9.1 Introduction

In the previous Unit, we have learnt about Active Methylene compounds. So far our study of the aromatic cyclic systems was restricted to only one aromatic ring. In this unit, we will study aromatic compounds having more than one aromatic ring. Such compounds are known Polynuclear Aromatic Hydrocarbons (PAHs). First we will learn the basic concept of polynuclear aromatic hydrocarbons followed by their properties and uses. In the next part of this unit, we will discuss the nomenclature of the derivatives of two most common polynuclear aromatic hydrocarbons i.e. naphthalene and anthracene.

You have already learnt about the aromaticity in Unit-19 of the course BCHCT-133. In this Unit we will not discuss aromaticity of these compounds in detail but we will recall Hückel’s rule and applied to naphthalene and
9.2 POLYNUCLEAR AROMATIC HYDROCARBONS: AN INTRODUCTION

Polynuclear aromatic hydrocarbon is an assembly of more than one aromatic ring in the molecule. Depending upon the mode of attachment of various rings, the polynuclear aromatic hydrocarbons may be classified into two broad classes: (i) isolated benzenoid hydrocarbons, and (ii) condensed or fused benzenoid hydrocarbons.

i) Isolated Benzenoid Hydrocarbons:
In isolated systems, two or more rings are joined to each other directly or through a carbon chain. Some of these are biphenyl, diphenylmethane and triphenylmethane. The structure of these compounds are given below.

<table>
<thead>
<tr>
<th>Biphenyl</th>
<th>Diphenylmethane</th>
<th>Triphenylmethane</th>
</tr>
</thead>
</table>

ii) Condensed or Fused Benzenoid Hydrocarbon:
The condensed or fused benzenoid hydrocarbons are those in which two or more benzene rings are fused together in such a way that each pair of rings shares two carbons. These include compounds like naphthalene, anthracene, phenanthrene etc.

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>Anthracene</th>
<th>Phenanthrene</th>
</tr>
</thead>
</table>

The condensed polynuclear aromatic hydrocarbons are by far the larger and the more important groups. A large number of these compounds have been found to possess carcinogenic (cancer producing) activity. In this unit, we will discuss the chemistry of naphthalene and anthracene only.

SAQ 1
What are different types of polynuclear aromatic hydrocarbons?
9.3 SOURCES

Polycyclic aromatic hydrocarbons are a group of semi-volatile organic compounds that are present in natural sources such as bitumen, coal, crude oil, wood, garbage and gasoline. These compounds are mainly emitted from exhaust fumes of vehicles, including automobiles, railways, ships, aircrafts, and other motor vehicles.

Polycyclic aromatic hydrocarbons can also be produced geologically, when organic sediments are chemically transformed into fossil fuels such as oil and coal. The rare minerals idrialite, curtisite, and carpathite consist almost entirely of polycyclic aromatic hydrocarbons, that originated from such sediments that were extracted, processed, separated, and deposited by very hot fluids. They may result from the incomplete combustion of organic matter in natural wildfires. Perylene can also be generated in anaerobic sediments from existing organic materials.

SAQ 2

Fill in the following blanks:

i) Polycyclic aromatic hydrocarbons are present in------ sources.

ii) ________can also be generated in anaerobic sediments from existing organic material.

iii) Polycyclic aromatic hydrocarbons are emitted from exhaust fumes of ________.

9.4 PROPERTIES AND USES

Generally polycyclic aromatic hydrocarbons have high melting point, boiling point and low vapor pressure. These are nonpolar and lipophilic compounds. These compounds are hydrophobic and are generally insoluble in water. The larger members are also poorly soluble in organic solvents and in lipids. The chemical stability, low water solubility, and high absorption capacity of polycyclic aromatic hydrocarbons contribute greatly to their persistence in the environment.

