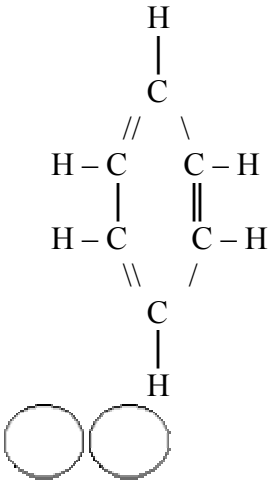
Benzene

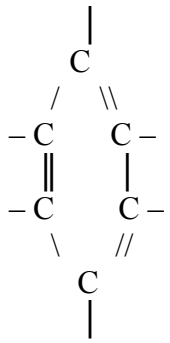
We defined aliphatic compounds (fat-like) now like alkane or open chain compounds and those cyclic compounds that resemble the open chain compounds.

Aromatic compounds are benzene and compounds that chemically resemble benzene.

The first scientist to propose benzene structure was Kekule. He based his work on isomer number.



A.



B

When studies of isomer showed that Kekule structure is wrong, he (Kekule) suggested that form A change to form B (i.e. An equilibrium existed between the two forms which is also wrong.).

Properties of Benzene

1. Flat i.e. planar molecule containing 6C and 6H.
2. Benzene undergoes substitution (ionic) reaction i.e. electrophilic substitution.
3. Does not react with Br_2/CCl_4, H_2/cat., $KMnO_4$ or with H_2SO_4 as do alkenes and alkynes. We can account for the stability by comparing heats of hydrogenation of benzene with other alkenes. Heat of hydrogenation is about 28 to 30 K cal/mol for each double bond. So we expect the heat of hydrogenation (H H) for benzene to be about 84-90 K cal, but it is 49.8 K cal i.e. the benzene ring is more stable than the hypothetical molecule cyclohexatriene by 36 K cal/mol. i.e. the resonance energy or stabilization energy or delocalization energy of benzene is 36 K cal/mol.

Further stability of the benzene ring can be explained in quantum mechanics. Electrons are described in terms of their wave nature; the energy of an e is inversely proportional to its wave length i.e. the longer the wave length, the lower is its energy.

The π e's have longer λ than e's in the molecular orbital of an isolated double bond where the motion of the e's is restricted to the vicinity of the two nuclei i.e. longer λ lower energy and more stable.

Bond length of C-C in benzene is 1.39 A^o intermediate in length between C-C single bond (1.53 A^o) and C-C DB (1.34 A^o). Hence we conclude that the actual structure of benzene is neither form A or B but a hybrid molecule. The contributing forms are identical and hence contribute equally to the actual structure of benzene, thus the ring is stabilized by resonance.

Bonding – molecular orbital theory

$3sp^2$ leaving one π e per C

The sp^2 is trigonal (120^o apart). Each C is bonded to two carbons on either side by an

overlap of sp^2 to sp^2 forming a sigma bond. Each C has a p orbital consisting of two lobes, one lying above and the other lying below the plane of the other $3sp^2$ orbitals. The p orbital of one C atom overlaps with the p orbitals of an adjacent carbon atom on either side resulting in two continuous doughnut-shaped electron clouds, one above and one below the plane of the atoms. It is this delocalization of the pi electrons (i.e. participation in several bonds) that makes the benzene molecule very stable.