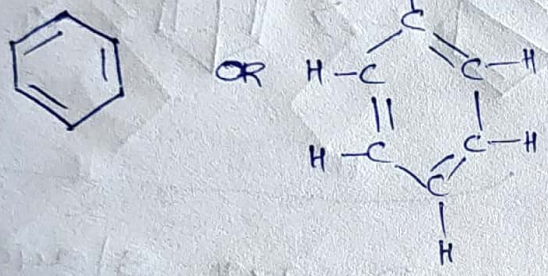
Structure & Stability of benzene

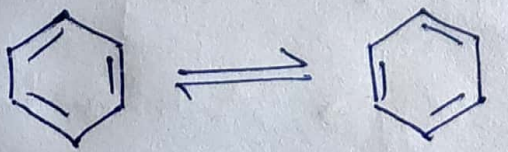
(a) Kekule's structure:

→ Suggested, 6 C atoms of benzene molecule might have hexagonal ring arrangement with alternate single & double bond blw them.



→ Later, Single & double bonds alternate in their position blw the carbons to yield two equivalent structure existing in dynamic equilibrium.

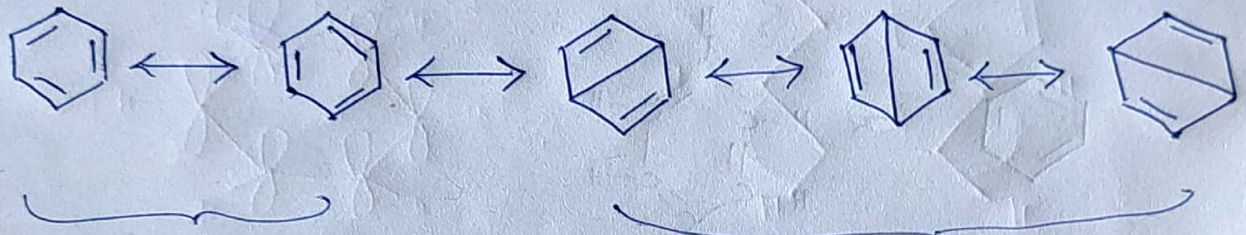
→ All six C–C bond in equal length 1.39 A° which is greater than C=C (1.34 A°) and less than C–C (1.54 A°)



→ Limitation : Could not explain stability towards strong oxidant like $KMnO_4$ or the substitution rxns.

(b) Resonance Concept :

→ Benzene molecule is a resonance hybrid of the following structure :



Kekule structures Dewar structures

→ Resonance energy = $-150.5\ kJmol^{-1}$

Resonance hybrid has lowest energy & hence greatest stability, than the contributing structures.

(c) Molecular orbital description

→ All the C atoms are sp^2 hybridised.

→ Each C atom of C_6H_6 are arranged in a planar triangular fashion. & the unhybridised P orbital ~~has~~ is ⊥r to the above plane.

→ Two adjacent C atoms by $sp^2 - sp^2$ head on overlap to form σ bonds.

→ Remaining one sp^2 orbital overlap with s orbital of Hydrogen to form σ bond

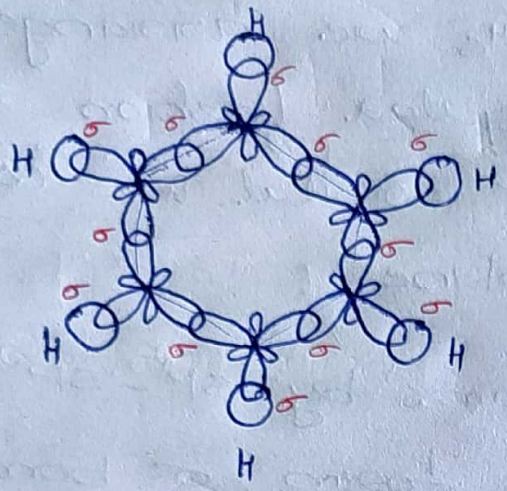
→ The six C–C σ bond forms hexagon structure with bond angle 120°

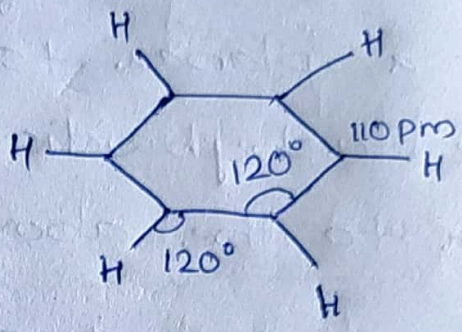
→ All C–H σ bond also lie in same plane.