Among the polycyclic aromatic hydrocarbons, naphthalene is a white crystalline solid. Naphthalene is a nonpolar compound and insoluble in polar solvents like water. Naphthalene is soluble in carbon tetrachloride, chloroform carbon disulfide, methanol, ethanol, diethylether benzene and toluene. Naphthalene is a solid that sublimes at standard atmospheric temperature with the sublimation point at around 355 K.

Naphthalene is used as an insecticide, in the form of naphthalene balls for protecting woolen clothings from insects. Polynuclear aromatic hydrocarbons are commonly used in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries. These compounds are also used in manufacture of pigments, dyes, plastics and pesticides. NASA’s Spitzer Space Telescope and James Webb Telescope include instruments for obtaining both images and spectra of light.
emitted by Polynuclear aromatic hydrocarbons associated with star formation. These images can trace the surface of star-forming clouds in our own galaxy or identify star forming galaxies in the distant universe.

**Effect on Human health**

Polycyclic aromatic hydrocarbons are carcinogenic in nature. Benzopyrene is the most common to cause cancer. Increased incidences of lung, skin and bladder cancers are associated with occupational exposure to polycyclic aromatic hydrocarbons. Long-term exposure to polycyclic aromatic hydrocarbons may cause eye cataracts or damage kidney and liver. Repeated skin contact to the naphthalene can result in redness and inflammation of the skin.

**SAQ 3**

Write “T” for true and “F” for false in the boxes for the following statements.

i) Polycyclic aromatic hydrocarbons have lower melting point.  
ii) Polycyclic aromatic hydrocarbons are polar in nature.  
iii) Smaller members of Polycyclic aromatic hydrocarbons are soluble in water.  
iv) Polycyclic aromatic hydrocarbons are carcinogenic in nature.  
v) Repeated skin contact to the naphthalene can result in inflammation of the skin.

**9.5 NOMENCLATURE OF NAPHTHALENE AND ANTHRACENE DERIVATIVES**

You may recall that in benzene the numbering starts at the position of a substituent, but in these compounds the numbering is fixed by convention and does not change with the position of a substituent. Various positions of naphthalene are numbered as shown below:

As indicated above we do not give any number to fussed carbon atoms. If you rotate the molecule upside down you will notice that positions 1 and 4 are same and positions 5 and 8 are same. Similarly positions 2 and 3 are same and positions 6 and 7 are same.
In case of only one substitution, say chlorine, in naphthalene only two isomers are possible i.e. 1-chloronaphthalene (α-chloronaphthalene) and 2-chloronaphthalene (β-chloronaphthalene).

If the rings contains two or more identical substituents the prefixes di, tri, etc are used, e.g. dichloro or trichloro i.e.

What name will you give to the following compound?

Can we call it 1,3,4-trichloronaphthalene? No. As mentioned above, here position 2 and 3 are same. Actually it is 1,2,4-trichloronaphthalene.
If more than one type of atoms or groups is attached, numbering of the compound will remain same but their names are arranged in alphabetical order, as shown below:

![1-bromo-2-chloronaphthalene](image1) ![2-bromo-1-chloronaphthalene](image2)

Now a question arises which is the 1-position in following compound? Will it be 1-chloro-4-nitronaphthalene or 4-chloro-1-nitronaphthalene? In such cases there is a IUPAC rule i.e.:

![1-chloro-4-nitronaphthalene](image3)

The priorities for selection of principal functional group are given below in the order of decreasing precedence. The order is: carboxylic acid, sulphonic acid, ester, acid anhydride, acyl halide, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, imine, alkyne, alkene, ethers, halides, nitro.

In this example nitro group comes after halogen (chlorine). Therefore, the name of this compound will be 1-chloro-4-nitronaphthalene not 4-chloro-1-nitronaphthalene.

Similarly,

![2-bromo-1,4-dichloronaphthalene](image4) ![2-bromo-1-chloro-4-nitronaphthalene](image5)

Now take the example of –OH substituted naphthalene.

