it is designated as position 1 (and not stated)



C₆H₅- group is called phenyl when it is a substituent

- ◆ Phenyl is abbreviated Ph or F
- ◆ 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

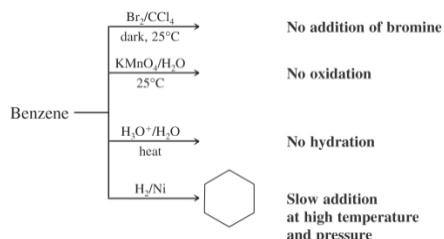


- ◆ The phenylmethyl group is called a benzyl (abbreviated Bz)



Reactions of Benzene

- ◆ Even though benzene is highly unsaturated, it does not undergo any of the regular reactions of alkenes



Reactions of Benzene

- ◆ Benzene can be induced to react with bromine if a Lewis acid catalyst is present
- ◆ The reaction is a *substitution* and not an addition!



Benzene produces only one monobrominated compound
All 6 carbon-hydrogen bonds are equivalent in benzene

◆The Kekule Structure for Benzene

- ◆ Kekule was the first to formulate a reasonable representation of benzene

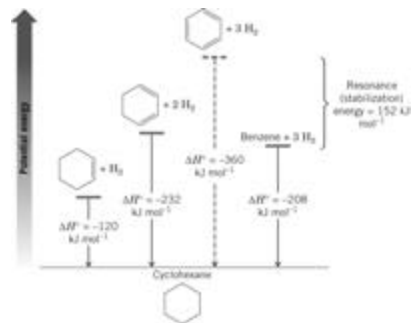


- ◆ The Kekule structure suggests alternating double and single bonds
 - One would expect there to be two different 1,2-dibromobenzenes
 - But there is only one
 - Kekule suggested an equilibrium between these compounds



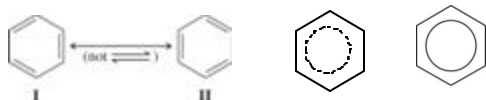
Doesn't explain stability!

What is the Stability of Benzene?



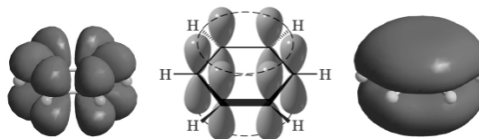
The Resonance Explanation of Benzene

- ◆ Benzene is particularly stable because it has two equivalent resonance structures
- ◆ C-C bond length is 1.39 Å
 - C-C single bond between sp^2 carbons (1.47 Å)
 - C-C double bond (1.33 Å)

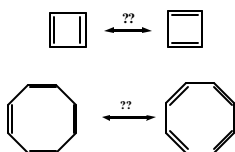


Molecular Orbital Picture of Benzene

- ◆ Each carbon in benzene is sp^2 hybridized with a p orbital
 - The p orbitals overlap around the ring to form a bonding molecular orbital with electron density above and below the plane of the ring



Simple resonance explanation is incomplete



Cyclooctatetraene rapidly decolorizes bromine

Molecular Orbital Theory gives superior explanation

Recap of MO Theory

- ◆ MO theory describes bonds as the combination of atomic orbitals that form a new set of orbitals called molecular orbitals (MOs).
- ◆ A molecular orbital occupies a region of space in a molecule where electrons are likely to be found.
- ◆ We will look only at qualitative version of a mathematically rigorous treatment
- ◆ For systems involving p bonds, we can focus only on p orbitals

The MO view of a double bond

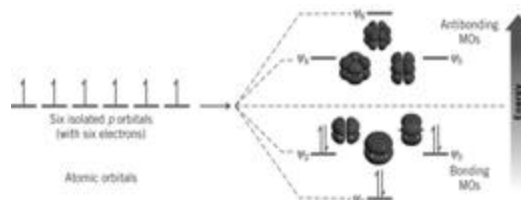
- The combination of two p orbitals can be constructive—that is, with like phases interacting—or destructive, that is, with opposite phases interacting.



