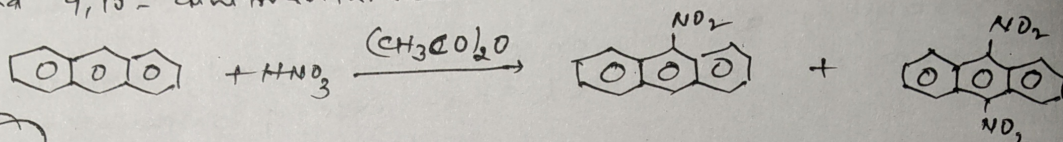


### ⑤ Nitration:

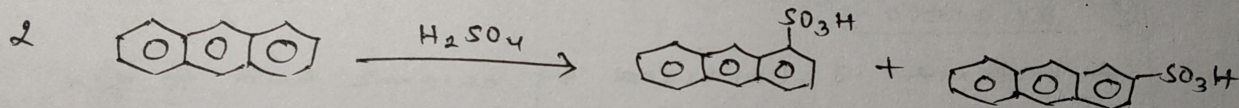
Anthracene undergoes nitration with concentrated nitric acid in acetic anhydride to give a mixture of 9-nitroanthracene and 9,10-dinitroanthracene.



**Note** → Nitrating mixture  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  gives 9,10-anthraquinone.

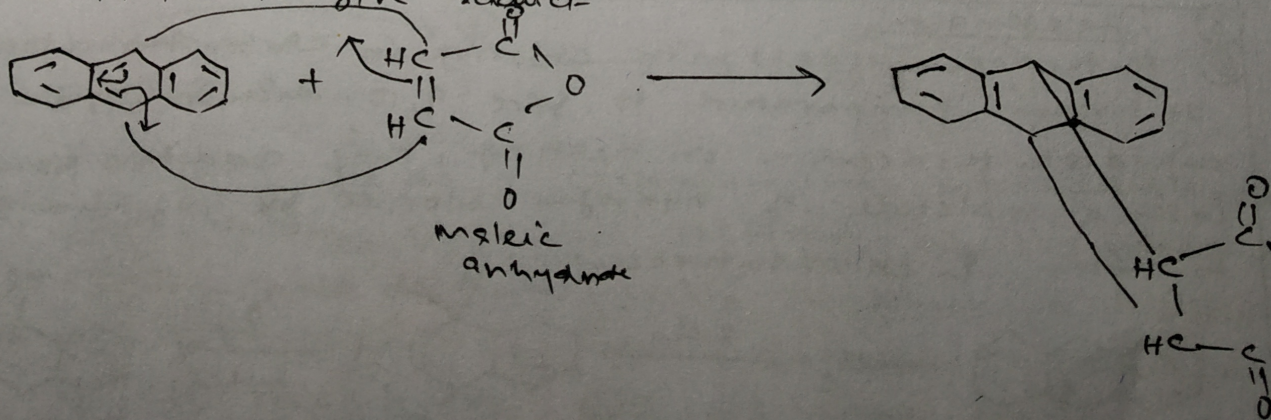
### ⑥ Sulphonation:

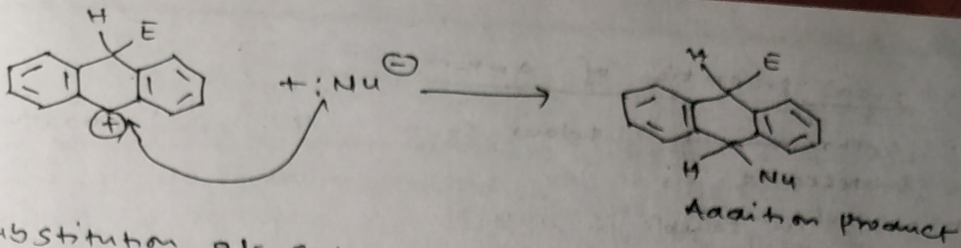
Anthracene undergoes sulphonation with concentrated sulphuric acid to give a mixture of 1-anthracenesulphonic acid and 2-anthracenesulphonic acid. At lower temperatures 1-anthracenesulphonic acid is the major product whereas at higher temperature 2-anthracenesulphonic acid is major product.



### ⑦ Diels-Alder Reaction:

Anthracene undergoes a Diels-Alder reaction with maleic anhydride to give adduct.