![1-naphthol](image6)

According to IUPAC nomenclature the name of above compound is 1-naphthol. Here naphthol is considered as a parent hydrocarbon, when halogen or any other groups are substituted to naphthol, they are named as a prefix of naphthol. For example:
Now let us discuss nomenclature of anthracene. Various positions of anthracene are numbered as shown below:

In case of only one substitution in anthracene, say chlorine, there is possibility of three isomers, i.e. 1-chloroanthracene, (\(\alpha\)-chloroanthracene), 2-chloroanthracene (\(\beta\)-chloroanthracene), and 9-chloroanthracene (\(\gamma\)-chloroanthracene).

Like naphthalene, if you rotate the molecule of anthracene upside down you will notice that positions 1 and 4 are same, positions 5 and 8 are same and positions 9 and 10 are same. Similarly positions 2 and 3 are same and position 6 and 7 are same.

Like naphthalene, if the rings contain two or more identical substituents the prefixes di, tri, etc are used.

Now take the example of disubstituted anthracene:

As mentioned above if more than one type of atoms or groups is attached to the anthracene their names are arranged in alphabetical order, as shown below:
2-chloro-4-methylantracene

2-chloro-4-methyl-6-nitroanthracene

SAQ 4

Give IUPAC name of the following compounds.

i) 

ii) 

iii) 

iv) 

9.6 AROMATICITY OF POLYNUCLEAR HYDROCARBONS

A hydrocarbon can be an aromatic compound if it follows the Hückel's Rule. Details of this rule you have studied in Unit 19 of Course BCHCT-133. Here we will only recall some important points of Hückel's Rule.

9.6.1 Hückel’s Rule

According to Hückel’s Rule, a compound can be aromatic if it has the following distinct properties:
a compound must contain \((4n + 2)\) \(\pi\) electrons, where “\(n\)” is any number i.e. 1, 2, 3, 4……. This means that only the ring with 2, 6, 10, 14,…… \(\pi\) electrons may be aromatic.

the compound must be co-planer.

In this Unit we will take the examples of naphthalene and anthracene.

**Naphthalene**

How can we explain the aromaticity of naphthalene? The naphthalene has 10 \(\pi\) electrons.

\[
\text{No. of } \pi\text{-electrons} = 10
\]

If \(n = 2\)

\[
4 \times 2 + 2 = 10 \pi\text{-electrons}
\]

Here, the Hückel’s rule is followed. It has 10 \(\pi\)-electrons, which are required for a compound to be aromatic. All the carbon atoms of naphthalene are \(sp^2\) hybridised and it is a planar molecule too. It is an excellent example of an aromatic system.

Similarly we can take the example of anthracene.

**Anthracene**

\[
\text{No. of } \pi\text{-electrons} = 14
\]

If \(n = 3\)

\[
4 \times 3 + 2 = 14 \pi\text{-electrons}
\]

Anthracene has 14 \(\pi\)-electrons (Hückel’s no.) and all the carbon atoms of anthracene are \(sp^2\) hybridised and it is a planar molecule. Therefore, it is also an aromatic compound.

**SAQ 5**

Anthracene is an aromatic compound. Explain.

### 9.7 REACTIONS OF NAPHTHALENE

Like, benzene, naphthalene undergoes usual electrophilic substitution reactions, oxidation and reduction. The naphthalene is more reactive towards these reactions than benzene. In this Unit we will concentrate mainly on reactions of naphthalene. Some important reactions of naphthalene are given in Table 9.1.
### Table: 9.1 Reactions of Naphthalene

