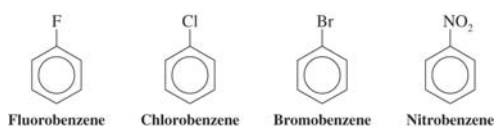


Chapter 14

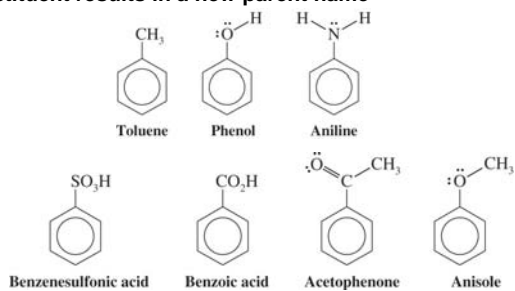
Aromatic Compounds

◆ Nomenclature of Benzene Derivatives

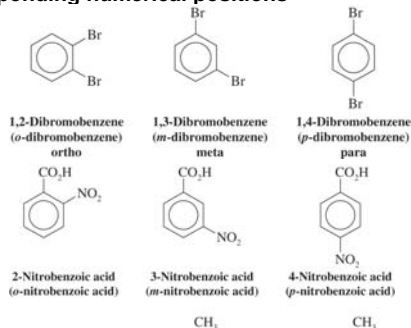
→ Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix



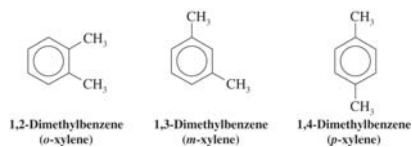
→ For other monosubstituted benzenes, the presence of the substituent results in a new parent name



→ 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

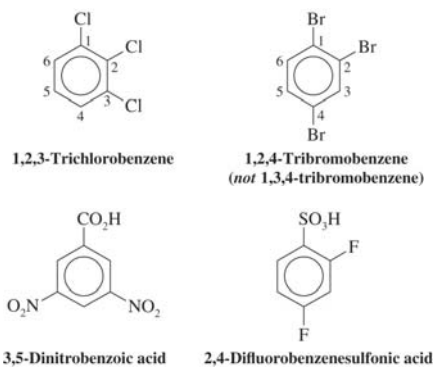


Chapter 14

3

→ 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

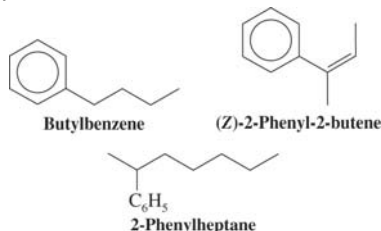


Chapter 14

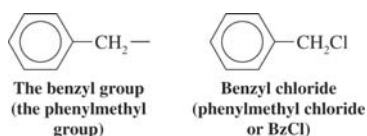
4

→ 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)



Chapter 14

5

◆ 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 in benzene

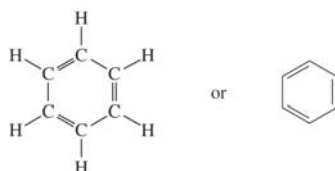


Chapter 14

6

◆ The Kekule Structure for Benzene

→ Kekule was the first to formulate a reasonable representation of 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



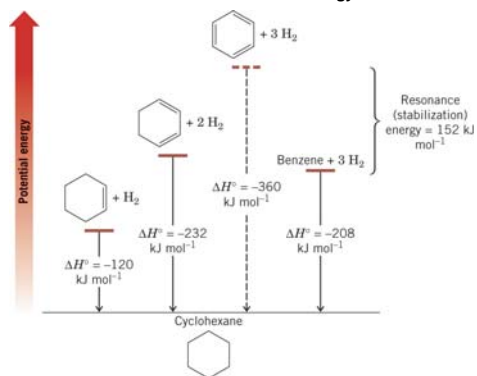
Chapter 14

7

◆ The Stability of Benzene

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

- ⌘ A reasonable 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 determined 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



Chapter 14

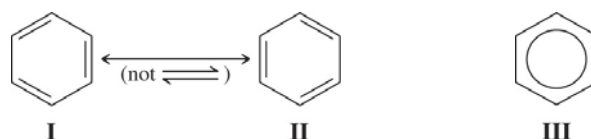
8

◆ 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 (1.47 Å) and a carbon-carbon double bond (1.33 Å)
- ⌘ Often the hybrid is represented by a circle in a hexagon (III)



