

Study of different classes of organic compounds

B.Sc Chemistry(Part-III)

organic chemistry

Paper-VII

Lecture-03

By

Dr. Supriya kumari

J.L.N college,Dehri-on-Sone(Rohtas)

V.K.S.U,Ara

supriyachemu@gmail.com

Polynuclear aromatic hydrocarbons

- Sometimes referred as polyaromatic hydrocarbons (PAHs) and polycyclic aromatic hydrocarbon
- Organic compounds containing only carbon and hydrogen atoms
- Multiple aromatic rings (electrons are delocalized in organic ring)
- Hydrocarbon made up of fused aromatic ring molecules
- Usually exist as colorless, white, or pale yellow-green solids.
- Made by fusing two or more benzene rings
- Uncharged, non-polar molecules.

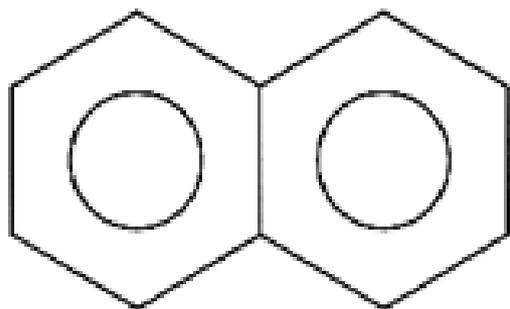
Occurance:

A class of chemicals that occur naturally in coal, crude oil, and gasoline.

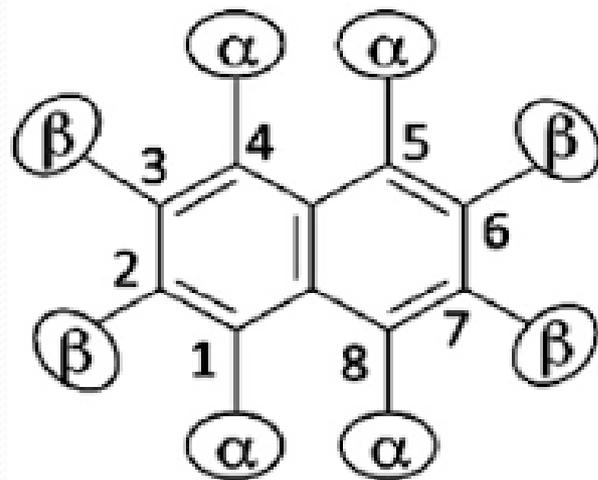
Produced by thermal decomposition when coal, oil, gas, wood, garbage, and tobacco are burned.

Naphthalene C₁₀H₈

- The simplest chemicals naphthalene, has two fused aromatic rings or bicyclic
- White crystalline solid
- Highly volatile, solid polycyclic hydrocarbon
- It has strong mothball odor.
- Obtained from either coal tar or petroleum distillation
- Flammable and potentially explosive



Naphthalene
C₁₀H₈



Physical characteristics

- **Molecular weight:** 128.1705 g/mol
- **Melting point:** 80.26 °C
- **Boiling point:** 218 °C
- **Formula:** C₁₀H₈
- **Density:** 1.14 g/cm³
- **Molecule point group** D_{2h}

Uses

- Used mainly as a precursor to other chemicals.
- Primarily used for manufacture phthalic anhydride(made from *o*-xylene)
- Used in moth repellents and **mothballs** (foridden in china)
- Used for manufacturing medicines and resin
- Used for making dyes(azo), plastics, and pesticides and insecticides (insect killing chemicals) like 1-naphthyl-*N*-methylcarbamate *carbaryl*
- Useful agrichemicals include naphthoxyacetic acids.

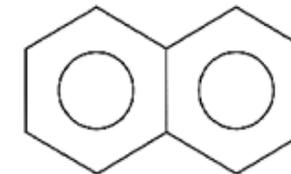
Laboratory uses

- Molten naphthalene provides an excellent solubilizing medium for poorly soluble aromatic compounds..

- Naphthalene is an aromatic benzene unit bonded to a diene
- Not extensively conjugated to it (at least in the ground state), which is consistent with two of its three resonance structures.

Naphthalene molecule is **aromatic** because it has five C=C (each having two pi electrons) in the closed loop

It obey Huckel's rule ($n=2$).