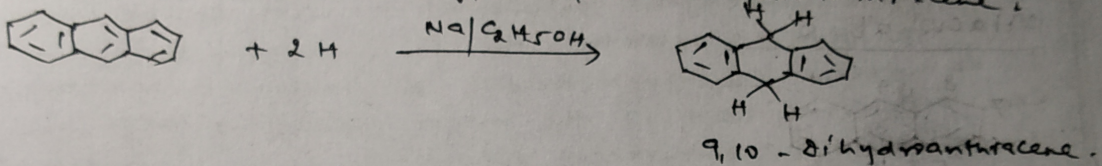




Substitution at C-1 or C-2 occurs only when the reaction is reversible (as in case of sulphonation),

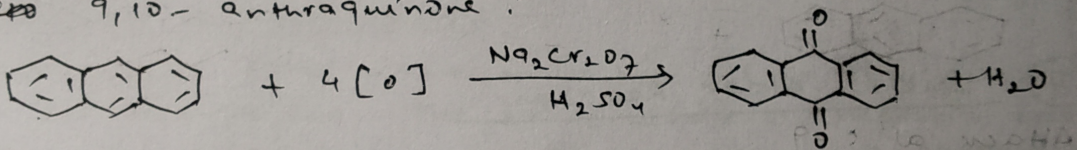
### ① Reduction

Anthracene undergoes reduction with sodium and ethyl alcohol to give 9,10-dihydroanthracene.



### ② Oxidation

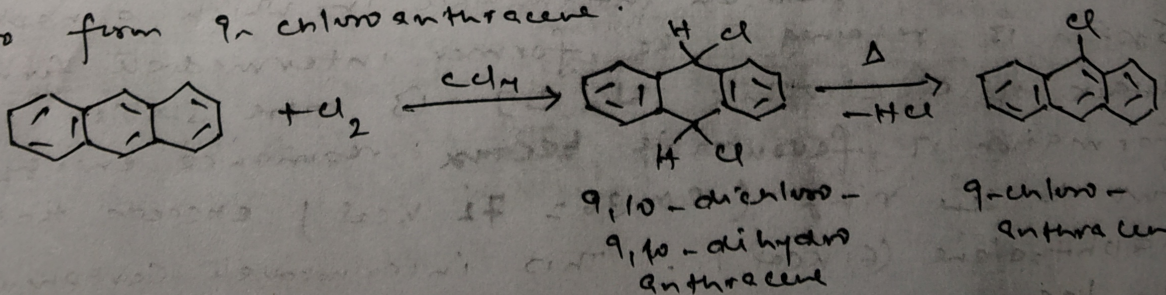
Anthracene is oxidised by chromic acid to give 9,10-anthraquinone.



### Electrophilic substitution reaction.

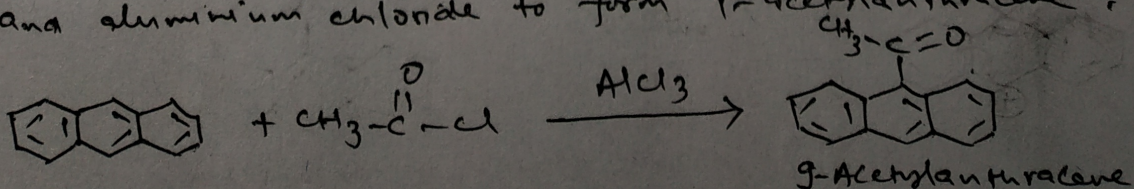
#### ③ Halogenation.

Anthracene reacts with chlorine in carbon tetrachloride at room temperature to give 9,10-dichloro-9,10-dihydroanthracene. On heating, this addition product loses a molecule of hydrogen chloride by 1,4-elimination to form 9-chloroanthracene.



#### ④ Friedel-Craft Acylation

Anthracene undergoes acylation with acetyl chloride and aluminium chloride to form 9-acetylanthracene.



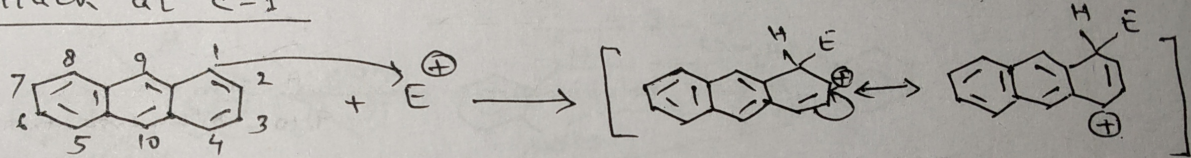
## Physical properties of Anthracene

- (i) Anthracene is a colour solid (m.p. 216°C) showing blue fluorescence.
- (ii) It is insoluble in water, sparingly soluble in organic solvents (ether, alcohol) etc but fairly soluble in hot benzene.