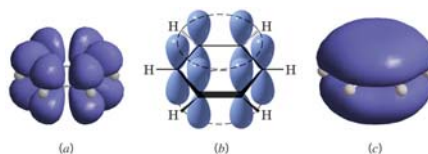
Chapter 14

9

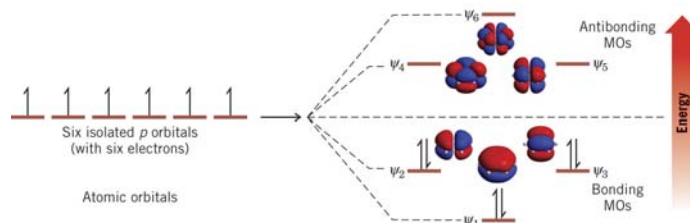
● The Molecular Orbital Explanation of the Structure of Benzene

→ 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



Chapter 14

10

◆ 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 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

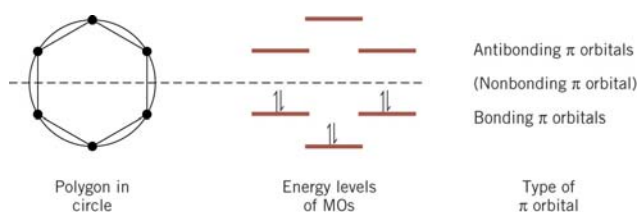
- ⌘ A polygon corresponding to the ring is inscribed in a circle with one point of the polygon pointing directly down
- ⌘ A horizontal line is drawn where vertices of the polygon touch the circle - each line corresponds to the energy level of the π MOs at those atoms
- ⌘ A dashed horizontal line half way up the circle indicates the separation of bonding and antibonding orbitals

→ 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

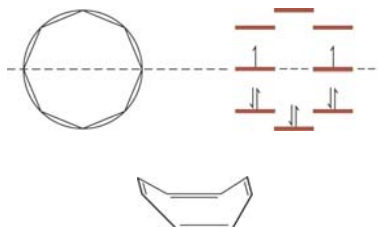
Chapter 14

11



→ 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



Chapter 14

12

● **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 $n=3,4$)**

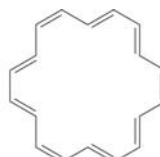
- ⌘ The [16] annulene is not aromatic



[14]Annulene
(aromatic)



[16]Annulene
(not aromatic)



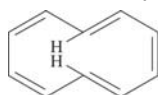
[18]Annulene
(aromatic)

Chapter 14

13

→ **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 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)

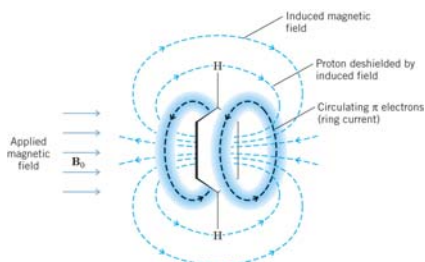
Chapter 14

14

- **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)



→ Generally protons at the periphery of aromatic compounds are highly deshielded

⌘ Deshielding of these protons is physical evidence for aromaticity

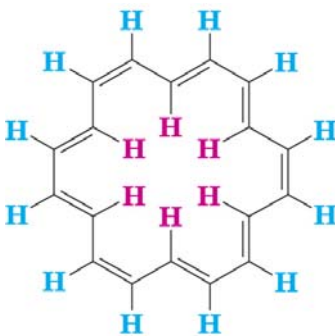
Chapter 14

15

→ The ring current of aromatic systems also provides regions of great shielding

⌘ In large annulenes the internal protons tend to be highly shielded

⌘ In [18]annulenes the protons along the outside of the ring (pink) appear at δ 9.3 whereas those on the inside of the ring (blue) appear at δ -3.0 (very highly shielded)



