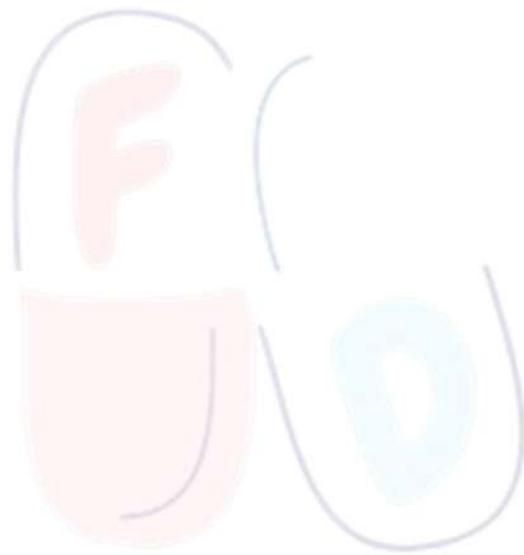


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# PHARMACEUTICAL ORGANIC CHEMISTRY - II

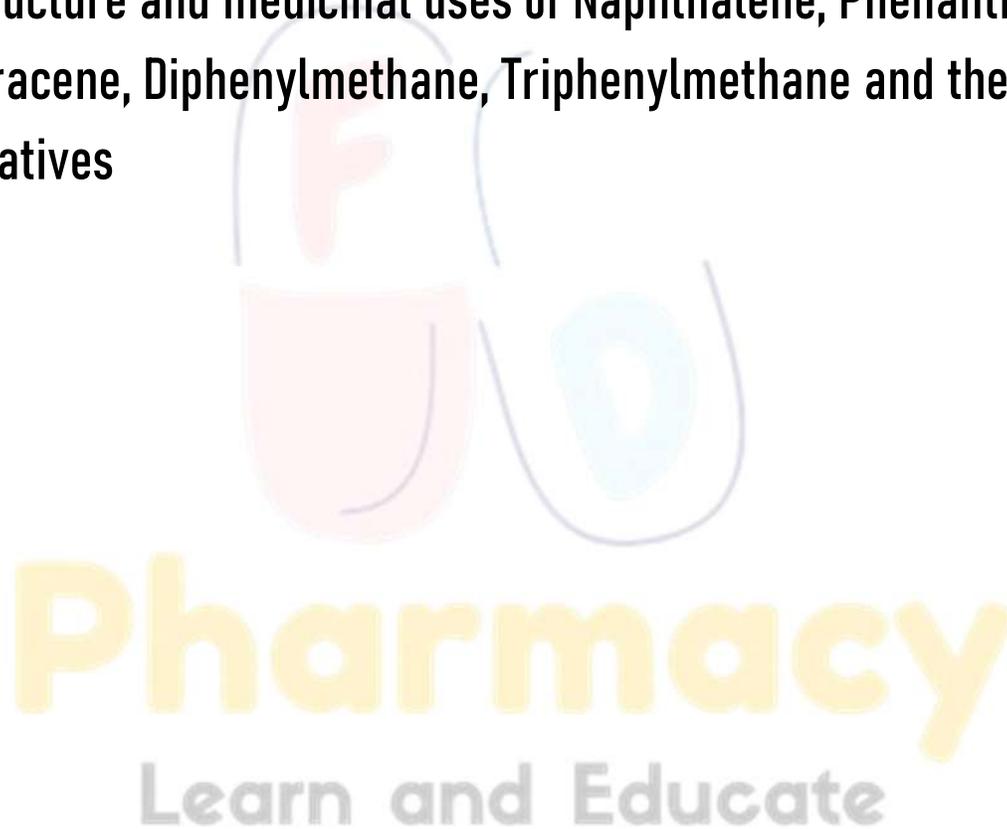
## UNIT 4

TOPIC :

- **Polynuclear hydrocarbons:**

- a. Synthesis, reactions

- b. Structure and medicinal uses of Naphthalene, Phenanthrene, Anthracene, Diphenylmethane, Triphenylmethane and their derivatives



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## Polynuclear Hydrocarbons

- Polynuclear hydrocarbons belong to the class of aromatic hydrocarbons that contain multiple aromatic rings made up entirely of carbon and hydrogen atoms.
- These rings may be either fused together (sharing common carbon atoms) or isolated (separated by linkages).
- They are also known as Polycyclic Aromatic Hydrocarbons (PAHs).