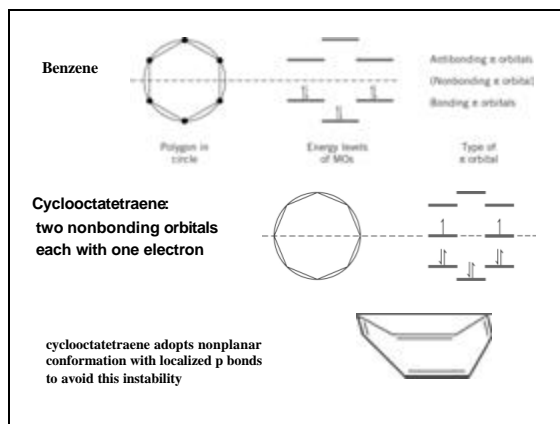
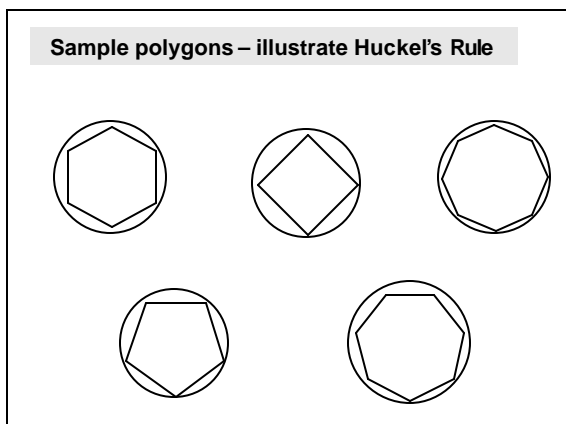
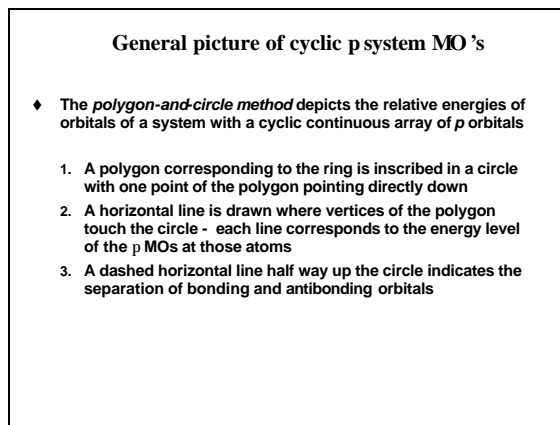
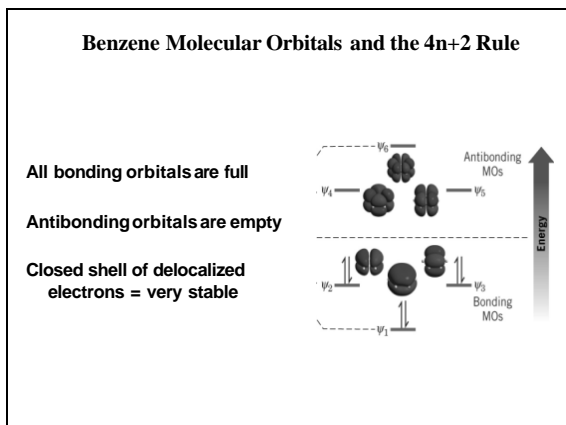
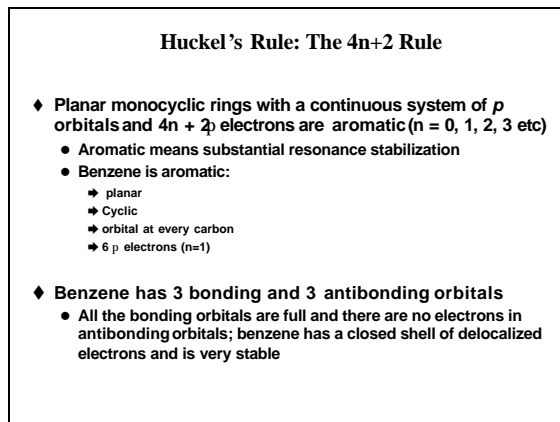
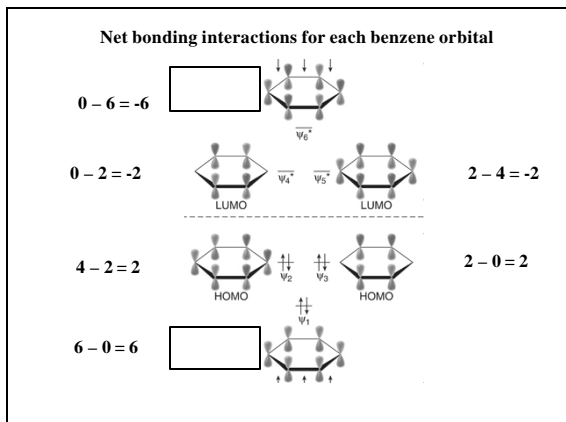
- When two p orbitals of similar phase overlap side-by-side, a p bonding molecular orbital results.
- When two p orbitals of opposite phase overlap side-by-side, a p^* antibonding orbital results.