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Electrophilic substitution</td>
</tr>
<tr>
<td>a)</td>
<td>Nitration</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Nitration Reaction" /></td>
</tr>
<tr>
<td>b)</td>
<td>Halogenation</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Halogenation Reaction" /></td>
</tr>
<tr>
<td>c)</td>
<td>Sulphonation</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Sulphonation Reaction" /></td>
</tr>
<tr>
<td>d)</td>
<td>Friedel-Crafts alkylation</td>
</tr>
<tr>
<td></td>
<td><img src="image" alt="Friedel-Crafts Alkylation Reaction" /></td>
</tr>
<tr>
<td>e)</td>
<td>Friedel-Crafts acylation</td>
</tr>
<tr>
<td>i)</td>
<td><img src="image" alt="Friedel-Crafts Acylation Reaction i" /></td>
</tr>
<tr>
<td>ii)</td>
<td><img src="image" alt="Friedel-Crafts Acylation Reaction ii" /></td>
</tr>
<tr>
<td>2.</td>
<td>Oxidation</td>
</tr>
<tr>
<td>a)</td>
<td><img src="image" alt="Oxidation Reaction a" /></td>
</tr>
<tr>
<td>b)</td>
<td><img src="image" alt="Oxidation Reaction b" /></td>
</tr>
</tbody>
</table>
Let us discuss each reaction in little detail.

9.7.1 Electrophilic Substitution Reactions

Like benzene, polynuclear hydrocarbons also undergo electrophilic substitution reactions i.e. Nitration, Halogenation, Sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation. The first substituent goes to 1-position (α-position); that means, the 1-position is more reactive than the 2-position (β-position). You can ask why it is so? We will explain this in section 9.7.2.

a) Nitration of Naphthalene

Nitration of naphthalene at room temperature occurs almost exclusively at 1-postion, giving 1-nitronaphthalene. This reaction does not require any catalyst.

\[
\text{Naphthalene} + \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{1-nitronaphthalene}
\]

b) Halogenation of Naphthalene

Chlorination and bromination of naphthalene in presence of FeCl₃ yield only one substituted product. 1-chloronaphthalene can form in presence of FeCl₃. Bromination does not required any Lewis acid.

\[
\text{Naphthalene} + \text{Cl}_2 \text{FeCl}_3 \rightarrow \text{1-chloronaphthalene}
\]

c) Sulfonation of Naphthalene

Reaction of naphthalene with sulfuric acid at 355 K, yields 1-naphthalenesulfonic acid as major product. If same reaction is carried out at a higher temperature (435K) it will give 2-naphthalenesulfonic acid as a major product. 1-naphthalenesulfonic acid is less stable than the 2-naphthalenesulfonic

\[
\text{Naphthalene} + \text{H}_2\text{SO}_4 \rightarrow \text{1-naphthalenesulfonic acid}
\]
acid because of repulsions between the $-\text{SO}_3\text{H}$ group and the hydrogen at 8-position.

\[
\text{Naphthalene} + \text{H}_2\text{SO}_4 \xrightarrow{355 \, \text{K}} \text{1-naphthalenesulfonic acid (Major product)}
\]

\[
\text{Naphthalene} + \text{H}_2\text{SO}_4 \xrightarrow{435 \, \text{K}} \text{2-naphthalenesulfonic acid (Major product)}
\]

d) Friedel-Crafts Alkylation

Reaction of naphthalene with alkyl halide in presence of $\text{AlCl}_3$ gives two different isomers i.e. 1-methylnaphthalene and 2-methylnaphthalene. The percentage of the two products depends on the size of the reagent.

\[
\text{Naphthalene} + \text{CH}_3\text{I} \xrightarrow{\text{AlCl}_3} \text{1-methylnaphthalene} + \text{2-methylnaphthalene}
\]

e) Friedel-Crafts Acylation

Naphthalene undergoes Friedel-Crafts acylation in the presence of acetyl chloride and aluminium chloride to give 1-acetonaphthalene and 2-acetonaphthalene. The orientation of substitution depends on the solvent used, as shown below:

\[
\text{Naphthalene} + \text{CH}_3\text{CCL} \xrightarrow{\text{AlCl}_3} \text{1-Accetonaphthalene} \quad \text{Solvent, } \text{C}_2\text{H}_4\text{Cl}_4
\]

\[
\text{Naphthalene} + \text{CH}_3\text{CCL} \xrightarrow{\text{AlCl}_3} \text{2-Accetonaphthalene} \quad \text{Solvent, } \text{C}_6\text{H}_5\text{NO}_2
\]

