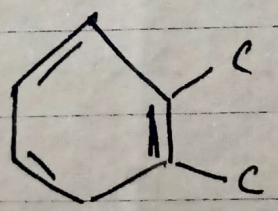
Structure of Naphthalene

(1) Classical Structure →

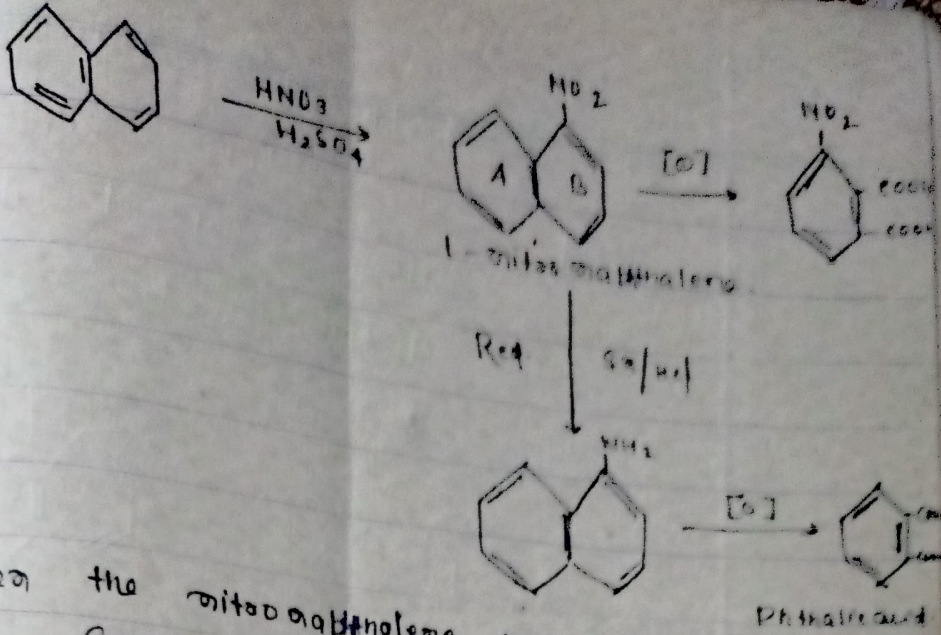
(i) Elemental analysis and molecular weight determinations shows that molecular formula of naphthalene is $C_{10}H_8$.

(ii) Dipole moment of naphthalene is zero. This indicates that naphthalene molecule is symmetrical.

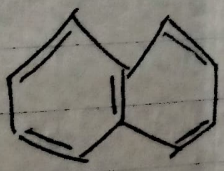
(iii) Oxidation - naphthalene with Oxygen and V_2O_5 at 470°C yields Pthalic anhydride. This indicates the presence of a benzene ring with two ortho side chains in the molecule.



(iv) Nitration of naphthalene produces a nitro naphthalene which Oxidation yields 3-nitro phthalic acid. The presence of Nitro group stabilises the benzene ring to which it is attached (ring B).

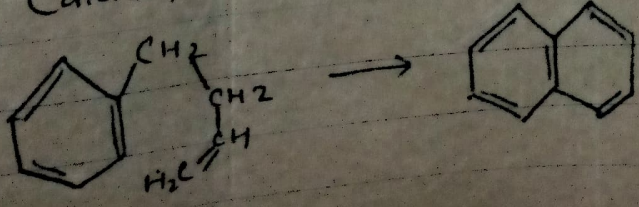


When the nitro naphthalene has reduced and corresponding amino naphthalene oxidised, Phthalic acid was obtained. In Phthalic acid two -COOH groups are attached to benzene ring in ortho position. Results clearly indicate that benzene ring in the Phthalic acid obtained by oxidation of- amino naphthalene. It is not the same ring as that originally containing nitro group in nitro naphthalene. These experimental evidence show that naphthalene consists of two benzene ring fused in ortho position. This has been shown below.

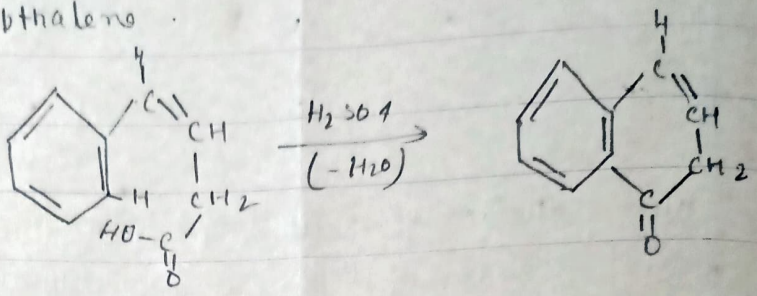


This structure of naphthalene has been confirmed by the following synthesis.

