Aromatic compounds are compounds that are similar to benzene in structure and chemical behavior. Benzene, C₆H₆, is a cyclic compound commonly written as a hexagon with alternating double and single bonds.

**CHAPTER SUMMARY**

6.1 Introduction to Aromatic Compounds

**Aromatic compounds** are compounds that are similar to **benzene** in structure and chemical behavior. Benzene, C₆H₆, is a cyclic compound commonly written as a hexagon with alternating double and single bonds.
6.2 Benzene: Structure and Bonding

A. Unusual Characteristics of Benzene

Benzene has two unusual features that are not necessarily apparent using classical molecular structures. First, it has an unexpected stability. This is evident in that benzene characteristically undergoes substitution reactions, in which the integrity of the benzene ring is maintained, rather than addition reactions that are characteristic of highly unsaturated compounds with double bonds. Even when addition reactions occur, as in the hydrogenation of benzene, the heat of reaction is significantly less than would be expected from hydrogenation of three carbon-carbon double bonds. The difference is known as the resonance energy.

Secondly, the carbon-carbon bond lengths are not as they appear in classical structures, three single and three double bonds; instead the bonds are all equal in length and intermediate between double and single bonds.

B. Bonding in Benzene

Benzene actually is a resonance hybrid of the two resonance forms written with alternating double and single bonds. The resonance hybrid is an average of the two and is often written with a circle inside the hexagon to denote bond lengths intermediate between double and single bonds. Each carbon in the benzene ring has a p-orbital. These parallel p-orbitals overlap continuously making all the carbon-carbon bonds identical.

C. Structure of Benzene - A Summary

Benzene is a flat six membered ring with the formula C₆H₆. All six carbons are equivalent, all six hydrogens are equivalent, and all the carbon-carbon bonds are equivalent and intermediate in length between a single bond and double bond. Each carbon is trigonal, sp²-hybridized, and has 120° bond angles. There is a p-orbital on each carbon and the six overlap continuously around the ring.

CONNECTIONS 6.1 Cancer and Carcinogens
6.3 Nomenclature of Aromatic Systems

A. Aromatic Hydrocarbon Ring Systems
   Napthalene, anthracene, and phenanthrene are simple fused ring aromatic systems.

B. Monosubstituted Benzenes
   Monosubstituted benzenes are named as derivatives of benzene or by common names such as toluene, benzaldehyde, benzoic acid, benzenesulfonic acid, phenol, and aniline.

C. Disubstituted Benzenes
   Disubstituted benzenes can be named using ortho (1,2), meta (1,3), and para (1,4) designations; either the numbers or o, m, p are acceptable.

D. Polysubstituted Benzenes
   When more than two groups are on a benzene ring, their positions must be numbered. If one of the groups is associated with a common name, the compound can be named as a derivative of the monosubstituted compound, numbering from the group designated in the common name.

E. Substituted Anilines
   Substituents on the nitrogen of aniline are located by capital N.

F. Aromatic Compounds Designated by a Prefix
   The prefix for benzene is phenyl. Benzene with a CH$_2$ group is benzyl.

CONNECTION 6.2 Gasoline

6.4 Electrophilic Aromatic Substitution

Because of its exceptional stability, benzene is resistant to chemical change and has substitution as its characteristic reaction. The special
electronic character of the system is preserved in substitution reactions whereas it would be destroyed with addition reactions. Because of its electron-rich pi electron system, benzene attracts electron-deficient species, electrophiles, that eventually replace a hydrogen on the ring.

A. Electrophilic Aromatic Substitution: The Reaction

The characteristic reaction of benzene and its derivatives is **electrophilic aromatic substitution**. In these reactions, a hydrogen on the benzene ring is replaced by a chlorine (**chlorination**), a bromine (**bromination**), an alkyl or acyl group (**Friedel-Crafts alkylation or acylation**), a nitro group (**nitration**), or a sulfonic acid group (**sulfonation**).