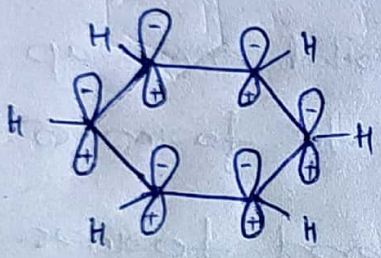
→ 6 mutually parallel unhybridised P orbitals above the hexagonal ring collectively overlap in sideways manner above & below the plane of carbon ring.

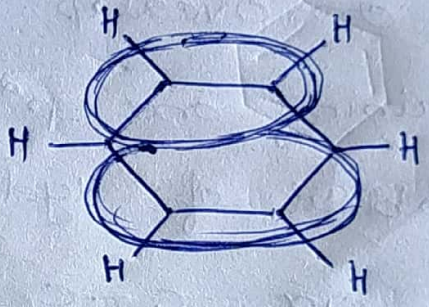
→ The two cyclic continuous delocalised Pi-lobes, above & below the ring are called electron delocalisation.

which cause lowering of energy & promotes stabilisation.









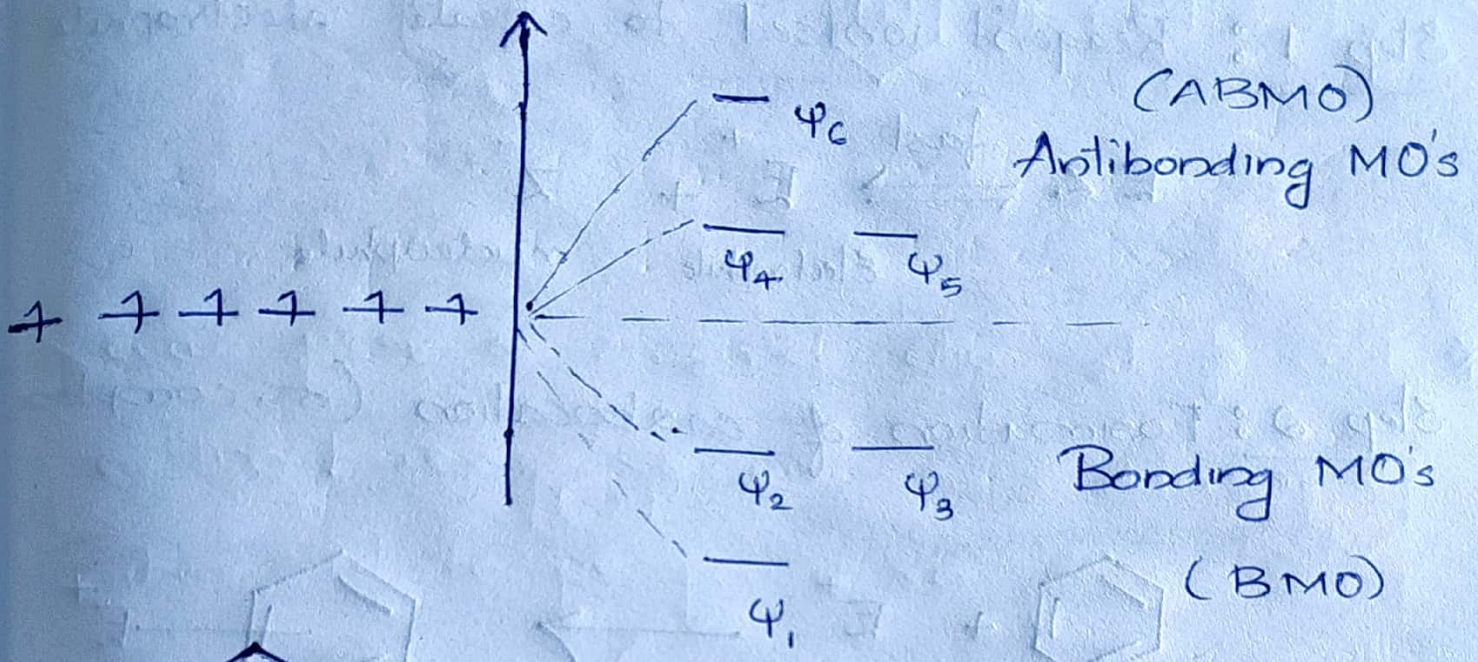
Delocalisation energy / resonance energy = −150.5 kJmol⁻¹

→ According to molecular orbital theory, the 6 overlaping P orbitals combine to form set of six π MO's.

~~3 are lower energy & other 3~~

3 are lower energy → Bonding MO (BMO)

& other 3 are higher energy → Antibonding MO (ABMO)



(ABMO)
Antibonding MO's

Bonding MO's
(BMO)

— Circle indicate π de localisation.