BENZENE & AROMATIC COMPOUNDS

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Learning Objectives

By the end of chapter four the students will:

- Understand the resonance description of structure of benzene
- Understand the hybridization in benzene
- Understand the relation between the stability of benzene and resonance energy
- Know the criteria of aromaticity and Huckel rule
- Understand the nomenclature rules of aromatic compounds and know the Common names of some aromatic compounds
- Understand the reactivity of aromatic compounds, know what are electrophiles and know the four types of electrophilic aromatic substitution reactions (halogenation, Freidel Crafts alkylation and acylation, nitration and Sulfonation).
- Know the reactions of alkyl side chains of aromatic compounds (halogenation, oxidation)
- Understand the orientation and reactivity of E.A.S reactions in monosubstituted benzene derivatives.
Benzene: Resonance description

Primary analysis revealed benzene had...

Molecular Formula of $\text{C}_6\text{H}_6$

Molecular Mass of 78

Hybridization = $\text{sp}^2$

Bond angles = 120°

Structure = Cyclic planner

All bond lengths in benzene to be equal and intermediate between single bond and double bond lengths (1.39 Å)

Resonance instead considers such molecules to be an intermediate or average (Called a Resonance Hybrid) between several structures that differ only in the placement of the valence electrons
The electrons in the π-bonds are delocalized around the ring (The circle represent six π-electrons distributed over the six atoms of the ring.)
Stability of Benzene

\[
\text{Benzene} \quad + \quad \text{H}_2 \quad \xrightarrow{\text{catalyst}} \quad \text{Cyclohexane} \quad \Delta H = 28.6 \text{ kcal/mol}
\]

\[
\text{Benzene} \quad + \quad 3 \text{ H}_2 \quad \xrightarrow{\text{catalyst}} \quad \text{Cyclohexane} \quad \Delta H = 85.8 \text{ kcal/mol}
\] (imaginary)

\[
\text{Benzene} \quad + \quad 3 \text{ H}_2 \quad \xrightarrow{\text{catalyst, heat, pressur}} \quad \text{Cyclohexane} \quad \Delta H = 49.8 \text{ kcal/mol}
\]

Benzene is more stable by 36 kcal/mol: **Resonance energy**
Characteristics of Aromatic Compounds

Aromatic compounds are compounds that resemble benzene in chemical behavior thus they tend to react by substitution rather than by addition and fulfill the aromaticity requirements.

To be classified as aromatic, a compound must have:
- Cyclic structure.
- Planar structure.
- Alternating $\Pi$ and $\delta$ bonds
- Fulfill Huckel rule i.e. the system must have $4n + 2$ pi electrons: thus by calculating $n$ value it will be an integral number i.e. $n=0, 1, 2, 3$.....
Examples of aromatic compounds

\[
\begin{align*}
4n+2 &= 6 \\
n &= 1
\end{align*}
\]

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\end{align*}
\]

\[
\begin{align*}
4n+2 &= 2 \\
n &= 0
\end{align*}
\]

\[
\begin{align*}
4n+2 &= 10 \\
n &= 2
\end{align*}
\]

\[
\begin{align*}
4n+2 &= 10 \\
n &= 2
\end{align*}
\]
Heterocyclic Aromatic compounds

Pyridine

Pyrrole

Furan

Thiophene

Naphthalene

Quinoline

1H-Indole
Examples of non aromatic compounds

- Carbon indicated by * is sp³

\[ n = \frac{1}{2} \]

\[ n = \frac{1}{2} + 2 = 8 \]

\[ n = 1.5 \]
Nomenclature of Aromatic Compounds

1. Monosubstituted Benzenes

a. IUPAC Names

- They are named as derivatives of benzene.
- No number is needed for mono-substituted benzene.

- \[
  \text{C(CH}_3\text{)}_3 \quad \text{CH}_2\text{CH}_3 \quad \text{NO}_2 \quad \text{Cl}
  \]

- \text{tert-Butyl-benzene}  
  \text{Ethyl-benzene}  
  \text{Nitro-benzene}  
  \text{Chloro-benzene}
Benzene ring has priority over side chains with alkyl, alkoxy groups, halogens, double and triple bonds.

Vinyl-benzene  Allyl-benzene  Ethynyl-benzene  Butyl-benzene  Methoxy-benzene

In some cases the side chains on aromatic ring contain functional groups of higher priorities (NH$_2$, OH, CHO,C=O, COOH, COOR) thus in this case the aromatic ring will be considered as a substituent and the side chain will be used to give the root name.

