Polynuclear Aromatic Hydrocarbons

Synthesis, Structure, and Reactions of Naphthalene, Anthracene, and Phenanthrene

Polynuclear aromatic hydrocarbons (PAHs) are aromatic compounds containing two or more fused benzene rings. Naphthalene, anthracene, and phenanthrene are important members of this class and show aromatic character, distinct structures, and characteristic chemical reactions.

1. Naphthalene (C■■H■)

Structure:

Naphthalene consists of two fused benzene rings sharing two carbon atoms. It is a planar molecule with 10 π-electrons, satisfying Huckel's rule for aromaticity. Positions 1,4,5,8 are called α-positions, while 2,3,6,7 are β-positions.

Synthesis:

- From coal tar by fractional distillation.
- By heating benzene vapours over red-hot iron or copper.
- By decarboxylation of naphthalene-2-carboxylic acid with soda lime.

Reactions:

- Nitration: Gives mainly α-nitronaphthalene.
- Sulphonation: At low temperature gives α-sulphonic acid; at high temperature gives β-sulphonic acid.
- Halogenation: Occurs readily in presence of catalysts.
- Oxidation: With alkaline KMnO■ gives phthalic acid.

2. Anthracene (C■■H■■)

Structure:

Anthracene consists of three linearly fused benzene rings. The central ring is more reactive due to lower aromatic stabilization. Positions 9 and 10 are the most reactive.

Synthesis:

- From coal tar.
- By Friedel–Crafts reaction followed by cyclization.
- By reduction of anthraquinone.

Reactions:

- Nitration and sulphonation mainly at 9,10-positions.
- Oxidation: Forms anthraquinone.
- Addition reactions: Adds halogens at 9,10-positions.
- Photochemical reaction: Forms dianthracene.

3. Phenanthrene (C■■H■■)

Structure:

Phenanthrene contains three fused benzene rings in an angular arrangement. It is more stable than anthracene due to greater resonance stabilization. Positions 9 and 10 are the most reactive.

Synthesis:

- From coal tar.
- By Haworth phenanthrene synthesis.
- By cyclization of suitable biphenyl derivatives.

Reactions:

- Electrophilic substitution mainly at 9,10-positions.
- Oxidation: Gives phenanthraquinone.
- Nitration and sulphonation under controlled conditions.
- Less reactive towards addition reactions compared to anthracene.