Reading: Chapter 8.1-8.13
Practice problems: in text problems and 23-27

Aromaticity: Reactions of Benzene and Substituted Benzenes

Representative Compounds

[Chemical structures of adrenaline and ephedrine]
Representative Compounds

amphetamine

methamphetamine

Representative Compounds

Aspirin
Reactions of Aromatic Compounds

Selective oxidations of alkylbenzenes using moderately strong oxidizing conditions (hot acidic KMnO$_4$ or K$_2$Cr$_2$O$_7$), however, the aromatic ring remains intact:

BENZENE – DETERMINATION OF RESONANCE ENERGY

The exceptional stability of aromatic compounds due to resonance can be estimated via hydrogenation reactions. Hydrogenation of cyclohexene is an exothermic reaction.

$\Delta H = -28.6 \text{ kcal/Mol}$
BENZENE – DETERMINATION OF RESONANCE ENERGY

Hydrogenation of 1,4-cyclohexadiene is also an exothermic reaction. The amount of heat released doubles because we have two double bonds.

\[ \text{H}_2 \rightarrow \]
\[ \Delta H = -57.2 \text{ kcal/Mol} \]

BENZENE – DETERMINATION OF RESONANCE ENERGY

Hydrogenation of a “theoretical” cyclohexatriene is expected to produce 85.8 kcal/Mol. Since here we have three double bonds, each would contribute 28.6 kcal/Mol.

\[ \text{H}_2 \rightarrow \]
\[ \Delta H = -49.8 \text{ kcal/Mol} \]

The real value is 49.8 kcal/Mol. The difference is “RESONANCE ENERGY.”
BENZENE – DETERMINATION OF RESONANCE ENERGY

\[ -36 \text{ kcal/mole} \]

\[ +3\text{H}_2 \]

\[ +3\text{H}_2 \]

\[ -49.8 \text{ kcal/mole} \]

\[ (-208 \text{ kJ}) \]

\[ (-120 \text{ kJ}) \]

\[ (-360 \text{ kJ}) \]

\[ (-152 \text{ kJ}) \]

\[ (28.6 \times 2) \]

Hypothetical 1,3,5-cyclohexatriene

Benzene

Aromaticity

- Uninterrupted arrangement of p bonds
- Cyclic molecule
- All atoms must have p orbital
- Molecule has to be planar
- Total number of p-electron pairs is odd (1,3,5…)
- Exceptionally stable molecules
Aromaticity

Cyclobutadiene: planar, cyclic, all atoms have $p$ orbitals, **2 pairs of $p$ electrons**

Benzene: planar, cyclic, all atoms have $p$ orbitals, **3 pairs of $p$ electrons**.

Cyclooctatetraene: nonplanar, cyclic, all atoms have $p$ orbitals, **4 pairs of $p$ electrons**.

Benzene: planar, ring, all atoms have $p$ orbitals, **3 pairs of $p$ electrons**.
BENZENE PI MOLECULAR ORBITALS

six p’s
six mo’s

top view

Aromaticity

cyclopentadien

cyclopentadienyl cation

cyclopentadienyl anion

4 p electrons
planar

4 p electrons
nonplanar

6 p electrons
planar
Cyclopentadienyl anion

Resonance contributors.
Overall every C atom has the same amount of negative charge

Cycloheptadienyl cation

6 p electrons planar
6 p electrons nonplanar
8 p electrons planar

sp³-atom
**Cycloheptadienyl cation**

Resonance contributors. Overall every C atom has the same amount of positive charge.

**Polycyclic Aromatic Rings**

- naphthalene, planar, 5 pairs
- azulene, planar, 5 pairs
Polycyclic Aromatic Rings

- Phenanthrene: planar, 7 pairs
- Anthracene: planar, 7 pairs
- Chrysene: planar, 9 pairs

Heterocyclic Aromatic Rings

- Pyridine
- Pyrrole
- Furan
- Thiophene
**Pyridine**

The lone pair is not part of the aromatic ring system. Electrons are located in $sp^2$-hybrid orbital.

**Pyrrol, Furan**

Lone pair part of p-system, N and O are $sp^2$ hybridized

Second lone pair
Located in $sp^2$-hybridized orbital
Pyrrol

Resonance contributors

Furan

Resonance contributors
Bicyclic Heterocyclic Aromatics

**Quinoline**

**Indole**

**Purine**

**Porphyрин, Chlorophyll, Heme**

Porphyрин ring system, four pyrrole rings are joined together by one-carbon bridges.

- In Heme: Fe(II) takes central atom position.
- In Chlorophyll: Mg(II) takes central atom position
Porphyrin, Chlorophyll, Heme
Naming

State the name of substituent and add the word “benzene”

- bromobenzene
- chlorobenzene
- nitrobenzene
- ethylbenzene
- methoxybenzene
- methylbenzene
- hydroxybenzene
- aminobenzene

Naming

Many trivial names in use

- anisole
- toluene
- phenol
- aniline
- styrene
- benzoic acid
- benzonitrile
Disubstituted Benzenes

1,2-dichlorobenzene
orthodichlorobenzene
o-dichlorobenzene

1,3-dichlorobenzene
meta-dichlorobenzene
m-dichlorobenzene

1,4-dichlorobenzene
paradichlorobenzene
p-dichlorobenzene

Relative positions are often indicated by *ortho*, *meta*, *para*

Disubstituted Benzenes

4-bromotoluene
para-bromotoluene

2-nitrophenol
ortho-nitrophenol