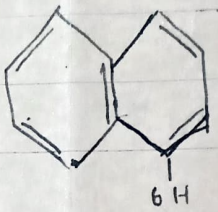
(i) When 4-phenyl-1-butene is passed over Calcium oxide, naphthalene is formed.



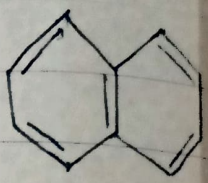
(2) From 4-phenyl-3-butenoic acid → When 4-phenyl-3-butenoic acid is heated with Conc. Sulphuric acid, 1-naphthol is formed this on distillation with Zn dust give naphthalene.



Rearrangement →



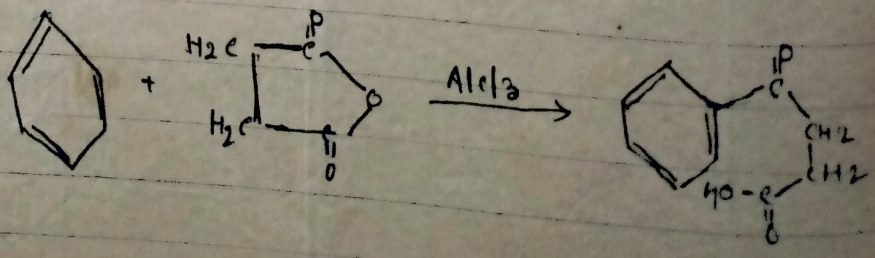
Zn dust →

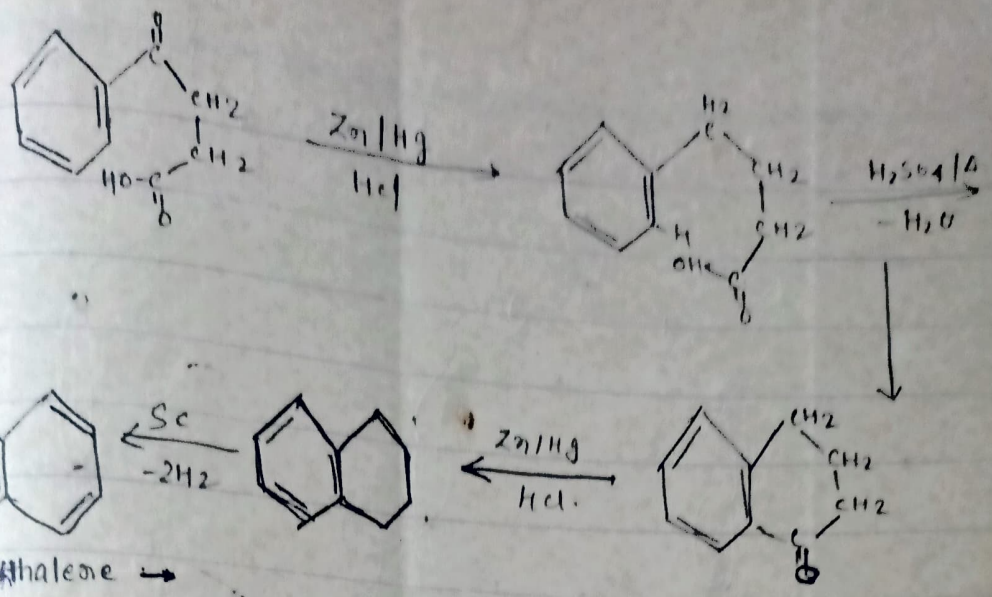


Naphthalene.

(4) Haworth Synthesis → This involves the following 5 step.

Step (i) Benzene and Succinic anhydride are heated in the presence of AlCl3 and the Ketonic acid produced is reduced by Clemmensen method. The ring is closed by heating with Conc. H_2SO_4 and the product is reduced to tetrahydronaphthalene by Clemmensen method. This Compound is then dehydrogenated by heating with Selenium or Palladised-Charcoal.

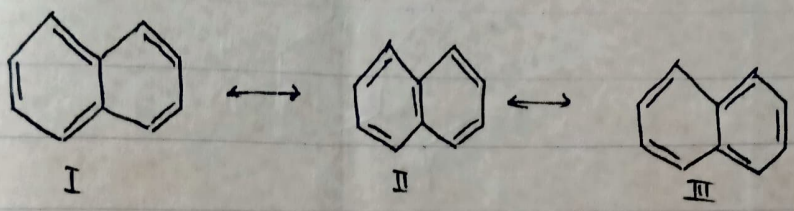




Naphthalene →

True - Structure of naphthalene ⟷

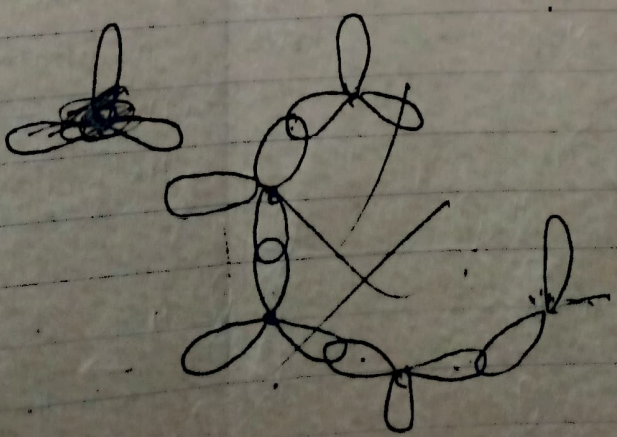
According to resonance theory, naphthalene is considered to be resonance hybrid of the following 3 - Canonical forms shown below.