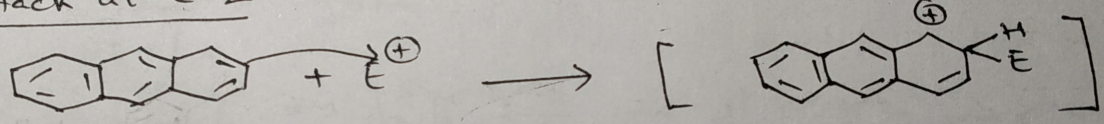
## Chemical properties of Anthracene

Anthracene undergoes addition and electrophilic substitution reactions. These reactions occur mainly at C-9 and C-10.

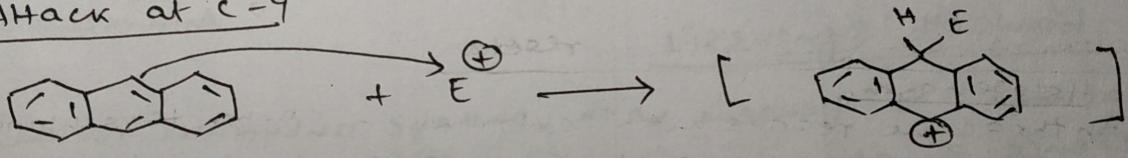
### Attack at C-1



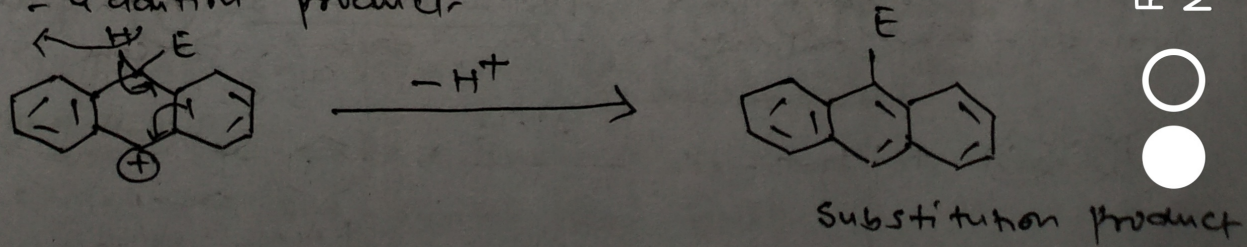
### Attack at C-2



### Attack at C-9



Attack at C-9 yields a carbocation intermediate in which two benzene rings are retained whereas attack at C-1 or C-2 yield an intermediate in which a naphthalene system is retained. The former intermediate formed by attack of electrophile at C-9 is more stable and its formation is favourable because resonance energy of two benzene rings ( $2 \times 36 = 72$  kcal) exceeds that of naphthalene (61 kcal). This intermediate carbocation can lose a proton to give the corresponding substitution product or it can react with a nucleophile to form a 9-10-addition product.

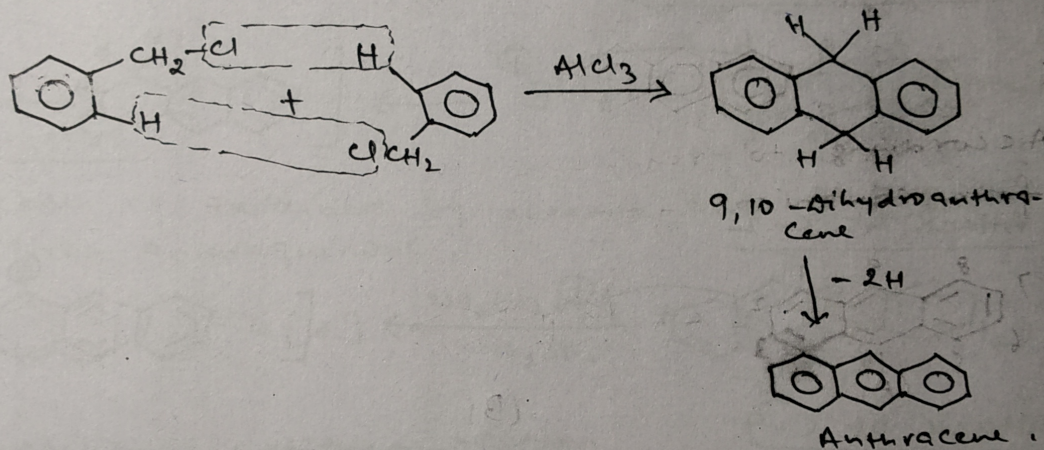


The resonance energy of anthracene is 84 kcal/mole. This is average  $\frac{84}{3} = 28$  kcal/mole per ring which is lower than that of benzene (36 kcal/mole). As a result anthracene is less aromatic than benzene and behaves more as an unsaturated aliphatic hydrocarbon.