B. Electrophilic Aromatic Substitution: The Mechanism

Electrophilic aromatic substitution is a three-step process. First, a positive electrophile is generated. This is followed by two-step substitution. In the first step, the positive electrophile bonds to the benzene ring and produces a resonance stabilized carbocation. Then hydrogen ion is lost from the ring as the carbocation is neutralized and the benzene ring is regenerated.

C. Orientation of Substitution

Groups already present on a benzene ring direct the orientation of substitution of incoming groups. **Electron-donating groups** (hydroxy, alkoxy, amino, halogens and alkyl groups) stabilize the intermediate carbocation and direct the incoming electrophile to the **ortho and para positions**; these groups are called **ortho, para directors**. **Electron-withdrawing groups** (carboxylic acid, aldehyde, ketone, cyano, nitro, and sulfonic acid) destabilize the carbocation and the incoming electrophile is directed to the **meta position**; these groups are called **meta directors**.

D. Activating and Deactivating Groups

Electron-donating groups increase the negative character of the ring and its attractiveness to electrophiles. As a result they increase reactivity and are called **activating groups**. Electron-withdrawing groups decrease
the negative character of the ring and are deactivating groups. The
directing and activating or deactivating effects of substituents must be
taken into account in devising synthesis schemes.

6.5 Oxidation of Alkylbenzenes

Alkyl side chains on benzene can be oxidized to carboxylic acids using
potassium permanganate.

CONNECTIONS 6.3  Herbicides

SOLUTIONS TO PROBLEMS

6.1 Molecular Formulas of Aromatic Compounds
(a) C₆H₅Br; (b) C₁₀H₈; (c) C₁₄H₁₀.

6.2 Bonding in Aromatic Compounds

6.3 Positional Isomers
Look very carefully. These compounds are very symmetrical and there are
some carbons that do not have a hydrogen to replace.
6.4 Nomenclature of Monosubstituted Benzenes
(a) bromobenzene; (b) isopropylbenzene; (c) butylbenzene; (d) iodobenzene

6.5 Nomenclature of Disubstituted Benzenes
(a) m-ethylbenzaldehyde; (b) p-dibromobenzene;
(c) o-chlorobenzenesulfonic acid; (d) m-nitroaniline

6.6 Nomenclature of Polysubstituted Benzenes
(a) 1-chloro-3-isopropyl-5-nitrobenzene; (b) 2,4-dibromobenzoic acid;
(c) 2,3,4,5,6-pentachlorophenol; (d) 5-bromo-2-chloroaniline

6.7 Nomenclature of Substituted Anilines
(a) N-butylaniline; (b) N-ethyl, N-methyl, para propylaniline;
(c) 5-bromo-2-chloro-N,N-dimethylaniline

6.8 Nomenclature Using Prefixes for Aromatic Groups
(a) 4-methyl-2-phenylhexane; (b) 1,4-diphenyl-2-butyne;
(c) p benzylbenzoic acid
6.9 Electrophilic Aromatic Substitution

p-xylene

\[
\begin{align*}
\text{CH}_3 & + \text{Reagents} \\
\text{CH}_3 & \text{in a-f} \\
\end{align*}
\]

a) \[
\begin{align*}
\text{CH}_3 & \text{Cl} \\
\text{CH}_3 & \\
\end{align*}
\]

b) \[
\begin{align*}
\text{CH}_3 & \text{Br} \\
\text{CH}_3 & \\
\end{align*}
\]

c) \[
\begin{align*}
\text{CH}_3 & \text{CH}_2\text{CH}_3 \\
\text{CH}_3 & \\
\end{align*}
\]

d) \[
\begin{align*}
\text{CH}_3 & \text{CCH}_3 \\
\text{CH}_3 & \\
\end{align*}
\]

e) \[
\begin{align*}
\text{CH}_3 & \text{NO}_2 \\
\text{CH}_3 & \\
\end{align*}
\]

(f) \[
\begin{align*}
\text{CH}_3 & \text{SO}_3\text{H} \\
\text{CH}_3 & \\
\end{align*}
\]

6.10 Electrophilic Aromatic Substitution - Chlorination

Generation of the Electrophile \[
\begin{align*}
\text{Cl}_2 & + \text{FeCl}_3 \rightarrow \text{Cl}^+ + \text{FeCl}_4^- \\
\end{align*}
\]