Two aromatic radials are known

Benzyl group  phenyl group (C$_6$H$_5^-$)  Benzylchloride
b. Common Names Of Monosubstituted Benzenes

- Toluene
- Styrene
- Phenol
- Benzaldehyde
- Benzoic acid
- Aniline
- Anisol

- o-Xylene
- m-Xylene
- p-Xylene
2. Nomenclature of Disubstituted and polysubstituted Benzenes

- All disubstituted benzenes (two groups are attached to benzene), can give rise to three possible positional isomers. The relative positions of the substituents are designated by numbers or, more commonly, by the prefixes ortho (*o*: 1,2), meta (*m*: 1,3) or para (*p*: 1,4).

![Chemical structures of dibromobenzenes](image)

1,2-Dibromobenzene 1,3-Dibromobenzene 1,4-Dibromobenzene

- When the substituents are different, they are of equal priorities they will should be listed in alphabetical order.
If one of the substituents is part of a parent compound, then the disubstituted or polysubstituted benzene is named as a derivative of that parent compound i.e. priorities determine the root name and substituents.
The physical properties of Benzene

- Benzene is toxic.
- Benzene is a colorless liquid.
- Benzene is non polar.
- Benzene is soluble in organic solvents but immiscible in water.
Electrophilic Aromatic Substitution Reactions

- **Halogenation**
  - $X_2, \text{FeX}_3$
  - $\text{Ph} + HX \quad (X=\text{Cl, Br})$

- **Alkylation**
  - $\text{Ph} + \text{RCl, AlCl}_3$
  - $\text{Ph} + \text{HCl}$

- **Nitration**
  - $\text{Ph} + \text{HONO}_2, \text{H}_2\text{SO}_4$
  - $\text{PhNO}_2 + \text{H}_2\text{O}$

- **Sulfonation**
  - $\text{Ph} + \text{SO}_3, \text{H}_2\text{SO}_4$
  - $\text{PhSO}_3\text{H}$

- **Acylation**
  - $\text{Ph} + \text{RCOCl, AICl}_3$
  - $\text{PhCOR}$
Side-Chain Reactions of Aromatic Compounds

a. Halogenation of an Alkyl Side Chain

\[
\text{Toluene} \xrightarrow{\text{Br}_2, \text{UV light}} \text{Benzyl Bromide} \quad + \quad \text{HBr}
\]

b. Oxidation of an Alkyl Side Chain

\[
\text{Toluene} \xrightarrow{\text{KMnO}_4} \text{Benzoic acid} \quad + \quad \text{CO}_2 \quad + \quad \text{H}_2\text{O}
\]

\[
\text{Toluene} \xrightarrow{\text{KMnO}_4} \text{Benzoic acid}
\]
Orientation effects of substituents in electrophilic aromatic substitution reactions of monosubstituted Benzenes

- Alkyl groups and groups with lone pairs (electron donating groups) direct new groups to ortho-, para-positions and speed-up the reaction (i.e. o & p directors and activating groups).

- Halogens direct new groups to ortho-, para- positions but they slow down the reaction (i.e. halogens are o & p directors and deactivating groups).

- Electron withdrawing groups such as nitro, nitrile, and carbonyl direct new groups to the meta-position and slow the reaction down (i.e. i.e. m directors and deactivating groups).
Orientation effects of substituents in electrophilic aromatic substitution reactions of monosubstituted Benzenes

<table>
<thead>
<tr>
<th>Ortho, para directors</th>
<th>Meta directors</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH, -OR</td>
<td>-NO₂</td>
</tr>
<tr>
<td>-NH₂, -NHR, -NR₂</td>
<td>-SO₃H</td>
</tr>
<tr>
<td>-C₆H₅</td>
<td>-COOH, -COOR</td>
</tr>
<tr>
<td>-CH₃, -R (alkyl)</td>
<td>-CHO, -COR</td>
</tr>
<tr>
<td>-F, -Cl, -Br, -I</td>
<td>-CN</td>
</tr>
</tbody>
</table>

OH

HNO₃ / H₂SO₄

o-Nitrophenol

53 %

OH

NO₂

m-Nitrophenol

47 %

NO₂

SO₃ / H₂SO₄

m-Nitrobezenesulfonic acid
Thank You for your kind attention!

Questions