Chapter 17
Aromatic Compounds
17.1 Introduction to Aromatic Compounds

- **Aromatic** compounds or **arenes** include benzene and benzene derivatives

![Benzene](image1.png) ![Toluene](image2.png) ![ortho-Xylene](image3.png)

- Benzene derivatives were originally isolated from fragrant oils
- Most aromatic compounds are odorless
17.1 Introduction to Aromatic Compounds

- **Aromatic** rings are a common feature in drugs

Lipitor (atorvastatin)

Zyprexa (olanzapine)

Norvasc (amlodipine)

Prilosec (omeprazole)

Prevacid (lansoprazole)

Plavix (clopidogrel)
17.1 Introduction to Aromatic Compounds

- Coal contains aromatic rings fused together and joined by nonaromatic functional groups
Buckyballs are $\text{C}_{60}$ spheres made of interlocking aromatic rings.
Buckyballs and Nanotubes

• Fullerenes can be made into tubes (cylinders) = nanotubes

• Single, double, and multi-walled carbon nanotubes have many applications:
  – Conductive Plastics, Energy Storage, Conductive Adhesives, Molecular Electronics, Thermal Materials, Fibres and Fabrics, Catalyst Supports, Biomedical Applications
17.2 Nomenclature of Benzene Deriv.

- Benzene is generally the parent name for monosubstituted derivatives
The following common names are accepted by IUPAC as parent names, and are frequently used:
17.2 Nomenclature of Benzene Deriv.

- If the substituent is larger than the ring, the substituent becomes the parent chain.

- Benzene rings are represented with “Ph” (for phenyl) or with a “ϕ” (phi) symbol.
17.2 Nomenclature of Benzene Deriv.

- The common name for dimethyl benzene derivatives is xylene

- *ortho*, *meta*, and *para* are used for the location of substituents on disubstituted benzene rings
17.2 Nomenclature of Benzene Deriv.

1. Identify the parent

2. Identify and Name the substituents

3. Number the parent chain and assign a locant to each substituent
   - Give the first substituent the lowest number possible

4. List the numbered substituents before the parent name in alphabetical order
   - Ignore prefixes (except iso) when ordering alphabetically
17.2 Nomenclature of Benzene Deriv.

1. Identify the parent chain (generally the aromatic ring)
   - Often a common name can be the parent chain

   ![Diagram of phenol with OH and Br substituents]

   Parent = phenol

2. Identify and Name the substituents
17.2 Nomenclature of Benzene Deriv.

3. Number the parent chain and assign a locant to each substituent
   – A substituent that is part of the parent name must be assigned locant NUMBER 1

4. List the numbered substituents before the parent name in alphabetical order
   – Ignore prefixes (except iso) when ordering alphabetically

   3,5-dibromophenol

• Practice with SkillBuilder 17.1
17.3 Structure of Benzene

- In 1866, August Kekulé proposed that benzene is a ring comprised of alternating double and single bonds.

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

- Kekulé suggested that the exchange of double and single bonds was an equilibrium process.
17.3 Structure of Benzene

- We now know that the two drawings are resonance contributors rather than in equilibrium

- Sometimes the ring is represented with a circle in it to avoid drawing resonance structures
17.4 Stability of Benzene

- Aromatic rings are remarkably stable
- Recall alkenes readily undergo addition reactions

\[
\text{Cyclohexane} + \text{Br}_2 \rightarrow \text{Bromo-cyclohexane} \\
\]

- Aromatic rings are stable enough that they do not undergo such reactions

\[
\text{Benzene} + \text{Br}_2 \rightarrow \text{No reaction} \\
\]
17.4 Stability of Benzene

- Heats of hydrogenation can be used to quantify aromatic stability.
17.4 Stability of Benzene

- MO theory can help us explain aromatic stability
- The 6 atomic p-orbitals of benzene overlap to make 6 MOs
17.4 Stability of Benzene

- The delocalization of the 6 pi electrons in the three bonding molecular orbitals accounts for the stability of benzene.
17.4 Stability of Benzene

- Not all fully conjugated rings have aromatic stability

\[
\begin{align*}
\text{Cyclobutadiene} & \quad \text{Cyclooctatetraene} \\
\end{align*}
\]

- Some fully conjugated cyclic compounds react like normal alkenes

\[
\begin{align*}
\text{Benzene} + \text{Br}_2 & \rightarrow \text{Brominated Benzene} + \text{Enantiomer} \\
\end{align*}
\]
17.4 Stability of Benzene

- Aromatic compounds must meet two criteria:
  1. A fully conjugated ring with overlapping p-orbitals
  2. Meets Hückel’s rule: an ODD number of e⁻ pairs or 4n+2 total π electrons where n=0, 1, 2, 3, 4, etc.