Two-Step Substitution \[
\begin{align*}
\text{HCl} & \rightarrow \text{Cl}^+ \\
\text{FeCl}_4^- & \rightarrow \text{Cl}^- + \text{HCl} + \text{FeCl}_3 \\
\end{align*}
\]

6.11 Electrophilic Aromatic Substitution - Bromination

Generation of the Electrophile \[
\begin{align*}
\text{Br}_2 & + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^- \\
\end{align*}
\]

Two-Step Substitution \[
\begin{align*}
\text{HBr} & \rightarrow \text{Br}^+ \\
\text{FeBr}_4^- & \rightarrow \text{Br}^- + \text{HBr} + \text{FeBr}_3 \\
\end{align*}
\]

6.12 Electrophilic Aromatic Substitution - Alkylation and Acylation

(a) Acylation
Chapter 6  Aromatic Compounds

6.13 Electrophilic Aromatic Substitution - Nitration

**Generation of the Electrophile**

\[
\text{HNO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}
\]

**Two-step Substitution**

\[
\begin{align*}
\text{CH}_3 & \quad \text{NO}_2^+ \\
\text{CH}_3 & \quad \text{NO}_2 \\
\text{CH}_3 & \quad + \quad \text{HSO}_4^- \\
\text{CH}_3 & \quad + \quad \text{H}_2\text{SO}_4
\end{align*}
\]

6.14 Electrophilic Aromatic Substitution - Sulfonation

**Generation of the Electrophile**

\[
2\text{H}_2\text{SO}_4 \longrightarrow \text{SO}_3\text{H}^+ \quad \text{HSO}_4^- + \text{H}_2\text{O}
\]

**Two-step Substitution**

\[
\begin{align*}
\text{CH}_3 & \quad \text{SO}_3\text{H}^+ \\
\text{CH}_3 & \quad \text{SO}_3\text{H} \\
\text{CH}_3 & \quad + \quad \text{HSO}_4^- \\
\text{CH}_3 & \quad + \quad \text{H}_2\text{SO}_4
\end{align*}
\]
6.15 Electrophilic Aromatic Substitution Reactions

\[
\begin{align*}
\text{a)} \quad & \begin{aligned}
    & \text{Br} \quad \text{NO}_2 \quad \text{Br} \\
    & \text{NO}_2 \\
\end{aligned} \\
\text{b)} \quad & \begin{aligned}
    & \text{NO}_2 \\
    & \text{CO}_2 \text{H} \\
\end{aligned} \\
\text{c)} \quad & \begin{aligned}
    & \text{CH}_2\text{CH}_3 \quad \text{SO}_3 \text{H} \\
    & \text{CN} \\
\end{aligned} \\
\text{d)} \quad & \begin{aligned}
    & \text{Br} \\
    & \text{OCH}_3 \\
\end{aligned}
\end{align*}
\]

6.16 Synthesis Problems

\[
\begin{align*}
\text{a)} \quad & \begin{aligned}
    & \text{H}_2\text{SO}_4 \\
    & \text{Cl}_2 \quad \text{FeCl}_3 \\
\end{aligned} \\
\text{b)} \quad & \begin{aligned}
    & \text{CH}_3\text{Cl} \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \\
    & \text{CH}_3 \quad \text{NO}_2 \\
\end{aligned} \\
\text{b)} \quad & \begin{aligned}
    & \text{Cl}_2 \quad \text{FeCl}_3 \\
    & \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \\
\end{aligned}
\end{align*}
\]

6.17 Activating and Deactivating Groups

(a) methoxybenzene > benzene > chlorobenzene
(b) phenol > p-nitrophenol > nitrobenzene
(c) p-methylaniline > toluene > m-chlorotoluene

6.18 Oxidation of Alkylbenzenes

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{KMnO}_4 \\
\text{CO}_2\text{H}
\end{align*}
\]
Chapter 6  Aromatic Compounds