## Types of Polynuclear Hydrocarbons

Polynuclear hydrocarbons are mainly divided into two types:

### ① Isolated Ring Compounds

- In these compounds, aromatic rings are not directly connected to each other.
- The rings are linked via a non-aromatic chain or a single atom.
- These compounds do not share any carbon atoms between the rings.

#### Examples:

- Diphenyl methane  
(Two benzene rings connected through a  $-\text{CH}_2-$  group)
- Triphenyl methane  
(Three benzene rings connected to a central carbon)

**Note:** These are less reactive in electrophilic substitution compared to fused ring systems.

### ② Fused Ring Compounds

- In these compounds, two or more benzene rings are fused, meaning they share one or more carbon atoms.
- The aromatic rings are directly joined and form a continuous  $\pi$ -system.
- These are more stable and highly aromatic in nature.

**Examples:**

- Naphthalene – 2 fused benzene rings
- Anthracene – 3 benzene rings in a straight line
- Phenanthrene – 3 benzene rings in an angular arrangement

These compounds are more reactive toward electrophilic substitution at specific positions.



## Synthesis of Polynuclear Hydrocarbons

### 1. Naphthalene

#### *a) From Coal Tar:*

- Naphthalene is a major constituent of coal tar (5-10%) and can be separated by fractional distillation.

#### *b) Haworth Synthesis:*

- Used for laboratory synthesis.
- Involves Friedel–Crafts acylation and reduction steps.

### 2. Anthracene

#### *a) From Coal Tar:*

- Present in the green oil fraction of coal tar.
- Separated by crystallization.

#### *b) Synthetic Method:*

- Cyclodehydration of o-benzylbenzoic acid gives anthracene.

### 3. Phenanthrene

- Also obtained from coal tar.
- Can be synthesized by Bardhan–Sengupta synthesis.

## Reactions of Polynuclear Hydrocarbons

### 1. Electrophilic Substitution Reactions (EAS):

Like benzene, PNHs undergo substitution reactions rather than addition.

#### *Naphthalene:*

- Reacts faster than benzene.
- Electrophile enters  $\alpha$ -position (1-position) due to resonance stability.
- Reactions:
  - Nitration: Forms 1-nitronaphthalene
  - Sulphonation: Forms 1-naphthalenesulphonic acid
  - Halogenation: Forms 1-halogenonaphthalene

#### *Anthracene:*

- Reactivity is high at 9,10-positions due to stabilization of carbocation.
- Reactions:
  - Nitration: Gives 9-nitroanthracene
  - Addition reactions at 9,10 positions forming dihydro derivatives

#### *Phenanthrene:*

- Reacts at 9-position.
- Reactions:
  - Nitration: Forms 9-nitrophenanthrene
  - Oxidation: Yields phenanthrenequinone

## 2. Oxidation Reactions:

### *Naphthalene:*

- Oxidized with  $\text{KMnO}_4 \rightarrow$  forms phthalic acid

### *Anthracene:*

- Oxidized at 9,10 positions  $\rightarrow$  forms anthraquinone

### *Phenanthrene:*

- Oxidation gives phenanthraquinone

## 3. Reduction Reactions:

### *Naphthalene:*

- With Na in ethanol  $\rightarrow$  forms tetralin (1,2,3,4-tetrahydronaphthalene)

### *Anthracene:*

- With reducing agents  $\rightarrow$  forms 9,10-dihydroanthracene

### *Phenanthrene:*

- Forms dihydrophenanthrene on reduction

## 4. Addition Reactions (less common):

- Reactivity is less due to aromatic stabilization.
- Under pressure or with catalysts, hydrogenation gives partially saturated compounds.

## 5. Other Important Reactions:

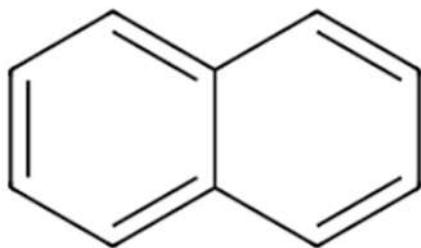
- **Friedel-Crafts Acylation/Alkylation:**
  - Can occur in PNHs, especially in  $\alpha$ -positions of naphthalene.
- **Diels-Alder Reaction:**
  - Anthracene acts as a diene and reacts at 9,10 positions with dienophiles.