- The following compounds do not meet Hückel’s rule:
  - Cyclobutadiene
  - Cyclooctatetraene

- Practice with Conceptual Checkpoint 17.8
17.4 Stability of Benzene

- We can explain Hückel’s rule using MO theory
- Consider the MOs for cyclobutadiene, which has 4 \( \pi \) electrons:

Lacks a closed-shell electron configuration, and unstable. It is **antiaromatic**
17.4 Stability of Benzene

- A similar MO analysis for cyclooctatetraene suggests that it is also **antiaromatic**
17.4 Stability of Benzene

- However, if the structure adopts a tub-shaped conformation, it can avoid being antiaromatic:

- The conjugation does not extend around the entire ring, so the system is neither aromatic nor antiaromatic. It is nonaromatic.
17.4 Stability of Benzene

- Predicting the shapes and energies of MOs can be simplified by drawing **Frost circles** to predict the relative MO energies.
17.4 Stability of Benzene

- **Frost circles** help to explain the $4n+2$ rule:

  ![Diagram showing bonding orbitals in different ring sizes]

- Note that the number of bonding orbitals is always an odd number - aromatic compounds will always have an odd number of electron pairs.

- **Practice with Conceptual Checkpoint 17.9**
17.5 Other Aromatic Compounds

• **Aromatic** compounds fulfill two criteria
  1. A fully conjugated ring with overlapping $p$-orbitals
  2. Meets **Hückel’s rule**: an ODD number of $e^-$ pairs or $4n+2$ total $\pi$ electrons where $n=0, 1, 2, 3, 4, \text{ etc.}$

• **Antiaromatic** compounds fulfill two criteria
  1. A fully conjugated ring with overlapping $p$-orbitals
  2. An EVEN number of electron pairs or $4n$ total $\pi$ electrons where $n=0, 1, 2, 3, 4, \text{ etc.}$

• When a compound fails criteria #1, it is **nonaromatic**
17.5 Other Aromatic Compounds

- Annulenes are rings that are fully conjugated

- Annulenes can aromatic, antiaromatic or nonaromatic

- Practice with Conceptual Checkpoint 17.10
17.5 Other Aromatic Compounds

- Aromatic rings can contain carbanions or carbocations
- Consider a 5-membered ring

- 6 \pi electrons must be present in order to be aromatic
17.5 Other Aromatic Compounds

- The **cyclopentadienyl anion** has a lone pair delocalized over each of the 5 carbon atoms, and is an **aromatic anion**

- The acidity of cyclopentadiene is attributed to the aromatic stability of its conjugate base
17.5 Other Aromatic Compounds

- Consider a 7-membered ring

- With $6\pi$ electrons, one of the carbon atoms has an empty p orbital, and the compound is cationic.

Three bonding MOs can accommodate six $\pi$ electrons.
17.5 Other Aromatic Compounds

- The **tropylium cation** is an **aromatic cation**: 

  ![Diagram of tropylium cation]

- **Practice with SkillBuilder 17.2**
17.5 Aromatic Heterocycles

- Heteroatoms (atoms other than C or H) can also be part of an aromatic ring

![Pyridine and Pyrrole structures](image)

$N$: $sp^2$-hybridized orbital

$p$ orbital
17.5 Aromatic Heterocycles

- If the heteroatom’s lone pair is necessary for aromaticity, it will be included in the **Hückel** number of \( \pi \) electrons

![Pyridine and Pyrrole](image)

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17.5 Aromatic Heterocycles

- If the lone pair is necessary for aromaticity, then the lone pair will not be as basic.

\[
pK_a = 5.2
\]

Still aromatic

\[
pK_a = 0.4
\]

nonaromatic
17.7 Reduction of Benzene

- Under forceful conditions, benzene can be reduced to cyclohexane

\[
\text{C}_6\text{H}_6 + 3\text{H}_2 \xrightarrow{\text{Ni}\atop 100\text{ atm}\atop 150^\circ\text{C}} \text{C}_6\text{H}_{12} \quad \Delta H^\circ = -208 \text{ kJ/mol}
\]

- However, alkenes can be selectively hydrogenated in the presence of a benzene ring:

\[
\text{C}_6\text{H}_5\text{CH} = \text{C} + \text{H}_2 \xrightarrow{\text{Pt}\atop 2\text{ atm}\atop 25^\circ\text{C}} \text{C}_6\text{H}_{11} \quad \Delta H^\circ = -117 \text{ kJ/mol}
\]