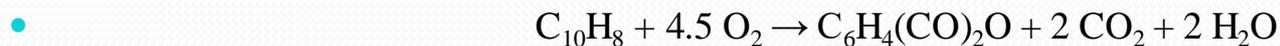


Naphthalene
 $C_{10}H_8$

Naphthalene is derived from coal tar

Oxidation and Reduction

- Oxidation with O₂ in the presence of vanadium pentoxide as catalyst gives phthalic anhydride



This reaction is the basis of the main use of naphthalene.

- Oxidation can also be effected using conventional stoichiometric chromate or permanganate reagents.
- Naphthalene forms the dark blue-green radical anion salts such as sodium naphthalenide with alkali metals,

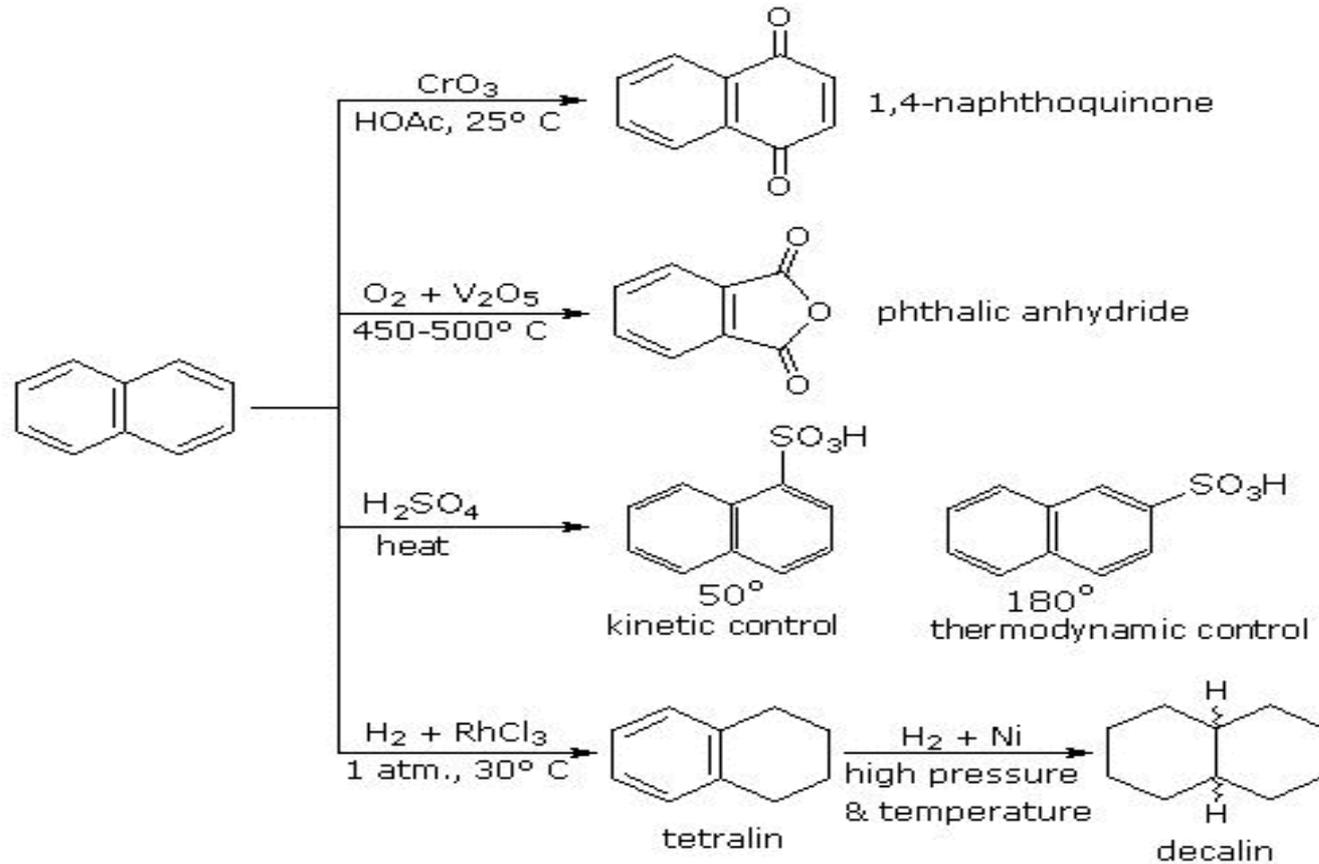


The naphthalenide salts are strong reducing agents.