6.19 Bonding Pictures:  Section 6.2B

6.20 Molecular Formulas:  Section 6.2
(a) C₁₆H₁₀  (b) C₂₀H₁₂

6.21 Nomenclature of Mono and Disubstituted Benzenes:
Section 6.3B-C
(a) fluorobenzene;  (b) hexylbenzene;  (c) t-butylbenzene;
(d) o-dichlorobenzene;  (e) m-dibromobenzene;  (f) p-bromochlorobenzene;
(g) m-iodobenzoic acid;  (h) o-difluorobenzene  (i) p-ethylbenzaldehyde;
(j) o-nitrophenol;

6.22 Nomenclature of Polysubstituted Benzenes:  Section 6.3D
(a) 2,4-dichlorotoluene;  (b) 3-bromo-5-methylaniline;
(c) 2-ethyl-5-methylbenzenesulfonic acid;  (d) 2,4,6-tribromophenol;
(o) 3-bromo-2-chloro-5-nitroethylbenzene;  (p) 1,3,5-trinitrobenzene

6.23 Nomenclature of Substituted Anilines:  Section 6.3E
(a) m- ethylaniline;  (b) N-ethylaniline;
(c) m-nitro-N,N-diethylaniline;  (d) 3,5-dichloro-N-ethyl-N-methylaniline

6.24 Nomenclature Using Benzene as a Prefix:  Section 6.3F
(a) 2,4-dimethyl-2-phenylpentane;  (b) p-benzylbenzaldehyde;
(c) 5-ethyl-2-phenyl-2-heptene

6.25 Nomenclature of Polynuclear Aromatic Compounds:
Section 6.3A
(a) 1-bromo-5-fluoronaphthalene;  (b) 1,4-dinitronaphthalene;
6.26 Nomenclature: Section 6.3

6.27 Positional Isomers: Section 6.3A
(a) 1,2,3-tribromobenzene; 1,2,4-tribromobenzene; 1,3,5-tribromobenzene
(b) 3-chloro-1,2-dibromobenzene; 1-chloro-2,4-dibromobenzene; 2-chloro-1,4-dibromobenzene; 2-chloro-1,3-dibromobenzene; 4-chloro-1,2-dibromobenzene; 5-chloro-1,3-dibromobenzene
(c) 1-bromo-2-chloro-3-fluorobenzene; 1-bromo-2-chloro-4-fluorobenzene; 2-bromo-1-chloro-4-fluorobenzene; 2-bromo-1-chloro-3-fluorobenzene; 4-bromo-2-chloro-1-fluorobenzene; 1-bromo-3-chloro-5-fluorobenzene; 2-bromo-4-chloro-1-fluorobenzene; 1-bromo-3-chloro-2-fluorobenzene; 1-bromo-4-chloro-2-fluorobenzene; 4-bromo-1-chloro-2-fluorobenzene;
(d) 1,2; 1,3; 1,4; 1,5; 1,6; 1,7; 1,8; 2,3; 2,6; and 2,7-dibromonaphthalenes
(e) 1,2; 1,3; 1,4; 1,10; 1,5; 1,6; 1,7; 1,8; 1,9; 2,3; 2,10; 2,6; 2,7; 2,9; and 9,10 dinitroanthracenes
6.28 Positional Isomers: Section 6.3

- **ortho**
  - Reactions at $+6^\circ C$ with $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ to produce two possible isomers.

- **meta**
  - Reactions at $-7^\circ C$ with $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ to produce three possible isomers.

- **para**
  - Reactions at $87^\circ C$ with $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ to produce only one possible isomer.

6.29 Positional Isomers: Section 6.3

- **a)**
  - Reaction with $\text{CH}_3$ groups.

- **b)**
  - Reaction with $\text{CH}_2\text{CH}_3$ groups.

