Chapter 11

Arenes and Aromaticity
Examples of Aromatic Hydrocarbons

Benzene

Toluene

Naphthalene
11.1 Benzene
1825 Michael Faraday isolates a new hydrocarbon from illuminating gas.

1834 Eilhardt Mitscherlich isolates same substance and determines its empirical formula to be $C_nH_n$. Compound comes to be called benzene.

1845 August W. von Hofmann isolates benzene from coal tar.

1866 August Kekulé proposes structure of benzene.
11.2
Kekulé and the Structure of Benzene
Kekulé proposed a cyclic structure for $\text{C}_6\text{H}_6$ with alternating single and double bonds.
Later, Kekulé revised his proposal by suggesting a rapid equilibrium between two equivalent structures.

Kekulé Formulation of Benzene

Later, Kekulé revised his proposal by suggesting a rapid equilibrium between two equivalent structures.
However, this proposal suggested isomers of the kind shown were possible. Yet, none were ever found.
Structural studies of benzene do not support the Kekulé formulation. Instead of alternating single and double bonds, all of the C—C bonds are the same length.

Benzene has the shape of a regular hexagon.
All C—C bond distances = 140 pm
All C—C bond distances = 140 pm

140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.
11.3
A Resonance Picture of Bonding in Benzene
Instead of Kekulé's suggestion of a rapid equilibrium between two structures:
express the structure of benzene as a resonance hybrid of the two Lewis structures. Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbons.
Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two Kekulé structures)
11.4  
The Stability of Benzene

benzene is the best and most familiar example of a substance that possesses "special stability" or "aromaticity"

aromaticity is a level of stability that is substantially greater for a molecule than would be expected on the basis of any of the Lewis structures written for it
Thermochemical Measures of Stability

heat of hydrogenation: compare experimental value with "expected" value for hypothetical "cyclohexatriene"

\[ \Delta H^\circ = -208 \text{ kJ} \]
Figure 11.2 (p 404)

3 x cyclohexene

120 kJ/mol

231 kJ/mol

208 kJ/mol

360 kJ/mol
"expected" heat of hydrogenation of benzene is $3 \times$ heat of hydrogenation of cyclohexene

$120 \text{ kJ/mol}$

$360 \text{ kJ/mol}$

$3 \times$ cyclohexene
observed heat of hydrogenation is 152 kJ/mol less than "expected"
benzene is 152 kJ/mol more stable than expected
152 kJ/mol is the resonance energy of benzene
hydrogenation of 1,3-cyclohexadiene (2H₂) gives off more heat than hydrogenation of benzene (3H₂)!

231 kJ/mol

208 kJ/mol
Cyclic conjugation versus noncyclic conjugation

Heat of hydrogenation = 208 kJ/mol

Heat of hydrogenation = 337 kJ/mol
Resonance Energy of Benzene

compared to localized 1,3,5-cyclohexatriene

152 kJ/mol

compared to 1,3,5-hexatriene

129 kJ/mol

extact value of resonance energy of benzene depends on what it is compared to, but regardless of model, benzene is more stable than expected by a substantial amount
11.5
An Orbital Hybridization View of Bonding in Benzene
Orbital Hybridization Model of Bonding in Benzene

Planar ring of 6 $sp^2$ hybridized carbons

Figure 11.3
Orbital Hybridization Model of Bonding in Benzene

Each carbon contributes a $p$ orbital.
Six $p$ orbitals overlap to give cyclic $\pi$ system; six $\pi$ electrons delocalized throughout $\pi$ system.
Orbital Hybridization Model of Bonding in Benzene

High electron density above and below plane of ring
11.6
The $\pi$ Molecular Orbitals of Benzene
6 p AOs combine to give 6 \( \pi \) MOs
3 MOs are bonding; 3 are antibonding
All bonding MOs are filled
No electrons in antibonding orbitals

Benzene MOs

Antibonding orbitals

Bonding orbitals

Energy
The Three Bonding $\pi$ MOs of Benzene