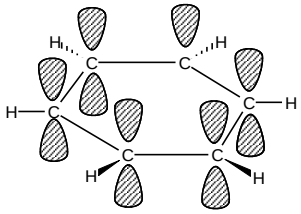
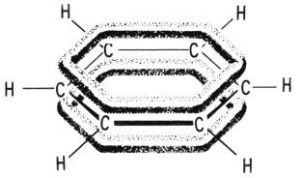
THE STRUCTURE OF BENZENE

- Benzene has the formula C_6H_6.
- Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom.
- The molecule is planar, and the six C-C bonds are the same length – intermediate between single and double.
- Each C atom is bonded to two other C atoms and one H atom by single covalent σ-bonds.
- This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring.
- Each p orbital overlaps with the neighbouring p orbitals to form a π-bond.
- The overall result is a ring of negative charge ("electron cloud") above and below the plane of the ring.

the six p orbitals before overlap



the π system formed



- The electrons in the π system do not belong to any particular C atom (or to a bond between two C atoms) - they are free to move throughout the whole π system - they are **delocalised**. As the electrons are delocalised and more spread out, they will repel each other less making the molecule more stable. Due to this delocalisation, the structure of benzene is represented by:

- Kekulé made a significant breakthrough and was the first chemists to realise that benzene had a ring structure with six carbon atoms each joined to one hydrogen atom. However, he thought that the ring contains three C=C double bonds and three C-C single bonds. This molecule would be a "triene" (“cyclohexa-1,3,5-triene”) with three C=C double bonds rather than a delocalised ring system. It would be drawn like this:

- There are some key pieces of evidence to support the delocalised structure rather than the Kekulé "triene" structure.

1) C-C bond length

- All the C-C bonds are the same length – and this length is in-between the length of C-C single and C=C double bonds.
- If benzene was a triene we would expect three longer C-C single bonds and three shorted C=C double bonds.

2) Addition reactions

- Benzene does not readily undergo addition reactions (e.g. benzene does not decolourise bromine water)
- If benzene was a triene, we would expect it to readily undergo addition reactions such as this – but it doesn’t.

3) Enthalpy of hydrogenation

- We would expect a triene to react with 3 H_2 to form cyclohexane releasing 360 kJ/mol of energy (3 x 120).
- It only releases 208 kJ/mol of energy showing that benzene is 152 kJ/mol more stable than the triene.
- This extra stability is due to the delocalisation of electrons and is known as the delocalisation stability.