- Naphthalene can be hydrogenated under high pressure in the presence of metal catalysts to give 1,2,3,4-tetrahydronaphthalene(C₁₀H₁₂), also known as tetralin.

Further hydrogenation yields decahydronaphthalene or decalin (C₁₀H₁₈).

Some Reactions of Naphthalene

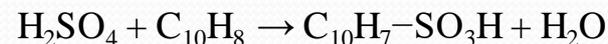


Reactions with electrophiles:

- In electrophilic aromatic substitution reactions naphthalene reacts more readily than benzene. For example, chlorination and bromination of naphthalene proceeds without a catalyst to give 1-chloronaphthalene and 1-bromonaphthalene, respectively. Likewise, whereas both benzene and naphthalene can be alkylated using Friedel–Crafts reactions Naphthalene can also be easily alkylated by reaction with alkenes or alcohols, using sulfuric or phosphoric acid catalysts.
- In terms of regiochemistry, electrophiles attack at the alpha position. The selectivity for alpha over beta substitution can be rationalized in terms of the resonance structures of the intermediate: For the alpha substitution intermediate, seven resonance structures can be drawn, of which four preserve an aromatic ring. For beta substitution, the intermediate has only six resonance structures, and only two of these are aromatic.

Sulfonation gives the "alpha" product naphthalene-1-sulfonic acid as the kinetic product but naphthalene-2-sulfonic acid as the thermodynamic product. The 1-isomer forms predominantly at 25 °C, and the 2-isomer at 160 °C.

Sulfonation to give the 1- and 2-sulfonic acid occurs readily:



Further sulfonation give di-, tri-, and tetrasulfonic acids.

Molecular geometry

- The molecule is planar, like benzene.
Unlike benzene, the carbon–carbon bonds in naphthalene are not of the same length. X-ray diffraction shows C1–C2, C3–C4, C5–C6 and C7–C8 bonds are about 1.37 Å (137 pm) in length, whereas the other carbon–carbon bonds are about 1.42 Å (142 pm) long.
- The molecule has bilateral symmetry across the plane of the shared carbon pair, as well as across the plane that bisects bonds C2-C3 and C6-C7, and across the plane of the carbon atoms because of this resonance
- There are two sets of equivalent hydrogen atoms:
 - I. The *alpha* positions, numbered 1, 4, 5, and 8,
 - II. The *beta* positions, 2, 3, 6, and 7.

Two isomers are then possible for mono-substituted naphthalenes, corresponding to substitution at an alpha or beta position.

Bicyclo[6.2.0]decapentaene is a structural isomer with a fused 4–8 ring system.

Electrical conductivity

- Pure crystalline naphthalene is a moderate insulator at room temperature, with resistivity of about $10^{12} \Omega \text{ m}$. The resistivity drops more than a thousand fold on melting, to about $4 \times 10^8 \Omega \text{ m}$.
- Both in the liquid and in the solid, the resistivity depends on temperature

Naphthalene derivatives

Naphthalene derivatives includes the following compounds

- Naphthoic acid $C_{11}H_8O_2$
- Naphthoyl chloride $C_{11}H_7ClO$
- 1-Naphthol $C_{10}H_8O$
- 1-Naphthaldehyde $C_{11}H_8O$
- 1-Nitronaphthalene $C_{10}H_7NO_2$
- Fluoronaphthalene $C_{10}H_7F$
- 1-Chloronaphthalene $C_{10}H_7Cl$
- 2-Chloronaphthalene $C_{10}H_7Cl$
- 1-Bromonaphthalene $C_{10}H_7Br$

Anthracene $C_{14}H_{10}$

- **Anthracene** is a solid polycyclic aromatic hydrocarbon (PAH) of formula $C_{14}H_{10}$, consisting of three fused benzene rings.
- It is a component of coal tar.
- Anthracene is noncarcinogenic
- Anthracene is colorless but exhibits a blue (400–500 nm peak) fluorescence under ultraviolet radiation.
- Follow Huckel's rule

Occurrence

Anthracene is generated during combustion processes.