## Naphthalene

### Structure:

- Naphthalene has a fused system of two benzene rings.
- Molecular formula:  $C_{10}H_8$



### Medicinal Uses:

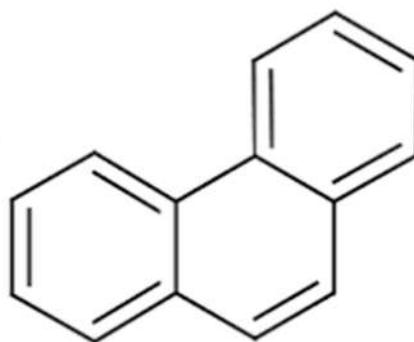
- ✓ **Antiseptic and insecticide** : Used in mothballs to repel insects.
- ✓ **Antifungal agent** : Used in some formulations for skin infections.
- ✓ **Intermediate in drug synthesis** : Used to prepare naphthylamines, which are precursors to antihistamines, antimalarials, and dyes.

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## Phenanthrene

### Structure:

- Phenanthrene has a three-ring angular fused structure.
- Molecular formula:  $C_{14}H_{10}$



### Medicinal Uses:

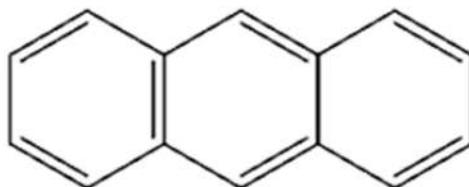
- ✓ **Backbone structure of steroids:** Phenanthrene nucleus is found in morphine, steroids, and cardiac glycosides.
- ✓ Used in synthesis of drugs with anti-inflammatory and antitumor activity.
- ✓ Precursor to phenanthroline, used in complexation and antimicrobial studies.

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## Anthracene

### Structure:

- Anthracene has a linear arrangement of three benzene rings.
- Molecular formula:  $C_{14}H_{10}$



Anthracene

### Medicinal Uses:

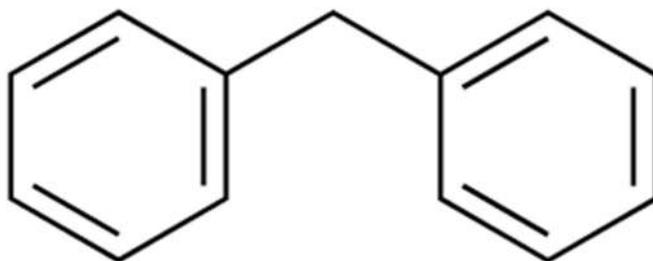
- ✓ Used in the manufacture of anthraquinone derivatives, like:
  - Aloe-emodin
  - Chrysophanol
- ✓ These are active constituents in laxatives like senna and rhubarb.
- ✓ Some derivatives show antiviral and anticancer activities.

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## Diphenylmethane

### Structure:

- Consists of two benzene rings connected through a CH<sub>2</sub> (methylene) bridge.
- Molecular formula: C<sub>13</sub>H<sub>12</sub>



### Medicinal Uses:

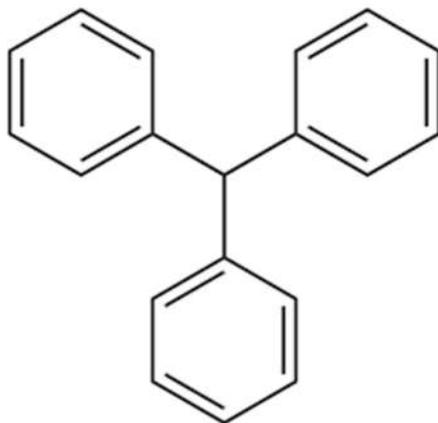
- ✓ Backbone of several antihistamines like:
  - Diphenhydramine (Benadryl)
- ✓ Found in:
  - Antiallergics
  - Antitussives
  - Sedatives
- ✓ Diphenylmethane derivatives are also used as antiemetics (e.g., meclizine).

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## Triphenylmethane

### Structure:

- Contains three phenyl rings attached to a central carbon atom (C).
- Molecular formula:  $C_{19}H_{16}$



### Medicinal Uses:

- ✓ Parent structure for triphenylmethane dyes:
  - Malachite green
  - Crystal violet
- ✓ These dyes possess antibacterial and antifungal properties.
- ✓ Used as:
  - Topical antiseptics
  - Biological stains in histopathology and microbiology.

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