Molecular Orbital Picture of Benzene

Six p orbitals must generate six p molecular orbitals for benzene

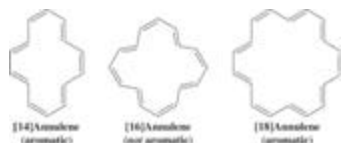


3 bonding MO's, 3 anti-bonding MO's



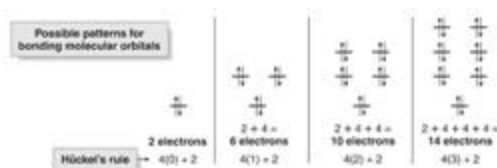
Annulenes and the $4n+2$ Rule

- Annulenes = monocyclic compounds with continuous p bonds
 - Named using a number in brackets to indicate ring size
 - Example: cyclooctatetraene is [8]annulene
 - An annulene is aromatic if it has $4n+2$ 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



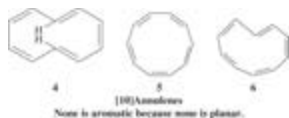
Why the $4n+2$ rule works

- For the compound to be aromatic, these MOs must be completely filled with electrons, so the "magic numbers" for aromaticity fit Hückel's $4n+2$ rule.



The [10]annulenes could 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 planar because of large angle strain in the flat molecules



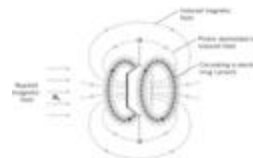
Cyclobutadiene is a [4]annulene and is not aromatic



NMR Evidence for Aromaticity

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

- Protons of benzene are highly deshielded (a singlet at δ 7.27)

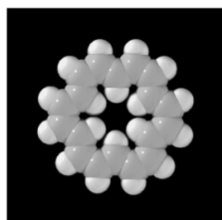


Protons on the periphery of aromatic compounds are deshielded

- Deshielding of these protons is physical evidence for aromaticity

Ring current of aromatic systems also produces regions of shielding

- In large annulenes, internal protons are highly shielded
- In [18]annulene the protons along the outside of the ring appear at δ 9.3 whereas those on the inside of the ring appear at δ -3.0 (above TMS = very highly shielded)



[18]Annulene.

A strained [10]-annulene



Vinyl protons
 δ 6.8-7.5

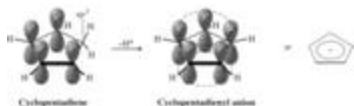
CH_2 group
at δ 0.5

Aromatic Ions

Cyclopentadiene is extraordinarily acidic ($pK_a = 16$)!



Cyclopentadienyl anion has 6 p electrons in a cyclic, continuous p-electron system, and hence follows the $4n + 2$ rule for aromaticity

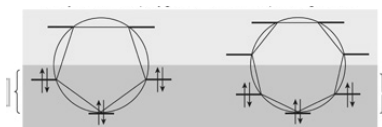


Aromatic Ions

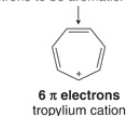
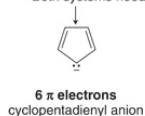
- ◆ Cycloheptatriene is not aromatic because its p electrons are not delocalized around the ring (CH_2 group is an "insulator")
 - Lose of hydride produces the aromatic cycloheptatrienyl cation (tropylium cation)



Why Huckel's Rule applies to ions

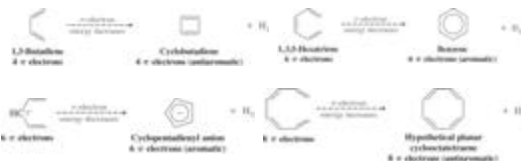


- Both systems have 3 bonding MOs.
- Both systems need 6 π electrons to be aromatic.