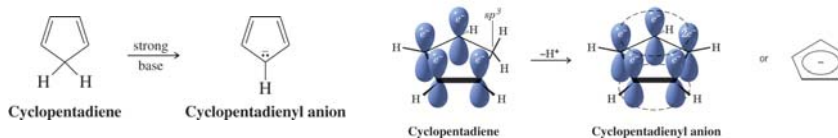
Chapter 14

16

• Aromatic Ions

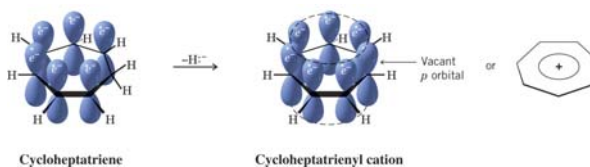
→ Cyclopentadiene is unusually acidic ($pK_a = 16$) because it becomes the aromatic cyclopentadienyl anion when a proton is removed

↳ 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 -hybridized CH_2 group is an "insulator")

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



Chapter 14

17

• 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

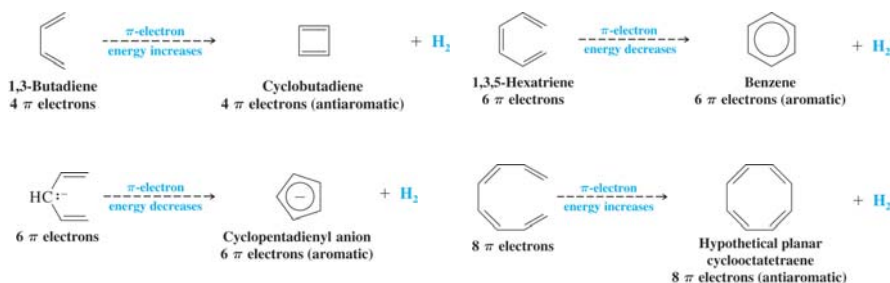
↳ If the ring has the same π -electron energy as the open chain, then it is nonaromatic

↳ If the ring has higher π -electron energy than the open chain, then it is antiaromatic

→ Benzene and cyclopentadienyl anion are aromatic

→ Cyclobutadiene is antiaromatic

↳ Cyclooctatetraene, if it were planar, would be antiaromatic



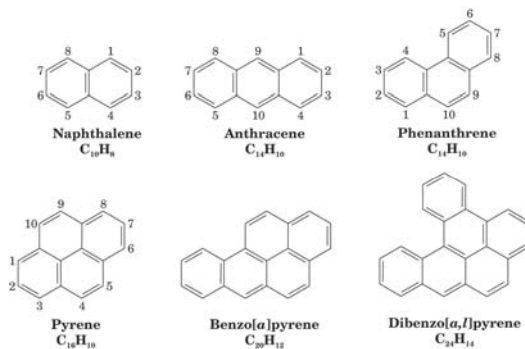
Chapter 14

18

◆ Other Aromatic Compounds

● Benzenoid Aromatic Compounds

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



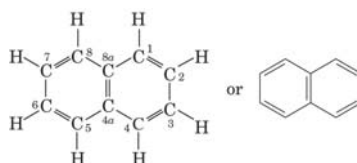
Chapter 14

19

→ Naphthalene can be represented by three resonance structures

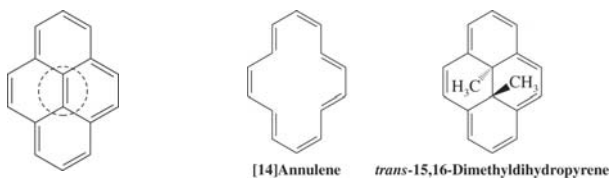
⌘ The most important resonance structure is shown below

⌘ Calculations show that the 10 π electrons of naphthalene are delocalized and that 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



Chapter 14

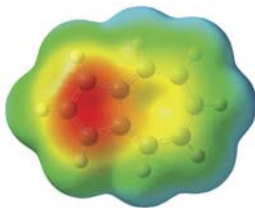
20

- **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



Chapter 14

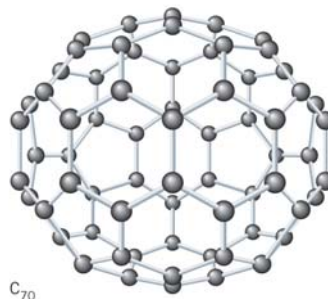
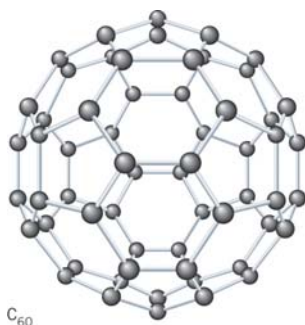
21