9.7.2 Mechanism of Electrophilic Substitution Reactions of Naphthalene:

Polynuclear aromatic hydrocarbons are more reactive towards electrophilic attach than benzene. The mechanism for electrophilic substitution of naphthalene is similar to that of electrophilic substitution of benzene.
The first substituent goes to 1-position (α-position); that means, the 1-position is more reactive than the 2-position (β-position). You can ask why it is so? To understand this, let us examine the resonance structures of the two intermediate carbocations resulting from the respective attacks.

Substitution at 1-Position

Following are the Resonance structures of carbocation formed during attack of electrophile on 1-carbon.

Substitution at 2-Position

Following are the Resonance structures of carbocation formed during attack of electrophile on 2-carbon.

In both cases, the positive charge can be distributed to five different positions, but these carbocations are not equivalent in energy. In the first case, the first two structures have their benzenoid ring intact and are consequently more stable than the remaining three structures. In the second case, only one resonance structure has a benzenoid ring intact. The resulting resonance hybrid has higher energy in the second case than in the first case. The intermediate carbocation in the first case in more stabilised by resonance, and its transition state is of lower
energy. For this reason the intermediate in the first case is formed faster and hence 1-position is more reactive.

9.7.3 Oxidation of Naphthalene

Benzene is not easily oxidised however naphthalene can be easily oxidised to products in which aromaticity is retained. For example Phthalic anhydride, which has commercial importance, can be synthesis by oxidation of naphthalene in good yield. This reaction probably proceeds through the formation of phthalic acid.

\[
\begin{align*}
\text{V}_2\text{O}_5 & \xrightarrow{\Delta} \text{Phthalic acid} \\
\text{COOH} & \xrightarrow{-\text{H}_2\text{O}} \text{Phthalic anhydride}
\end{align*}
\]

Under controlled conditions, naphthalene is oxidized to 1,4-naphthoquinone, but the yield is usually low.

\[
\begin{align*}
\text{CH}_3\text{COOH}/\text{Cr}_2\text{O}_3 & \xrightarrow{285-290 \text{K}} \text{1,4-naphthoquinone}
\end{align*}
\]

9.7.4 Reduction of Naphthalene

Unlike benzene, naphthalene can be partially hydrogenated by reducing agents. Naphthalene can be reduced with sodium and ethanol.

\[
\begin{align*}
\text{Na, C}_2\text{H}_5\text{OH} & \xrightarrow{\text{No reaction}} \\
\text{Na, C}_2\text{H}_5\text{OH} & \xrightarrow{350 \text{ K}} \text{1,4-dihydronapthalene}
\end{align*}
\]

\[
\begin{align*}
\text{Na, C}_2\text{H}_5\text{OH} & \xrightarrow{305 \text{ K}} \text{1,2,3,4-tetrahydronapthalene (tetralin)}
\end{align*}
\]

The decahydronaphthalene (decalin) is obtained by complete hydrogenation of naphthalene only by vigorous catalytic hydrogenation.
SAQ 6

Give the product of the following reactions.

i) \[ \text{+ CH}_3\text{I} \rightarrow \text{AlCl}_3 \]

ii) \[ \text{+ HNO}_3 + \text{H}_2\text{SO}_4 \text{ room temp.} \]

iii) \[ \text{Na, C}_2\text{H}_5\text{OH} \]

iv) \[ \text{CH}_3\text{COOH/Cr}_2\text{O}_3 \text{ 285-290 K} \]

9.8 SUMMARY

In this unit we have explained to you the following points:

