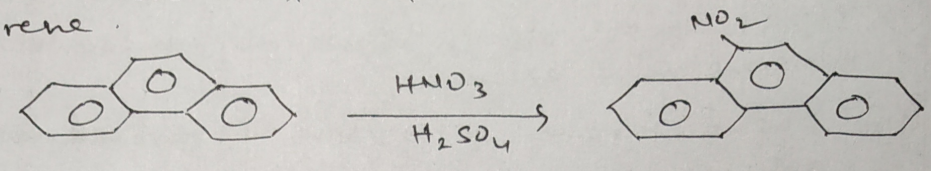
(3) Nitration.

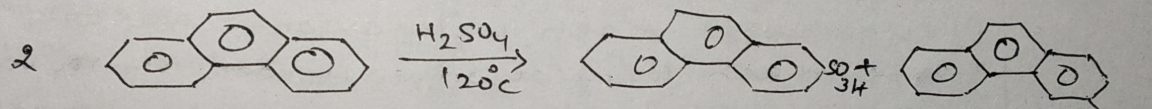
Phenanthrene undergoes nitration with concentrated nitric acid and sulphuric acid to give 9-nitrophenanthrene.



9-Nitroanthracene.

(4) Sulphonation.

Phenanthrene reacts with concentrated sulphuric acid at 120°C to give a mixture of 2-phenanthrene sulphonic acid and 3-phenanthrene sulphonic acid

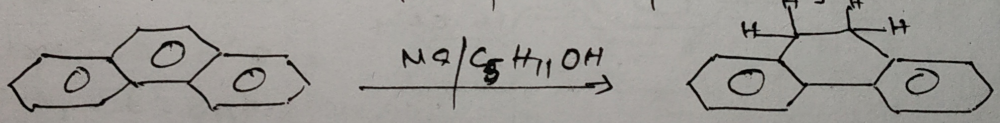


2-phenanthrene sulphonic acid

3-phenanthrene sulphonic acid.

(5) Reduction.

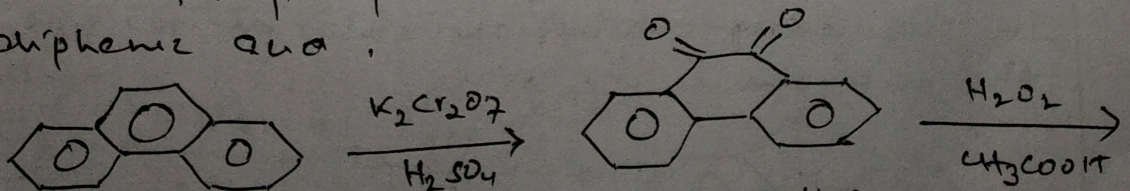
Phenanthrene undergoes reduction with sodium and isopentanol to form 9,10-dihydrophenanthrene.



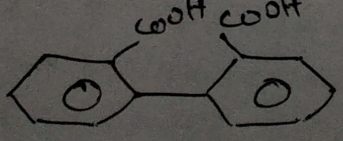
9,10-dihydrophenanthrene.

(6) Oxidation.

Phenanthrene undergoes oxidation with potassium dichromate and sulphuric acid or chromium trioxide in acetic acid to form 9,10-phenanthrenequinone (mp = 206°C). Further oxidation of this with hydrogen peroxide in acetic acid gives diphenic acid.



9,10 phenanthrenequinone



Diphenic acid.

Properties of Phenanthrene

Physical.

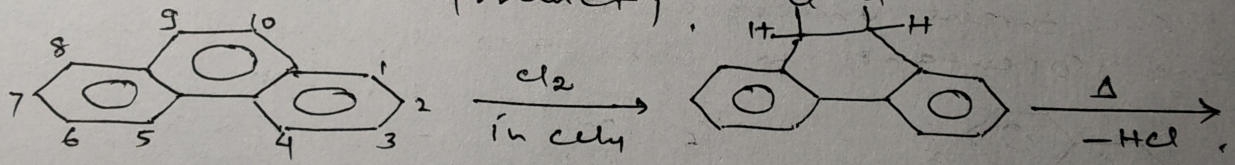
(i) Phenanthrene is a colourless solid having m.p 100°c.
(ii) It is insoluble in water but dissolve readily in ethanol benzene and ether.
(iii) Phenanthrene gives blue fluorescence in benzene solution.

