(A) Fused Ring Hydrocarbons

- **Naphthalene, anthracene** and **phenanthrene** are obtained from coal tar, naphthalene being the most abundant (5%) of all constituents of coal tar.
- Uses: moth balls, which contain naphthalene, are used as insect repellants (naphthalene is very volatile).
- Many synthetic dyes contain naphthalene moiety.

\[ \text{Naphthalene, Anthracene, Phenanthrene} \]

Aromatic character of naphthalene, anthracene and phenanthrene:
Naphthalene, anthracene and phenanthrene are classified as aromatic because of their properties, which resemble those of benzene.

(i) Experimental point of view

- Undergo electrophilic substitution reactions.
- Like benzene, they are unusually stable as indicated from their low heats of hydrogenation and combustion.
- As the number of aromatic rings increases, the resonance energy per ring decreases, this means the larger compounds have less aromatic stability, and as a result they start to display more (alkene) reactivity.
  - Resonance energy of naphthalene = 61 kcal mol\(^{-1}\)
  - Resonance energy of anthracene = 84 kcal mol\(^{-1}\)
  - Resonance energy of phenanthrene = 92 kcal mol\(^{-1}\)
  - Resonance energy of benzene = 36 kcal mol\(^{-1}\)
(ii) Theoretical point of view:

They have the structure required for aromatic compounds

- Flat ($sp^2$-hybridized); cyclic
- $\pi$-cloud above and below the plane due to ???
- Hückel’s rule ???

A cyclic ring molecule follows Hückel's rule when the number of its $\pi$-electrons equals $4n+2$ where $n$ is zero or any positive integer

i.e. $4n+2 = \text{No. of } \pi\text{-electrons}$

- For $n = 0$, The No. of $\pi$-electrons is 2 $\pi$-electrons
- For $n = 1$, The No. of $\pi$-electrons is 6 $\pi$-electrons (e.g. benzene)
- For $n = 2$, The No. of $\pi$-electrons is 10 $\pi$-electrons

Resonance structures and bond lengths of naphthalene, anthracene and phenanthrene:

There is $n+1$ principal resonance structures for polynuclear aromatic hydrocarbon containing $n$ benzene rings fused together in a linear manner.

The different carbon-carbon bond lengths reveal the decreased aromaticity of fused polynuclear aromatic hydrocarbons. Phenanthrene is an angular polynuclear aromatic hydrocarbon.

- As the number of fused rings increases, the number of resonance structures increases. Naphthalene is a hybrid of three resonance structures whereas benzene is a hybrid of two.
Anthracene is a resonance hybrid of mainly 4 resonance structures.

<table>
<thead>
<tr>
<th>Q</th>
<th>Answer</th>
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<tbody>
<tr>
<td>&gt; How many isomers for monosubstitution of naphthalene ($C_8H_8X$)?</td>
<td>2 isomers</td>
</tr>
<tr>
<td>&gt; How many isomers for monosubstitution of anthracene ($C_{14}H_{10}X$)?</td>
<td>3 isomers</td>
</tr>
<tr>
<td>&gt; How many isomers for monosubstitution of phenanthrene ($C_{14}H_{12}X$)?</td>
<td>5 isomers</td>
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<tr>
<td>&gt; How many isomers for disubstitution of naphthalene ($C_8H_6X_2$)?</td>
<td>10 isomers</td>
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<tr>
<td>&gt; How many isomers for disubstitution of naphthalene ($C_8H_6XY$)?</td>
<td>14 isomers</td>
</tr>
<tr>
<td>&gt; How many isomers for disubstitution of anthracene ($C_{14}H_8X_2$)?</td>
<td>15 isomers</td>
</tr>
<tr>
<td>&gt; How many isomers for disubstitution of phenanthrene ($C_{14}H_8X_2$)?</td>
<td>25 isomers</td>
</tr>
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</table>

(I) Naphthalene

Naphthalene is the simplest fused aromatic compound, and is comprised of two fused benzene rings.
Naphthalene can be represented by 3 different Kekulé structures, but is more commonly drawn with the circle notation.

Structure elucidation of naphthalene

1- Molecular Formula: \( \text{C}_8\text{H}_8 \)

2- Oxidation of naphthalene gives phthalic acid

3- Naphthalene \( \text{\textit{nitration}} \) Nitronaphthalene \( \text{\textit{oxygenation}} \) Nitrophthalic acid

So nitro group is present in benzene ring

4- Naphthalene \( \text{\textit{nitration}} \) Nitronaphthalene \( \text{\textit{reduction}} \) Aminonaphthalene \( \text{\textit{oxygenation}} \) Phthalic acid

The benzene ring in phthalic acid produced by oxidation of aminonaphthalene is not the same ring as that obtained by oxidation of nitronaphthalene.
The structure of naphthalene is confirmed by method of its analysis:

1- Howarth method

Other way of cyclization

- The reaction occurs if R is o- or p- directing group such as NH₂, NHR, OH, OR, R, halogen.
- If R is m- directing group (e.g. NO₂, CN, COOH, COCH₃, SO₃H) no reaction occur.
- The above reaction gives β-substituted naphthalene.
Synthesis of 1-alkyl naphthalene

\[ \text{benzene} \quad + \quad \text{succinic anhydride} \xrightarrow{\text{AlCl}_3} \quad \text{4-oxo-4-phenylbutanoic acid} \xrightarrow{\text{Zn-Hg-HCl}} \quad \text{4-phenylbutanoic acid} \]

\[ \text{conc. H}_2\text{SO}_4 \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{1-tetralone} \xrightarrow{1) \text{RMgX}} \xrightarrow{2) \text{HOH}} \quad \text{1-alkyl naphthalene} \]

2- From β-benzylidene – propenoic acid

\[ \text{β-Benzylidene-3-propenoic acid} \xrightarrow{\text{conc. H}_2\text{SO}_4} \xrightarrow{\text{H}_2\text{O}} \quad \text{naphthalene} \]

Chemical Reactions of naphthalene

1. Reduction

\[ \text{Naphthalene} \xrightarrow{\text{Na, EtOH}} \quad 1,4-\text{dihydronaphthalene} \]

\[ \text{Naphthalene} \xrightarrow{\text{Na, isoamyl alc.}} \quad \text{1,2,3,4-tetrahydronaphthalene} \]

\[ \text{Naphthalene} \xrightarrow{\text{H}_2, \text{Ni}} \quad \text{Decahydronaphthalene} \]

Decalene
2. Oxidation

Naphthalene → 1,4-naphthoquinone

1) CrO₃, AcOH
2) H₂O/Zn

Naphthalene → Phthalaldehyde

O₂, V₂O₅

Naphthalene → Phthalic anhydride

KMnO₄, H⁺

3. Addition of Cl₂

Naphthalene → 1,4-dichloro-1,4-dihydronaphthalene

Cl₂

Naphthalene → 1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene

excess Cl₂
4. Electrophilic substitution reaction

Q. Naphthalene undergoes electrophilic substitution at position 1 not 2, Explain?

Answer

At position 1; carbocation intermediate stabilize by two resonances. So carbocation is more stable position 1 than 2
Examples of electrophilic substitution