### Synthesis of Anthracene

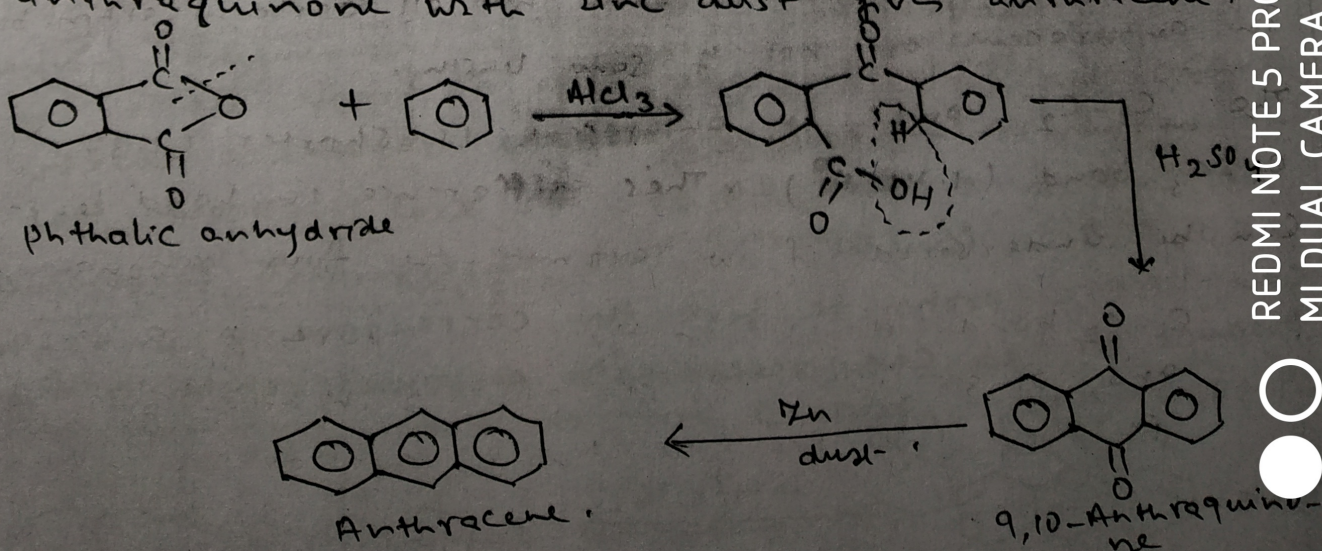
#### ① By Friedel-Craft's reaction.

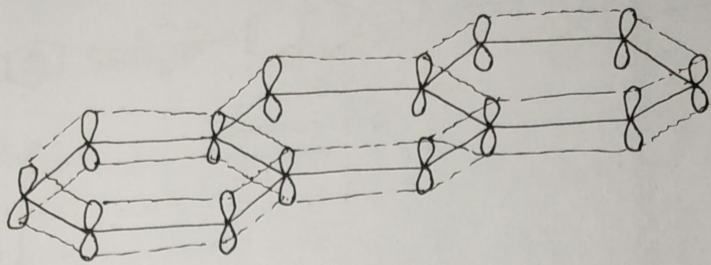
Benzyl chloride reacts with itself to form 9,10-dihydroanthracene which readily loses two hydrogen atoms to give anthracene.



#### ② Haworth Synthesis

Treatment of benzene with phthalic anhydride in the presence of aluminum chloride gives o-benzoyl benzoic acid. This is then heated with concentrated sulphuric acid to give 9,10-anthraquinone. Distillation of anthraquinone with zinc dust gives anthracene.





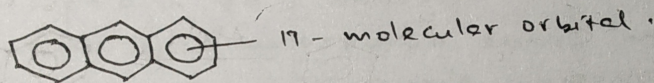
Anthracene shows aromatic properties because resulting  $\pi$ -molecular orbital satisfies the Hückel's rule.