Chemical properties

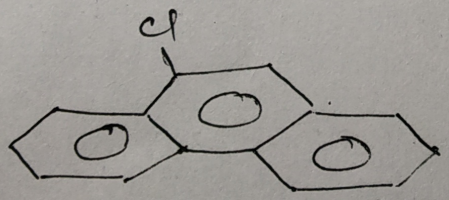
Phenanthrene undergoes oxidation, reduction, addition and electrophilic substitution reactions. These reactions mainly occur at the C-9 and C-10 positions.

(1) Reaction with halogens

Phenanthrene reach with chlorine in CCl_4 at room temperature to give 9,10-dichloro-9,10-dihydro phenanthrene (an addition product). On heating, this loses a molecule of HCl to give 9-chlorophenanthrene (a substitution product).



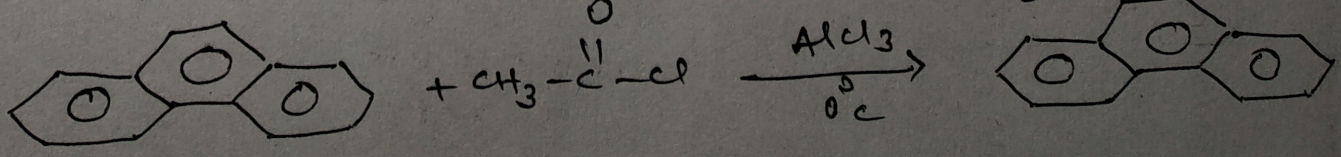
9,10-Dichloro-9,10-dihydro phenanthrene



9-chlorophenanthrene.

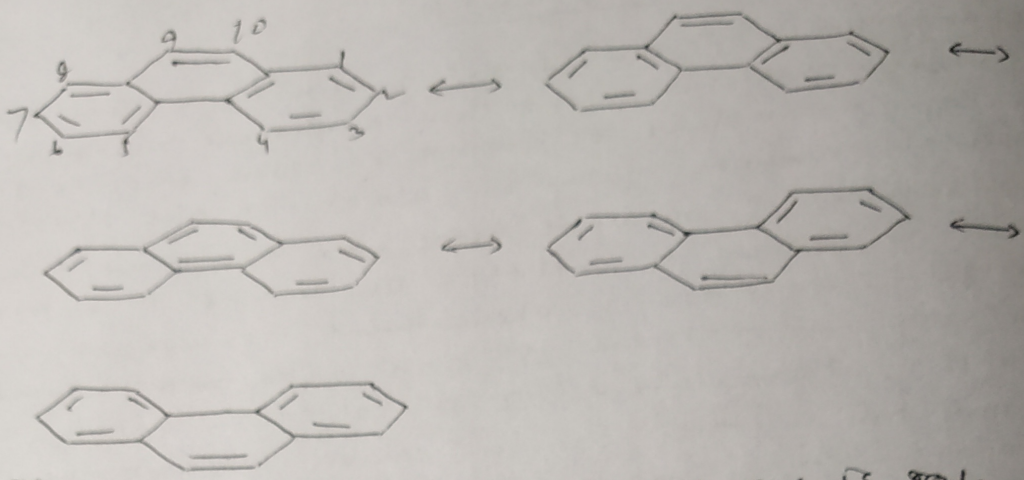
(2) Friedalcraft acylation.

Phenanthrene undergoes acylation with acetyl chloride in presence of aluminium chloride to give 9-acetyl phenanthrene.



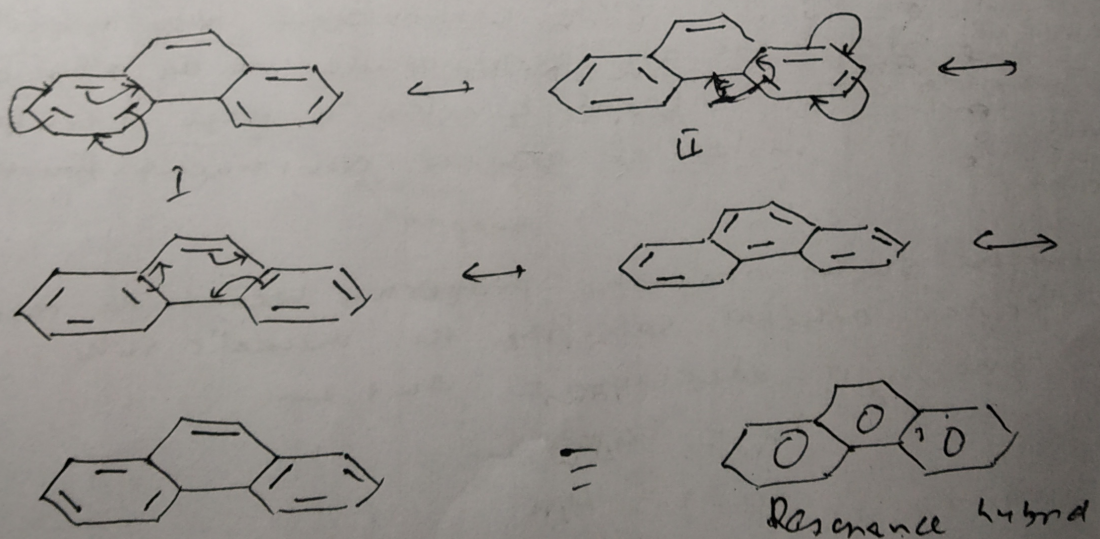
Phenanthrene.

