Aromaticity

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Discovery of Benzene

- Aromatic class was first used to classify anything that was fragrant (had aroma)
- Isolated in 1825 by Michael Faraday who determined C:H ratio to be 1:1.
- Synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be C₆H₆.
- Other related compounds with low C:H ratios had a pleasant smell, so they were classified as aromatic.

Kekulé Structure
- Proposed in 1866 by Friedrich Kekulé, shortly after multiple bonds were suggested.
- Failed to explain existence of only one isomer of 1,2-dichlorobenzene.
Unusual Reactions

- Alkene + KMnO₄ → diol (addition)
  Benzene + KMnO₄ → no reaction
- Alkene + Br₂/CCl₄ → dibromide (addition)
  Benzene + Br₂/CCl₄ → no reaction
- With FeCl₃ catalyst, Br₂ reacts with benzene to form bromobenzene + HBr (substitution!). Double bonds remain.

- All cyclic conjugated hydrocarbons were proposed to be aromatic.
- However, cyclobutadiene is so reactive that it dimerizes before it can be isolated.
- And cyclooctatetraene adds Br₂ readily like an alkene.
Modern Theory of the Benzene Structure

The Resonance Theory

- Structures I and II are equal resonance contributors to the real structure of benzene

\[ \text{I} \quad \leftrightarrow \quad \text{II} \]

- Benzene is particularly stable because it has two equivalent and important resonance structures

- Each carbon-carbon bond is 1.397 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)

Aromaticity - Benzene
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.

MO diagram

Energy diagram
MO Rules for Cyclobutadiene

Energy Diagram for Cyclobutadiene
Polygon Rule

The energy diagram for an annulene has the same shape as the cyclic compound with one vertex at the bottom.
Aromaticity, Anti and Non-Aromaticity

Aromatic

• Structure must be cyclic with conjugated pi bonds.
• Each atom in the ring must have an unhybridized $p$ orbital.
• The $p$ orbitals must overlap continuously around the ring. (Usually planar structure.)
• Follow Huckel's number (4n+2) (next slide).

Anti and Non Aromaticity

• Antiaromatic compounds are cyclic, conjugated, with overlapping $p$ orbitals around the ring, but do not follow Huckel’s number.
• Nonaromatic compounds do not have a continuous ring of overlapping $p$ orbitals and may be nonplanar.
Hückel’s Rule

• If the compound has a continuous ring of overlapping $p$ orbitals and has $4n + 2$ electrons ($\Pi e^-$), it is aromatic.
• If the compound has a continuous ring of overlapping $p$ orbitals and has $4n$ electrons, it is antiaromatic.

**Examples**
• When $n = 0$; $\pi e^-$ are $4 \times 0 + 2 = 2$ (does not exist)
• When $n = 1$; $\pi e^-$ are $4 \times 1 + 2 = 6$ (benzene)
• When $n = 2$; $\pi e^-$ are $4 \times 2 + 2 = 10$ (not aromatic because not planar)
• When $n = 3$; $\pi e^-$ are $4 \times 3 + 2 = 14$
• 4 and 8 $\pi e^-$ systems are antiaromatic (both cyclobutadiene and cyclooctatetraene are conjugated but do not have Hückel’s number)
Anti Aromatic Compounds

• Planar, cyclic molecules with $4n\pi$ electrons are much less stable than expected (antiaromatic)
• They will distort out of plane and behave like ordinary alkenes
• $4$- and $8$-electron compounds are not delocalized (single and double bonds)
• Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature
• Cyclooctatetraene has four double bonds, reacting with Br$_2$, KMnO$_4$, and HCl as if it were four alkenes

![Diagram of Diels-Alder reaction]

Cyclooctatetraene
Four double bonds; eight $\pi$ electrons
Cyclopentadienyl Ions

- The cation has an empty $p$ orbital, 4 electrons, so antiaromatic.
- The anion has a nonbonding pair of electrons in a $p$ orbital, 6 e$^-$s, aromatic.

Acidity of Cyclopentadiene: $pK_a$ of cyclopentadiene is 16, much more acidic than other hydrocarbons.
Tropylium Anion and Annulene Dianion

- The cycloheptatrienyl cation has 6 $p$ electrons and an empty $p$ orbital.
- Aromatic: more stable than open chain ion.

Cyclooctatetraene easily forms a -2 ion.
- Ten electrons, continuous overlapping $p$ orbitals, so it is aromatic.
Pyridine and Pyrrole and Basicity of N

- Heterocyclic aromatic compound.
- Nonbonding pair of electrons in $sp^2$ orbital, so weak base, $pK_b = 8.8$.
- Pyrrole is also aromatic, but lone pair of electrons is delocalized, so much weaker base.

Pyrimidine has two basic nitrogens.  
Imidazole has one basic nitrogen and one nonbasic.  

Purine
Other Heterocyclics and Aromatics

Other Heterocyclics

- Pyrrole
- Furan
- Thiophene

Fused Ring Hydrocarbons

- Naphthalene
- Anthracene
- Pyrene
- Benzo[a]pyrene

Aromaticity - Benzene
Key Concepts

• Why benzene is aromatic.
• MO theory
• Aromatic, non aromatic and anti-aromatic.
• Aromatic ions
• Other compounds that are aromatic.