Aromatic, Antiaromatic, and Nonaromatic Compounds

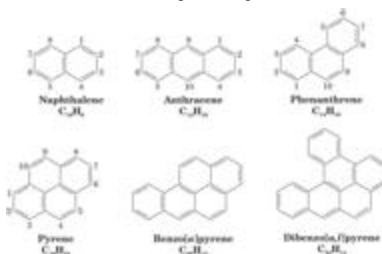
- ◆ A comparison of annulenes with their acyclic counterparts provides a measure of the stability conferred by aromaticity
 - If the ring has lower p-electron energy than the open chain, then it is **aromatic**
 - If the ring has the same p-electron energy as the open chain, then it is **nonaromatic**
 - If the ring has higher p-electron energy than the open chain, then it is **antiaromatic**



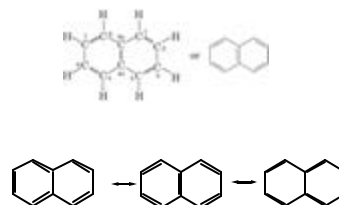
Other Aromatic Compounds

Benzenoid Polycyclic Aromatic Compounds

◆ Two or more benzene rings fused together

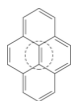


- ◆ Naphthalene can be represented by three resonance structures
 - The 10 p electrons of naphthalene are delocalized and that it has substantial resonance energy



Pyrene has 16 p electrons, a non-Huckel number, yet is known to be aromatic

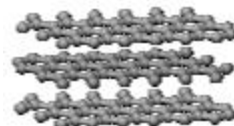
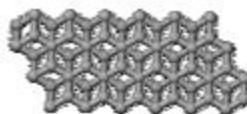
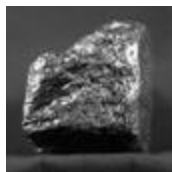
- By ignoring the central double bond, the periphery of pyrene has 14 p electrons, a Huckel number, and on this basis it resembles the aromatic [14]annulene



[14]annulene from: E.J. Corey, H. H. Kwart, J. K. Stille, J. Am. Chem. Soc. 81, 5661 (1959)

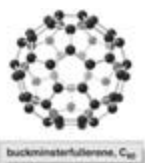
NMR: Methyl singlets at δ 4.25 d

Graphite = the ultimate aromatic

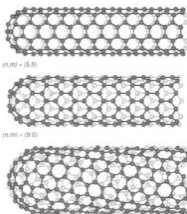


New Forms of Carbon – 1985, 1991

- Buckminsterfullerene (C_{60}) is a third elemental form of carbon.
- Buckminsterfullerene is completely conjugated, but it is not aromatic since it is not planar.
- It undergoes addition reactions with electrophiles in much the same way as ordinary alkenes.
- Carbon nanotubes are rolled graphite (1990's)



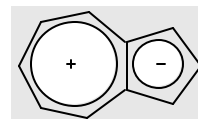
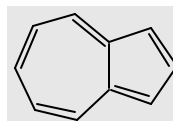
Buckminsterfullerene, C_{60}



(10,10) - (5,5)

(10,10) - (5,5)

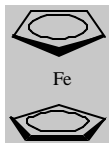
Azulene – the blue hydrocarbon



- Stable 10 pi electron system
- Dark blue crystals
- Has a dipole moment of 1.0 Debye (vs 1.8 for chloromethane)



Ferrocene – a remarkable aromatic compound



- Ferrocene discovered in 1951
- Orange crystals that sublime rather than melt
- Air stable and stable to $> 500^\circ\text{C}$
- Sandwich structure with all carbons equivalent

Heterocyclic Aromatic Compounds

- Heterocyclic compounds have an element other than carbon as a member of the ring
 - Common names dominate
 - Numbering always starts at the heteroatom
 - If there is a cyclic p system, Huckel's rule applies



Pyridine



Pyrrole



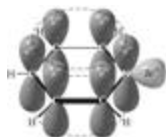
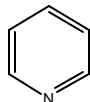
Furan