$$\text{no. of } \pi\text{-electrons} = 4n + 2$$

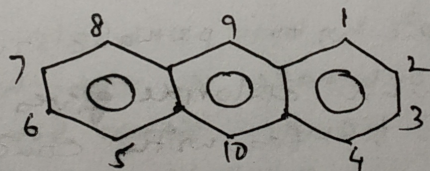
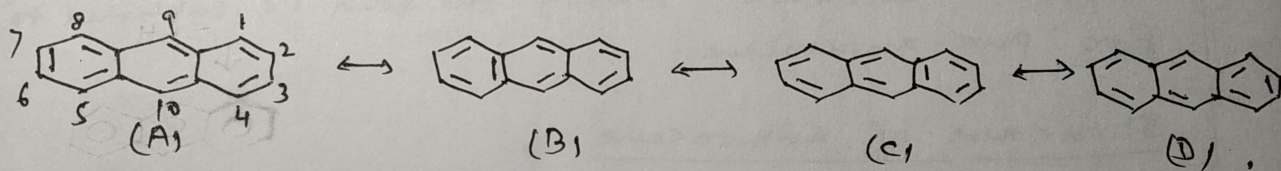
$$14 = 4n + 2$$

$$12 = 4n$$

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



According to resonance theory, anthracene has following four canonical forms.



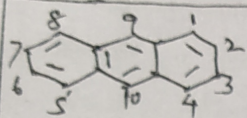
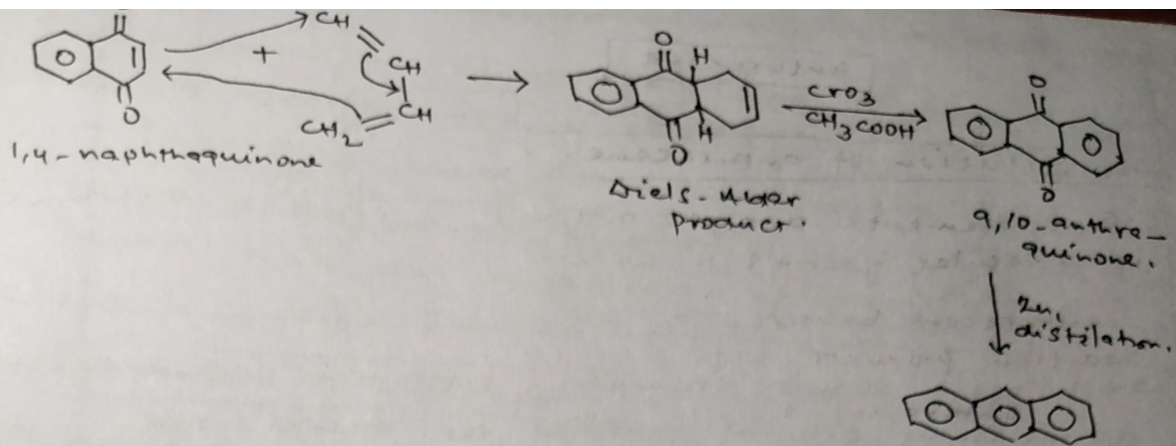
X-ray diffraction studies show that all carbon-carbon bonds in anthracene are not of same length.

The  $C_1-C_2$  bonds in anthracene is shorter ( $1.37 \text{ \AA}$ ) than  $C_2-C_3$  bond ( $1.42 \text{ \AA}$ ). This difference in bond lengths can be understood if we examine the four resonance forms.

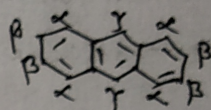
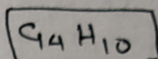
$C_1-C_2$  bonds double in three structures (A, B, C) and single only in structure D whereas  $C_2-C_3$  bond is single in structure (A, B, C) and double in only D.

Therefore, we can expect that  $C_1-C_2$  bond has more double bond character and shorter bond length than  $C_2-C_3$  bond.





Anthracene



Anthracene occurs in coal-tar and it is obtained from the green oil fraction (bp  $270-360^\circ\text{C}$ ). On cooling this fraction crude anthracene crystallises out. Crude anthracene contains phenanthrene and carbazole as impurities. It is purified by washing it successively with solvent naphtha to remove phenanthrene and pyridine to remove carbazole. Finally the solid is sublimed to give pure anthracene.

### Structure of Anthracene.

All the fourteen carbon atoms in anthracene is  $\text{sp}^2$  hybridised. The  $\text{sp}^2$  hybrid orbitals overlap with each other and with s-orbitals of ten hydrogen atoms forming C-C and C-H  $\sigma$ -bonds. Since bonds result due to overlap of trigonal  $\text{sp}^2$  orbitals, all the carbon and hydrogen atoms in anthracene lie in the same plane.

Also each carbon atom in anthracene has an unhybridised p-orbital containing one electron. These p-orbitals are perpendicular to the plane of  $\sigma$ -bonds. The lateral overlap of these p-orbitals produces a  $\pi$ -molecular orbital containing fourteen electrons. One half of this  $\pi$ -molecular orbital lie above and other half lie below the plane of  $\sigma$ -bonds.