6.30 Reactions of Aromatic Compounds: Section 6.4

First look at the reagent and decide what is going to substitute for a hydrogen on the benzene ring - a halogen, alkyl, acyl, nitro, or sulfonic acid group. Then look at the groups on the ring and determine where they direct - ortho/para or meta. Place the incoming group where it is directed by the existing groups. See Example 6.5 in the text.
6.31 Reactions of Aromatic Compounds: Section 6.4
See explanation on problem 6.30.
6.32 Reaction Mechanisms: Section 6.4B
Following is the general mechanism for electrophilic aromatic substitution. First the electrophile is generated. Then two-step substitution occurs: the electrophile bonds to the ring forming a carbocation followed by elimination of a hydrogen ion to regenerate the benzene ring.

The mechanism is the same for all cases, only the electrophile differs. Following are the equations for generation of the electrophiles.

- a) \( E^+ = Cl^+ \quad Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^- \)
- b) \( E^+ = CH_3CH_2C^+ \quad CH_3CH_2CCl + AlCl_3 \rightarrow CH_3CH_2C^+ + AlCl_4^- \)
- c) \( E^+ = CH_3CHCH_3 \quad CH_3CHCH_3 + AlCl_3 \rightarrow CH_3CHCH_3 + AlCl_4^- \)
- d) \( E^+ = NO_2^+ \quad HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O \)
- e) \( E^+ = SO_3H \quad 2 H_2SO_4 \rightarrow SO_3H + HSO_4^- + H_2O \)

Below is a specific example using acylation, part (b).
In this reaction, the catalyst is regenerated when hydrogen ion reacts with the aluminum tetrachloride anion.

\[
\text{AlCl}_4^- + H^+ \rightarrow \text{AlCl}_3 + HCl
\]

**6.33 Reactions of Aromatic Compounds:** Section 6.4
To predict each product, first determine what group will be introduced on the benzene ring. If one or more groups are already on the ring, determine where they direct (o,p or m) and bond the incoming group accordingly.

a) \( A = \text{C}_6\text{H}_5\text{SO}_3\text{H} \quad B = \text{C}_6\text{H}_4\text{SO}_3\text{H} \)

b) \( C = \text{C}_6\text{H}_6 \quad D = \text{C}_6\text{H}_4\text{CH}_2\text{CH}_3\text{NO}_2 \quad + \text{C}_6\text{H}_4\text{CH}_2\text{CH}_3 \)

c) \( E = \text{C}_6\text{H}_5\text{CH}=\text{CH}_3 \quad F = \text{C}_6\text{H}_4\text{SO}_3\text{H} \quad G = \text{C}_6\text{H}_4\text{BrSO}_3\text{H} \)
6.34 Oxidation of Alkylbenzenes: Section 6.5

\[
\begin{align*}
\text{a)} & \quad \text{CO}_2\text{H} \\
\text{b)} & \quad \text{CO}_2\text{H} \\
\text{c)} & \quad \text{CH}_3 \\
\text{A} & = \quad \text{CO}_2\text{H} \\
\text{B} & = \quad \text{CO}_2\text{H} \\
\text{C} & = \quad \text{Br}
\end{align*}
\]

6.35 Synthesis: Section 6.4 and 6.5
To make m-bromobenzoic acid from toluene one should first oxidize the methyl group to a carboxylic acid, which is a meta director, and then introduce the bromine. If the bromine is introduced first, it will go ortho and para since the methyl group is an ortho/para director.

6.36 Synthesis: Section 6.4
The chlorine is an ortho/para director and the sulfonic acid group is a meta director. Since the desired product is p-chlorobenzenesulfonic acid, the chlorine should be introduced first so it can direct the sulfonic acid group para.

6.37 Synthesis: Sections 6.4-6.5
Draw the compound you are trying to synthesize. Determine the reagents needed to introduce each group. Then determine the order in which to introduce groups. For example, in a disubstituted benzene, cover one group with your finger. Does the remaining group direct so that the group you have covered would go where you want it?

\[
\begin{align*}
\text{a)} & \quad \text{Br}_2 \xrightarrow{\text{FeBr}_3} \quad \text{Br} \\
& \quad \text{Cl}_2 \xrightarrow{\text{FeCl}_3} \quad \text{Cl}
\end{align*}
\]
6.38 Synthesis: Sections 6.4-6.5
6.39 Reaction Mechanisms: Sections 5.1B and 6.4B