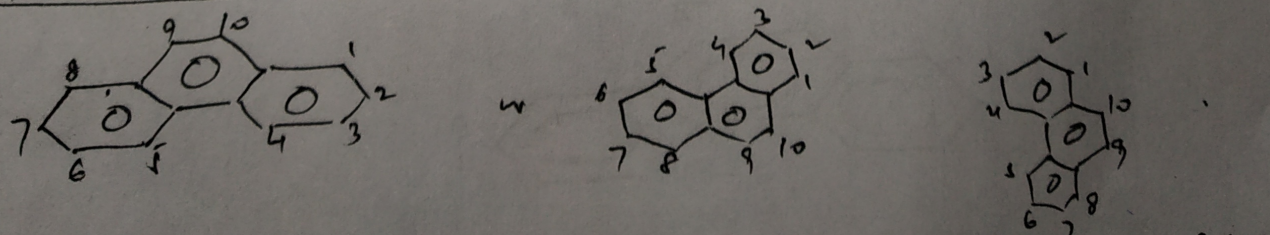
9-acetylphenant



The resonance energy of phenanthrene is 92 kcal/mole.

It is obvious from resonating structures of phenanthrene that four out of five resonating structures have double bond in C_9-C_{10} positive. i.e C_9-C_{10} has 4/5 double bond character which explain the tendency of the compound to give 9,10 - addition products

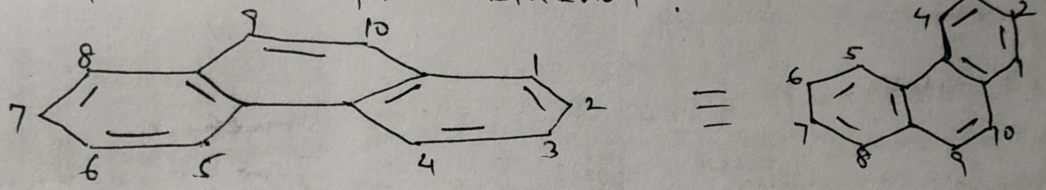




There are 5 monosubstituted products possible 1, 2, 3, 4 and 9
If two substituents are identical then 21 disubstituted isomers are possible.

Phenanthrene

Phenanthrene is an isomer of anthracene. But phenanthrene is much more important than anthracene biologically since its nucleus is found in some important natural products such as alkaloids and steroids. Phenanthrene is obtained along with anthracene from green oil fraction of coal tar. On cooling this fraction we get solid mass of phenanthrene, anthracene and carbazole. Treatment of this with ~~kerosene~~ solvent naphtha, phenanthrene is dissolved in naphtha. Evaporation of this solution crude phenanthrene is obtained which may be purified by recrystallisation of picrate from ethanol.



Structure of phenanthrene

Phenanthrene is a planar molecule. All fourteen carbon atoms are sp^2 hybridised. The sp^2 orbitals overlap with each other and with s orbitals of ten ~~bg~~ hydrogen atoms to ~~form~~ C-C and C-H σ-bonds. Each carbon atom also possesses a p orbital and these are perpendicular to the plane containing the σ-bonds. The Lateral overlap of these p orbitals produces a π-molecular orbital containing fourteen electrons

Phenanthrene shows aromatic properties because the resulting π-molecular orbital satisfies the Huckel's rule.

no. of π-electrons = $4n + 2$

$14 = 4n + 2$

$14 - 2 = 4n$

$n = \frac{12}{4} = 3$