- **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})



Chapter 14

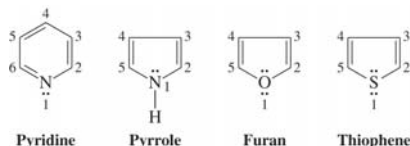
22

◆ Heterocyclic Aromatic Compounds

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

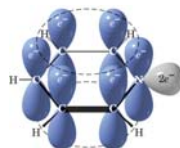
→ Example of aromatic heterocyclic compounds are shown below

⌘ 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 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

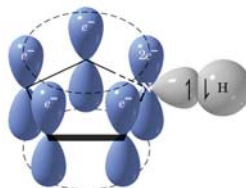


Chapter 14

23

→ 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



Chapter 14

24

◆ 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

⌞ In large annulenes protons pointing into the ring are highly shielded

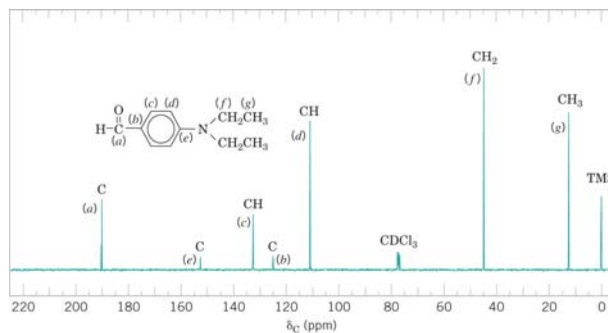
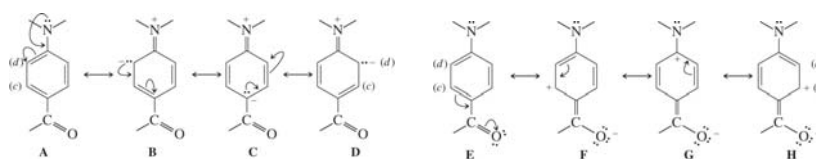
● ¹³C NMR Spectra

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

⌞ DEPT spectra will show these carbons to have one or no protons attached

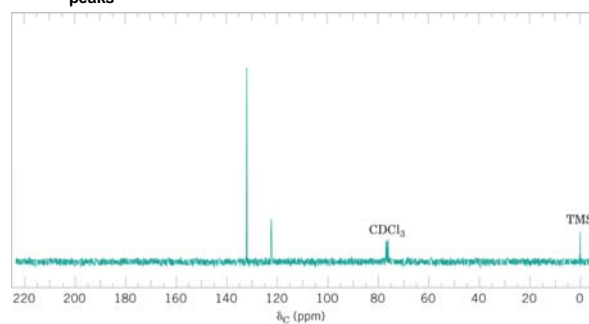
→ Example : the spectrum of 4-*N,N*-diethylaminobenzaldehyde

⌞ 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



Chapter 14

27

● Infrared Spectra of Substituted Benzenes

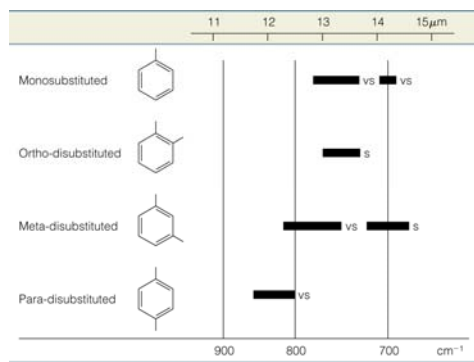
→ Benzene derivatives show several characteristic frequencies

⌘ 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



Chapter 14

28

- **Ultraviolet-Visible Spectra of Aromatic Compounds**

- Benzene derivatives give an absorption band of moderate intensity near 205 nm and a less intense band at 250-275 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 ($C_6H_5CH_2^+$), which rearranges to a tropylium ion ($C_7H_7^+$)

- Another common ion is the phenyl cation ($C_6H_5^+$)