Chapter 16
Aromatic Compounds

Discovery of Benzene

- 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 $C_6H_6$.
- 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.

\[
\begin{align*}
\text{H} & \quad \text{C}^-\quad \text{C}^-\quad \text{H} \\
\text{H} & \quad \text{C}^-\quad \text{C}^-\quad \text{H} \\
\end{align*}
\]

Resonance Structure

Each \( sp^2 \) hybridized C in the ring has an unhybridized \( p \) orbital perpendicular to the ring which overlaps around the ring.
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.

Unusual Stability

Hydrogenation of just one double bond in benzene is **endothermic**!
Annulenes

- 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.
- Look at MO’s to explain aromaticity.

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.
Chapter 16: Aromatics

MO’s for Benzene

- The six electrons fill three bonding pi orbitals.
- All bonding orbitals are filled (“closed shell”), an extremely stable arrangement.

Energy Diagram for Benzene

- The six electrons fill three bonding pi orbitals.
- All bonding orbitals are filled (“closed shell”), an extremely stable arrangement.
MO’s for Cyclobutadiene

- Following Hund’s rule, two electrons are in separate orbitals.
- This diradical would be very reactive.

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.

Aromatic Requirements

- 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.)
- Compound is more stable than its open-chain counterpart.
Anti- and Nonaromatic

- Antiaromatic compounds are cyclic, conjugated, with overlapping $p$ orbitals around the ring, but the energy of the compound is greater than its open-chain counterpart.
- 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, it is aromatic.
- If the compound has a continuous ring of overlapping $p$ orbitals and has $4N$ electrons, it is antiaromatic.
[N]Annulenes

- [4]Annulene is antiaromatic (4\(N\) e\(^+\)s)
- [8]Annulene would be antiaromatic, but it’s not planar, so it’s nonaromatic.
- [10]Annulene is aromatic except for the isomers that are not planar.
- Larger 4\(N\) annulenes are not antiaromatic because they are flexible enough to become nonplanar. =>

MO Derivation of Hückel’s Rule

- Lowest energy MO has 2 electrons.
- Each filled shell has 4 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 Ion

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

\[
\begin{align*}
\text{H} & \rightarrow \text{H}^+ \\
\text{OH} & \rightarrow \text{H}^+ \quad \text{H}_2\text{O} \\
\end{align*}
\]

Dianion of [8]Annulene

- Cyclooctatetraene easily forms a -2 ion.
- Ten electrons, continuous overlapping \( p \) orbitals, so it is aromatic.

\[
\begin{align*}
\text{[8]Annulene} & + 2 \text{K} \rightarrow \text{[8]Annulene}^- \\
\text{ten pi electrons} & \quad \text{[8]Annulene}^- + 2 \text{K}^+ \\
\end{align*}
\]
Pyridine

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

\[
\text{Pyridine, } pK_b = 8.8 \quad \text{pyridinium ion, } pK_a = 5.2
\]

Pyrrole

Also aromatic, but lone pair of electrons is delocalized, so much weaker base.

\[
\text{Pyrrole, } pK_b = 13.6 \quad \text{N-protonated pyrrole, } pK_a = 0.4
\]
Basic or Nonbasic?

Pyrimidine has two basic nitrogens.

Imidazole has one basic nitrogen and one nonbasic.

Purine?

Other Heterocyclics

Pyrrrole

Furan

Thiophene

Copyright © 2005 Pearson Prentice Hall, Inc.
Fused Ring Hydrocarbons

- Naphthalene

- Anthracene

- Phenanthrene

Reactivity of Polynuclear Hydrocarbons

As the number of aromatic rings increases, the resonance energy per ring decreases, so larger PAH’s will add Br₂.

(mixture of cis and trans isomers) =>
Larger Polynuclear Aromatic Hydrocarbons

- Formed in combustion (tobacco smoke).
- Many are carcinogenic.
- Epoxides form, combine with DNA base.

Allotropes of Carbon

- Amorphous: small particles of graphite; charcoal, soot, coal, carbon black.
- Diamond: a lattice of tetrahedral C’s.
- Graphite: layers of fused aromatic rings.
Diamond

- One giant molecule.
- Tetrahedral carbons.
- Sigma bonds, 1.54 Å.
- Electrical insulator.

Graphite

- Planar layered structure.
- Layer of fused benzene rings, bonds: 1.415 Å.
- Only van der Waals forces between layers.
- Conducts electrical current parallel to layers.
Some New Allotropes

- Fullerenes: 5- and 6-membered rings arranged to form a “soccer ball” structure.
- Nanotubes: half of a $C_{60}$ sphere fused to a cylinder of fused aromatic rings.

Fused Heterocyclic Compounds

Common in nature, synthesized for drugs.

L-tryptophan, an amino acid

LSD, a hallucinogen
Common Names of Benzene Derivatives

- phenol
- toluene
- aniline
- anisole
- styrene
- acetophenone
- benzaldehyde
- benzoic acid

Disubstituted Benzenes
The prefixes ortho-, meta-, and para- are commonly used for the 1,2-, 1,3-, and 1,4- positions, respectively.

- 1,2 or ortho
- 1,3 or meta
- 1,4 or para

- o-dichlorobenzene
- m-chloroperbenzoic acid
- p-nitrophenol
3 or More Substituents

Use the smallest possible numbers, but the carbon with a functional group is #1.

\[
\begin{align*}
\text{1,3,5-trinitrobenzene} & \quad \text{2,4,6-trinitrophenol} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Common Names for Disubstituted Benzenes

\[
\begin{align*}
\text{m-xylene} & \quad \text{mesitylene} & \quad \text{o-toluic acid} & \quad \text{p-cresol} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{O} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{H}_3\text{C} & \quad \text{CH}_3 & \quad \text{H}_3\text{C} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{OH}
\end{align*}
\]
Phenyl and Benzyl

Phenyl indicates the benzene ring attachment. The benzyl group has an additional carbon.

\[
\text{phenyl bromide} \quad \text{benzyl bromide}
\]

Physical Properties

- Melting points: More symmetrical than corresponding alkane, pack better into crystals, so higher melting points.
- Boiling points: Dependent on dipole moment, so \textit{ortho} > \textit{meta} > \textit{para}, for disubstituted benzenes.
- Density: More dense than nonaromatics, less dense than water.
- Solubility: Generally insoluble in water.
IR and NMR Spectroscopy

- C=C stretch absorption at 1600 cm\(^{-1}\).
- \(sp^2\) C-H stretch just above 3000 cm\(^{-1}\).
- \(^1\)H NMR at \(\delta\)7-\(\delta\)8 for H’s on aromatic ring.
- \(^{13}\)C NMR at \(\delta\)120-\(\delta\)150, similar to alkene carbons.

Mass Spectrometry

\[
\text{Ph} \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\]

\(n\)-butylbenzene
UV Spectroscopy

End of Chapter 16

Homework: 27, 28, 31, 32, 34, 35, 37, 45, 46, 50