- Polynuclear aromatic hydrocarbon (PAHs) is an assembly of more than one benzene ring in the molecule. One is isolated benzenoid hydrocarbon and the other is condensed or fused benzenoid hydrocarbons.
- PAHs are present in natural sources such as, coal, crude oil, wood, garbage and gasoline.
- PAHs are emitted from exhaust fumes of vehicles.
- Generally PAHs have high melting point, boiling point and low vapor pressure.
- PAHs are nonpolar and lipophilic.
- PAHs are commonly used in pharmaceuticals, agricultural products and photographic products.
- NASA’s Spitzer Space Telescope and James Webb Telescope include instruments for obtaining both images and spectra of light emitted by polynuclear aromatic hydrocarbon associated with star formation.
- The numbering of these compounds is fixed by convention and does not change with the position of a substituent.
- PAHs follow Hückel’s Rule and hence are aromatic.
Like, benzene, naphthalene undergoes usual electrophilic substitution reactions, oxidation and reduction.

Naphthalene is generally white crystalline solid with the sublimation point at around 355 K.

Naphthalene is a nonpolar compound and insoluble in polar solvents like water. Naphthalene is soluble in carbon tetrachloride, chloroform, carbon disulfide, methanol, ethanol, diethylether benzene and toluene.

9.9 TERMINAL QUESTIONS

1. What are isolated benzenoid hydrocarbons? Give an example.

2. Give the numbering of anthracene

3. What is Hückel's Rule?

4. Draw the resonance structure of carbocation formed during nitration at 1-carbon of naphthalene.

5. Give the IUPAC name of the following compounds.

   a) \[
   \text{OH}
   \]

   b) \[
   \text{OH}
   \]

   c) \[
   \text{OH}
   \]

9.10 ANSWERS

Self Assessment Questions

1. There are two types of polynuclear aromatic hydrocarbons, i.e. i) isolated benzenoid hydrocarbons and ii) condensed or fused benzenoid hydrocarbons.

2. i) natural; ii) Perylene; iii) vehicles

3. i) F; ii) F; iii) F; iv) T and v) T

4. i) 2-Chloronaphthalene; ii) 1,3-dichloronaphthalene; iii) 2-bromo-1,4-dichloronaphthalene; iv) 9,10-dimethylanthracene

5. No. of \(\pi\)-electrons = 14

   If \(n\) = 3

   \(4 \times 3 + 2 = 14\) \(\pi\)-electrons.

   Since 14 is Hückel’s no, it is an aromatic compound.

6. i) 

\[
\begin{align*}
\text{CH}_3 + \text{CH}_3 & \xrightarrow{\text{AlCl}_3} \text{CH}_3 \\
& \xrightarrow{\text{CH}_3} \text{CH}_3
\end{align*}
\]
ii) \[
\begin{align*}
\text{ } + \text{HNO}_3 + \text{H}_2\text{SO}_4 \quad \text{room temp.}
\end{align*}
\]

iii) \[
\begin{align*}
\text{Na, C}_2\text{H}_5\text{OH}
\end{align*}
\]

iv) \[
\begin{align*}
\text{CH}_3\text{COOH/Cr}_2\text{O}_3 \\
285-290 \text{K}
\end{align*}
\]

Terminal Questions

1. In isolated systems, two or more rings are joined to each other directly or through carbon chain. Example

2. 

3. According to Huckel’s rule, a compound must contain \((4n + 2)\) \(\pi\) electrons, where \(n\) is any number ie. 1,2,3,4,……. This means that only the ring with 2, 6, 10, 14,……. \(\pi\) electrons may be aromatic

4. 

5. a) \[
\begin{align*}
\text{1-naphthol}
\end{align*}
\]

b) \[
\begin{align*}
\text{2-naphthol}
\end{align*}
\]

c) \[
\begin{align*}
\text{2-naphthol}
\end{align*}
\]