Thiophene

Pyridine

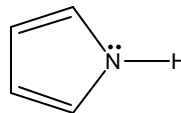
- ◆ An sp^2 hybridized nitrogen in place of a C-H in benzene
- ◆ The p orbital on nitrogen is part of the aromatic p system of the ring
- ◆ The nitrogen lone pair is in an sp^2 orbital orthogonal to the p orbitals of the ring; these electrons are not part of the aromatic system
- ◆ The lone pair on nitrogen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



$$4n+2 = 6 \text{ p electrons}$$

Pyrrole

- ◆ The nitrogen in pyrrole is sp^2 hybridized and the lone pair resides in the p orbital
 - This p orbital with its two electrons 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

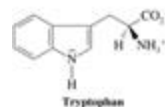
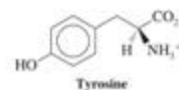
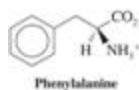


$$4n+2 = 6 \text{ p electrons}$$

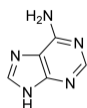
- ◆ In furan and thiophene one electron pair on the heteroatom is also in a p orbital which is part of the aromatic system
- ◆ The remaining non-bonded pair does not participate in the system



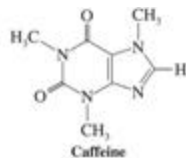
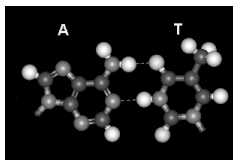
Several amino acids have aromatic rings



Purine rings



adenine



Caffeine

Spectroscopy of Aromatic Compounds

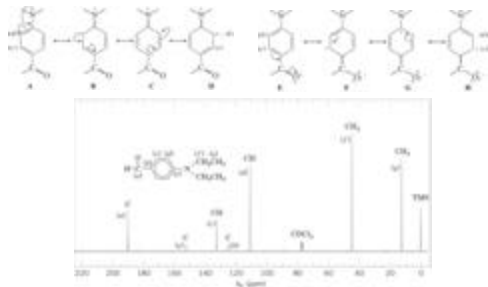
◆ ^1H NMR Spectra

- Protons of benzene derivatives are highly deshielded and appear in the region δ 6.0 to δ 9.5
 - ➔ A ring current is induced in the benzene ring that reinforces the applied magnetic field in the region of the protons in benzene

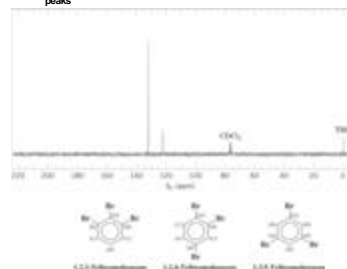
◆ ^{13}C NMR Spectra

- Aromatic carbons generally appear in the δ 100-170 region
 - ➔ DEPT spectra will show these carbons to have one or no protons attached

- ◆ Example : the spectrum of 4,N,N-diethylaminobenzaldehyde
 - The assignment of carbons (d) and (c) is possible because carbons (d) should have higher electron density than carbons (c), based on resonance structures

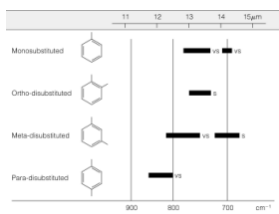


- ◆ Given a molecular formula or mass spectrometric data, ^{13}C NMR can be used to recognize compounds with high symmetry
 - The spectrum below corresponds to the last isomer which can have only two peaks



● Infrared Spectra of Substituted Benzenes

- ◆ Benzene derivatives show several characteristic frequencies
 - C-H Stretching occurs near 3030 cm^{-1}
 - Stretching motions of the ring give bands at $1450\text{-}1600\text{ cm}^{-1}$ and two bands near 1500 and 1600 cm^{-1}
- ◆ Monosubstituted benzenes show two strong absorptions at $690\text{-}710\text{ cm}^{-1}$ and $730\text{-}770\text{ cm}^{-1}$
- ◆ Disubstituted benzenes show the following absorptions



◆ Ultraviolet-Visible Spectra of Aromatic Compounds

- Benzene derivatives give an absorption band of moderate intensity near 205 nm and a less intense band at $250\text{-}275\text{ nm}$

◆ Mass Spectra of Aromatic Compounds

- The major ion in the mass spectrum of alkyl benzenes is $m/z\ 91$, which corresponds to a benzyl cation ($\text{C}_6\text{H}_5\text{CH}_2^+$), which rearranges to a tropylium ion (C_7H_7^+)
- Another common ion is the phenyl cation (C_6H_5^+)