1. From the elemental analysis and molecular weight determination, the molecular formula of anthracene comes $C_{14}H_{10}$.

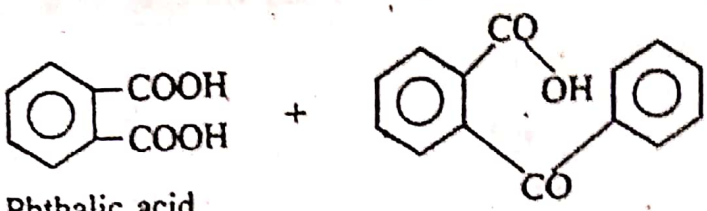
2. The molecular formula of anthracene $C_{14}H_{10}$ suggests that it is related to benzene and naphthalene.

$$\underset{\text{Benzene}}{C_6H_6} \xrightarrow{+(4C+2H)} \underset{\text{Nephthalene}}{C_{10}H_8} \xrightarrow{+(4C+2H)} \underset{\text{Anthracene}}{C_{14}H_{10}}$$

Like benzene and naphthalene, it also shows addition and substitution reactions.

3. Anthracene reacts with Br_2 to give bromoanthracene, which on caustic fusion gives hydroxy-anthracene. The latter, on vigorous oxidation forms phthalic acid and o-benzoyl benzoic acid—

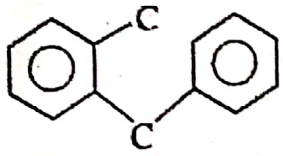
$$\underset{\text{Anthracene}}{C_{14}H_{10}} \xrightarrow{Br_2} C_{14}H_9Br \xrightarrow[\text{fusion}]{KOH} C_{14}H_9OH \xrightarrow{[O]}$$



Phthalic acid

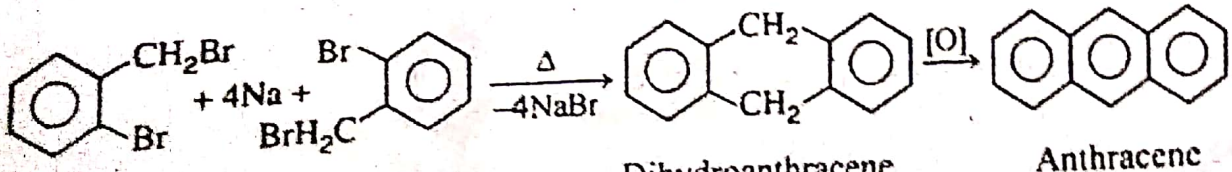
o-benzoylbenzoic acid

This confirms the presence of two benzene rings in anthracene with the following skeleton—



Accommodating the 10 H-atoms and maintaining the tetravalency of all C-atom, the middle ring must be closed. Therefore, three benzene rings are fused together in linear fashion in the anthracene molecule—

This structure is confirmed by the following synthesis of anthracene—



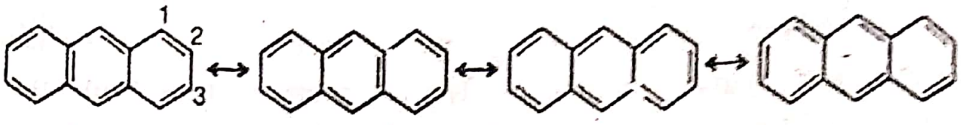
o-Bromobenzyl bromide

Dihydroanthracene

Anthracene

Modern Approach : According to modern views, all the 14 C-atoms of anthracene lie at the corners of three fused hexagons in linear fashion. Each sp^2 hybridised C-atom is attached to three others by σ - bonds. All C & H-atoms lie in a plane. There is a π - electron cloud formed by the overlap of $2p_z$ orbitals above and below the plane of C-atoms. The resonance energy of anthracene is 351.5 kJ mol^{-1}.

The various cannonical forms of anthracene are given below—

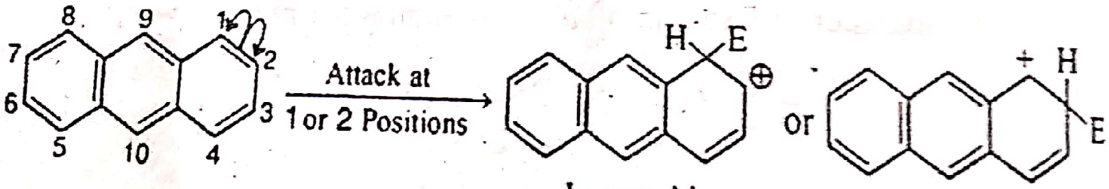


I II III IV

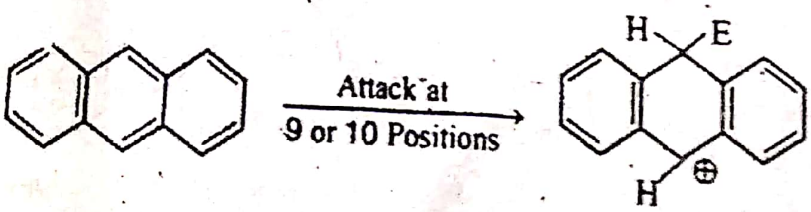
The $C_1 - C_2$ bond is double in three out of four cannonical structures and therefore it has 3/4 double bond character. The $C_2 - C_3$ bond is double only in one case, hence it has 1/4 double bond character.

Q.48. Why are the 9 and 10-positions of anthracene very reactive ?
Or, How would you account for the greater reactivity of positions 9 & 10 of anthracene ?

Ans. : 9 and 10-positions of anthracene are terminals of the quininoid structure and these are very reactive. Further, the carbocation formed by electrophillic (E^+) attack at 1 or 2 positions leaves a naphthalene ring intact involving loss of 351.5 – 256.2 = 95.3 kJ mol^{-1}, while carbocation formed by electrophillic attack at 9 or 10 positions leaves two benzene ring intact, thus there is a loss of only 50.3 kJ mol^{-1} of resonance energy (351.5 – 2 × 150.6). Therefore, the carbocation formed by attack at 9 and 10 positions is more stable and its formation is more readily favoured. Hence, anthracene is very reactive at 9 : 10 positions—



Less stable



More stable