Electrophilic Addition

Electrophilic Aromatic Substitution
6.40 Reaction Mechanisms: Sections 4.4B and 6.4B.1

**Electrophilic Aromatic Substitution**

**Generation of the Electrophile**

\[ \text{Br}_2 + \text{FeBr}_3 \rightarrow \text{Br}^+ + \text{FeBr}_4^- \]

**Two-step Substitution**

\[ \begin{align*}
\text{C}_6\text{H}_5^- + \text{Br}^+ & \rightarrow \text{C}_6\text{H}_5^+ \\
\text{C}_6\text{H}_5^+ + \text{H}^+ & \rightarrow \text{C}_6\text{H}_5 \quad \text{(Propagating step)}
\end{align*} \]

**Free-radical Chain Bromination**

**Initiation**

\[ \text{Br}_2 \xrightarrow{\text{light}} 2 \text{Br}^- \]

**Propagation**

\[ \begin{align*}
\text{C}_6\text{H}_5^- + \text{Br}^- & \rightarrow \text{C}_6\text{H}_5^- + \text{HBr} \\
\text{C}_6\text{H}_5^- + \text{Br}^- & \rightarrow \text{C}_6\text{H}_5^- + \text{Br}^-
\end{align*} \]

6.41 Reaction Mechanisms: Sections 4.5C, 5.1B, and 6.4B.2

The mechanism of electrophilic substitution for the synthesis of ethylbenzene is one of two-step substitution: the electrophile bonds and forms a carbocation which is neutralized upon elimination of hydrogen ion.

\[ \begin{align*}
\text{C}_6\text{H}_5^- + \text{CH}_3\text{CH}_2\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5^+ + \text{H}^+ \\
\text{C}_6\text{H}_5^+ & \rightarrow \text{C}_6\text{H}_5
\end{align*} \]

The difference in the three procedures described is in the way the electrophile is generated.
6.42 Activating and Deactivating Groups
a) nitrobenzene < benzene < phenol
b) chlorobenzene < benzene < aniline
c) benzoic acid < p-methylbenzoic acid < p-xylene
d) nitrobenzene < p-nitrotoluene < toluene < p-xylene

6.43 Activating and Deactivating Groups

a) The nitro group is deactivating; as a result, substitution occurs on the other ring.

b) The methoxy group is activating and directs substitution to the ring it occupies.

6.44 Physical Properties: Section 2.9
(a) Ethylbenzene has a greater molecular weight.
(b-d) The compound with the highest melting point in each case is the most symmetrical and consequently, forms a very strong and stable crystal lattice.
6.45 **Gasoline:** Connection 6.2

1) Hydrocarbons with 5-10 carbons  
2) Branched hydrocarbon chains  
3) Unsaturated, cyclic and especially aromatic hydrocarbons

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \text{CCH}_2\text{CHCH}_3 \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\end{align*}
\]

Research Octane Number 100 101 91 107

6.46 **Production of Gasoline:** Connection 6.2  
   a) Isomerization;  
   b) Cracking;  
   c) Isomerization or Aromatization;  
   d) Alkylation or Polymerization;  
   e) Alkylation;  
   f) Aromatization

6.47 **Basicity of Aniline**  
Any group that increases the availability of the electron pair of nitrogen will increase basicity and those that decrease availability will decrease basicity. Electron-withdrawing groups like nitro pull electrons from the ring and from the amine group whereas releasing groups do the opposite. Thus electron-withdrawing groups decrease basicity and electron-releasing groups increase basicity. Since resonance effects occur between positions in an ortho or para relationship, these groups will have greater effect if ortho or para rather than meta.

**ACTIVITIES WITH MOLECULAR MODELS**

1. Make a molecular model of benzene if your model kit allows this to be done effectively. Note that the molecule is entirely planar, that all carbons are equivalent, that all hydrogens are equivalent, and that each carbon is trigonal with 120° bond angles.
2. How many different places on a benzene ring can you replace one hydrogen with a bromine?

3. How many places on a benzene ring can you substitute two bromines for two hydrogens?