Coal tar, which contains around 1.5% anthracene, remains a major source of this material.

Common impurities are phenanthrene and carbazole.

Physical characteristics

Formula: $C_{14}H_{10}$

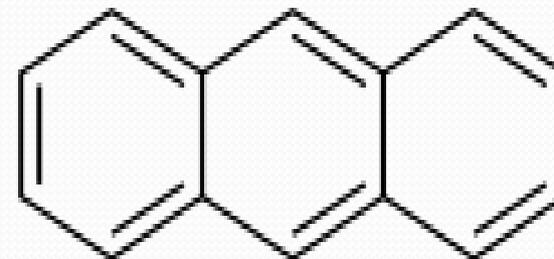
Molar mass: 178.23 g/mol

Boiling point: 340 °C

Density: 1.25 g/cm³

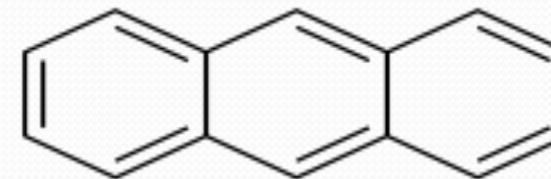
Classifications: Polycyclic aromatic hydrocarbon

Higher classifications: Polycyclic aromatic hydrocarbon



Athracene derivatives

- Derivatives having a hydroxyl group are :
1-hydroxyanthracene and 2-hydroxyanthracene, homologous to phenol and naphthols
- Anthracene may also be found with multiple hydroxyl groups, as in 9,10-dihydroxyanthracene



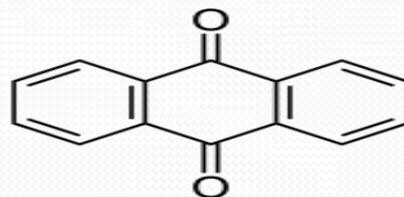
Solubility

Anthracene is insoluble in water

Quite soluble in **carbon** disulfide and somewhat soluble in ethanol, methanol, benzene, chloroform, and other organic solvents.

- **Reaction with electrophiles**

Chemical oxidation with hydrogen peroxide and vanadyl acetylacetonate readily give anthraquinone $C_{14}H_8O_2$



Anthraquinone

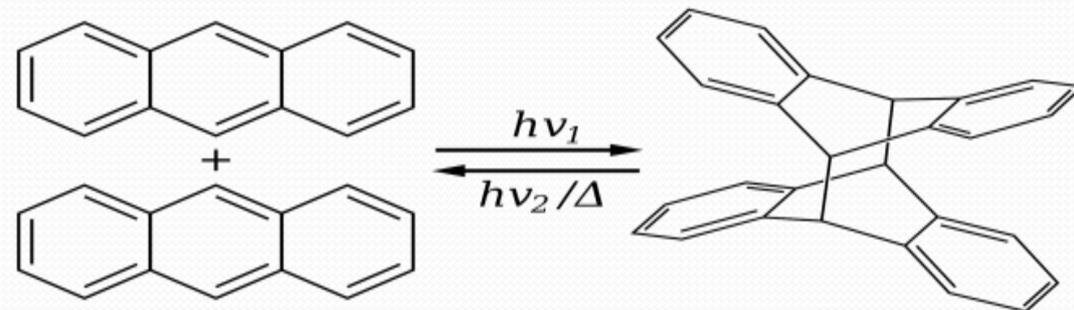
Reduction

Reduction of anthracene with alkali metals yields the deeply colored radical anion salts $M^+[anthracene]^-$ where ($M = Li, Na, K$).

Hydrogenation gives 9,10-dihydroanthracene, preserving the aromaticity of the two flanking rings.

Cycloadditions

Anthracene photodimerizes by the action of UVlight:



Preparation of anthracene.

Pieces of porous pumice stone of a size that will conveniently pass into a combustion tube are added to a paste **prepared** from 100 g of good zinc dust and 30 ml of alcohol. The mixture is stirred to incorporate the pumice and paste.