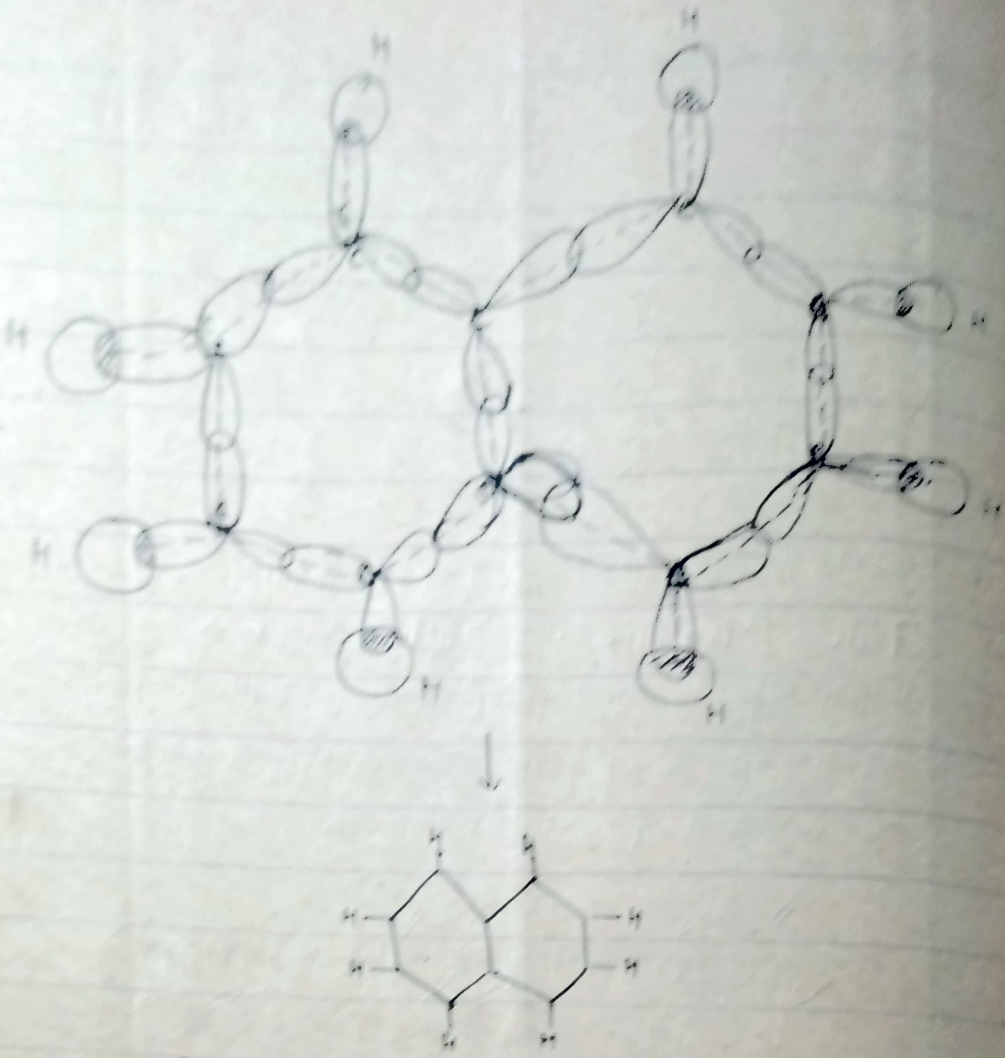


I II III

Orbital Structure of naphthalene ⟷

All ten Carbon atoms in naphthalene are sp^2 hybridised the sp^2 hybrid orbitals overlap with each other and with s - orbital of 8 H - atoms forming C-C - and C-H, σ bonds. All the σ - bonds lie in one Plane. This has been confirmed by X - ray diffraction studies.





Formation of σ bonds in naphthalene.

These p- orbitals are perpendicular to plane containing σ - bonds. The lateral overlap of these p- orbitals produces a π M.O. containing 10 electrons. One half of this π M.O. lies above and another half lies below the plane of σ - bonds. Naphthalene shows aromatic character because the resulting π M.O. satisfies the Huckel's rule ($n=2$, $4n+2$)