Chapter 15 (pp. 498-515)

Benzene and Aromaticity

Suggested Problems:
15.4, 15.10, 15.19, 15.27, 15.31, 15.32, 15.33, 15.35, 15.36, 15.38, 15.41

15A Introduction and Nomenclature
15B Stability of Aromatic Compounds/Huckel’s Rule
15C Aromatic Ions
15D Aromatic Heterocycles
15E Polycyclic Aromatic Compounds
Effect of Aromatic Stabilization on Reactions with Benzene

**ADDITION**

- Benzene + Br₂ → Benzene with Br⁺⁻⁻⁻⁻⁻ Bond
- Benzene + Br₂ → No reaction

**Bonds broken**
- Br-Br bond
- 2 C-Br

**Bonds made**
- π bond
- Br-Br bond

**If reaction occurred**
- π bond
- 2 C-Br

**BUT would lose AROMATIC STABILIZATION**

**INSTEAD - SUBSTITUTION**

- Benzene + FeBr₃/Br₂ → Benzene with Br⁺⁻⁻⁻⁻⁻ Bond

**AROMATIC STABILIZATION**
Heat evolved upon catalytic hydrogenation ($\Delta H^\circ$)

A MEASURE OF ALKENE STABILITY

$$\begin{align*}
\text{ALKENE} & \quad \xrightarrow{\text{H}_2/\text{Pd-C}} \quad \text{ALKANE} \\
\text{ENERGY} & \quad \text{(-) 27.4 kcal/mol} \\
& \quad \text{(-) 28.3 kcal/mol} \\
& \quad \text{(-) 30.3 kcal/mol}
\end{align*}$$
Catalytic hydrogenation of benzene and various cyclohexenes

Magnitude of aromatic stabilization = 36 kcal/mol
Benzene (C₆H₆) is not “cyclohexatriene!”

C=C 1.34Å
C-C 1.54Å

Each sp² hybridized C in the ring has an unhybridized p orbital perpendicular to the ring which overlaps around the ring.

1879
Landenberg
Criteria for Aromaticity

1. Cyclic
2. Unhybridized p orbital in continuous cyclic system
3. Able to adopt a planar geometry
4. Fulfills Huckel’s Rule and includes \((4n + 2)\) electrons
   \[ n = 0, 1, 2, 3, 4 \ldots \text{ (the 2, 6, 10, 14\ldots electrons)} \]

Initially, all cyclic conjugated hydrocarbons were proposed to be aromatic

However, cyclobutadiene is so reactive that it dimerizes before it can be isolated

Cyclooctatetraene adds \(\text{Br}_2\) readily.

Look at Molecular Orbitals (MOs) to explain aromaticity in benzene-like molecules
Constructing Molecular Orbitals

• $\pi$ molecular orbitals are the sideways overlap of $p$ orbitals

• $p$ orbitals have 2 lobes. Plus (+) and minus (-) indicate the opposite phases of the wave function, not electrical charge

• When lobes overlap constructively, (+ and +, or - and -) a bonding MO is formed

• When + and - lobes overlap, waves cancel out and a node forms; antibonding MO
MO Rules for Benzene

• Six overlapping p orbitals must form six molecular orbitals

• Three will be bonding, three antibonding

• Lowest energy MO will have all bonding interactions, no nodes

• As energy of MO increases, the number of nodes increases

• System symmetric so 2 pairs of degenerate orbitals
Energy Diagram for Benzene

6 atomic orbitals - 6 molecular orbitals
System symmetric so 2 pairs of degenerate orbitals

The six electrons fill three bonding pi orbitals.
All bonding orbitals are filled ("closed shell"), an extremely stable arrangement (AROMATIC STABILIZATION).
Following Hund’s rule, two electrons are in separate orbitals because they are at same energy.

Most stable if filled with an electron pair (as with benzene)

If cyclobutadiene adopted a coplanar geometry - two of the molecular orbitals would each have a single unpaired electron - very unstable. Applies to any (4 n) system

Cyclobutadiene is ANTIAROMATIC
Aromatic

All bond lengths same

(4n + 2)

benzene

(cyclobutadiene)

cyclooctatetraene

Anti-aromatic

Combination of single and double bonds

(vacant orbitals not shown)

N filled shells

aromatic: (4N + 2) electrons

antiaromatic: 4N electrons

N shells missing 2 electrons

energy
The Acidity of the Pyridinium Ion

- Heterocyclic aromatic compound.
- Nonbonding pair of electrons in \( sp^2 \) orbital, so weak base, \( pK_b = 8.8 \).

\[
\text{pyridine, } pK_b = 8.8 \quad \text{versus} \quad \text{pyridinium ion, } pK_a = 5.2
\]
The Acidity of Protonated Pyrrole

Also aromatic, but lone pair of electrons is delocalized: much weaker base.
Aromatic Cations and Anions
Many Benzene Derivatives are Useful Drugs

- Acetyl salicylic acid (ASPIRIN)
- Ibuprofen (ADVIL)
- Bronchodilator (ALBUTEROL)
- Procaine (NOVOCAINE)
- Acetaminophen (TYLENOL)
- Naproxen (ALEVE)
- Appetite suppressant (FENFLURAMINE)
- Rocecoxib (VIOXX)