Phenanthrene $C_{14}H_{10}$

- Phenanthrene is a polycyclic aromatic hydrocarbon composed of three fused benzene rings.
- The name 'phenanthrene' is a composite of phenyl and anthracene.
- It is found in cigarette smoke and is a known irritant, photosensitizing skin to light in its pure form,
- It appears as a colorless, crystal-like solid but can also look yellow.

Physical characteristics

Formula: $C_{14}H_{10}$

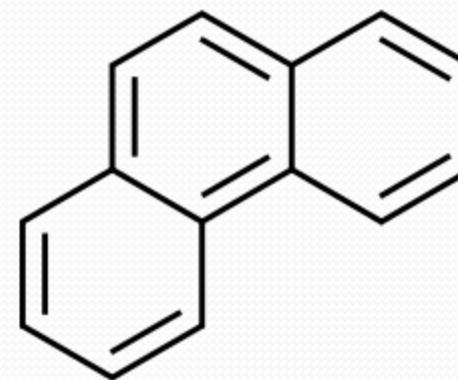
Melting point: 101 °C

Molar mass: 178.23 g/mol

Boiling point: 336 °C

Density: 1.18 g/cm³

Point group: C_{2v}



Natural occurrences

- Ravatite is a natural mineral consisting of phenanthrene. (Ravatite represents a small group of organic minerals)
- It is found in small amounts among a few coal burning sites.

Uses of Phenanthrene

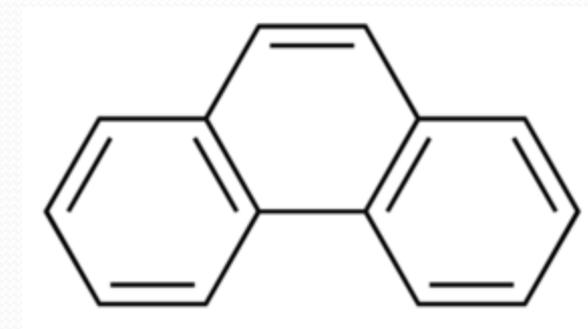
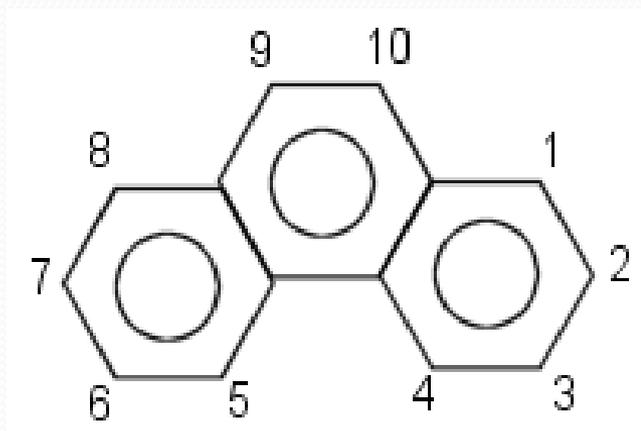
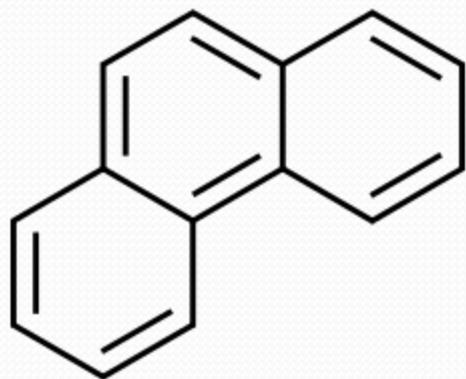
- Used to make dyes, plastics and pesticides, explosives and drugs.
- Used to make bile acids, cholesterol and steroids.
- The compound with a phenanthrene skeleton and nitrogens at the 4 and 5 positions is known as phenanthroline.

Chemistry

Phenanthrene is nearly insoluble in water

Soluble in most low polarity organic solvents such as toluene, carbon tetrachloride, ether, chloroform, acetic acid and benzene.

One of the five contributing structures has three fused benzene ring moieties,
two of the structures have a benzene ring fused to a 10 π -electron annulene
and the remaining two are 14 π -electron annulenes, which are aromatic by the Huckel Rule



Uses:

- Used for making dyes stuffs and plastics
- Used for making Explosives
- Used for Sythesis of drugs
- Used for making bile acids,cholestrol and steroids

Difference between phenanthrene and anthracene?

Anthracene is fused linearly, whereas **phenanthrene** is fused at an angle.

This **difference** in fusions causes the **phenanthrene** to have five resonance structures which is one more than **anthracene**.

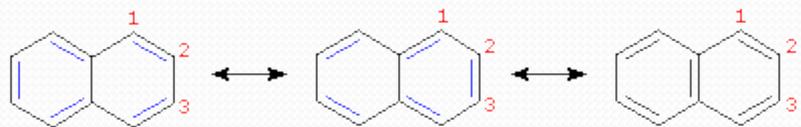
- **Phenanthrene** is **more stable than anthracene** due to the larger **stability** of the π -system of the former, which is **more** aromatic.
- When two electrons are removed, i.e., dicationic systems are analyzed, the reverse trend is obtained, so the linear isomer is **more stable than** the kinked one.

Oxidation and Reduction Reaction

- Reactions of phenanthrene typically occur at the 9 and 10 positions, including:
- Organic oxidation to phenanthrenequinone with chromic acid
- Organic reduction to 9,10-dihydrophenanthrene with hydrogen gas and Raney nickel
- Electrophilic halogenation to 9-bromophenanthrene with bromine
- Aromatic sulfonation to 2 and 3-phenanthrenesulfonic acids with sulfuric acid
- Ozonolysis to diphenylaldehyde

Resonance Structures of Aromatic Fused Rings

Napthalene



10 π -electron annulenes

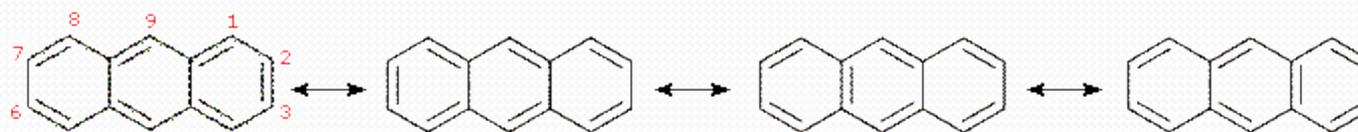
2 benzene rings

Resonance Energy = 61 kcal/mole (less than twice benzene)

(30.5 kcal per ring)

The C-C bond lengths in benzene are all 1.40 Å
The C¹-C² bond length in naphthalene is 1.36 Å
The C²-C³ bond length in naphthalene is 1.42 Å

Anthracene



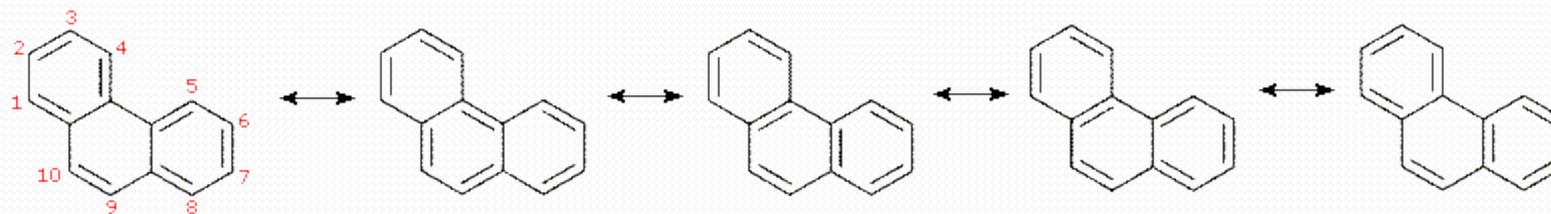
14 π -electron annulenes

benzene + 10 π -electron annulene

Resonance Energy = 83 kcal/mole

(27.7 kcal per ring)

Phenanthrene



14 π -electron annulenes

3 benzene rings

benzene + 10 π -electron annulene

Resonance Energy = 91 kcal/mole

(30.3 kcal per ring)

Exercises

Q1- What is the key difference between Phenanthrene and Anthracene?

Q2- Why Naphthalene, Anthracene and Phenanthrene is aromatic?

Q3- What are the different uses of Naphthalene, Anthracene and Phenanthrene?

Q4- which is more stable Phenanthrene and Anthracene and why?

Q5- Why (which position) Anthracene is more reactive than naphthalene ?