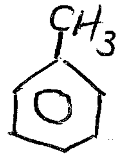
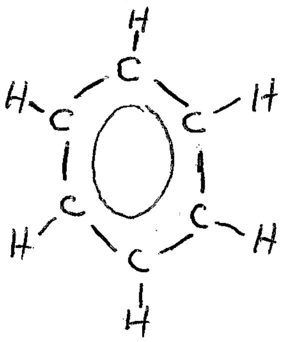
Arenes (A2)

- aromatic hydrocarbons
- general formula C_nH_{2n-6} ; $n \geq 6$
- $n=6$, C_6H_6 – benzene 
- $n=7$, C_7H_8 – methylbenzene (toluene)  or $C_6H_5CH_3$

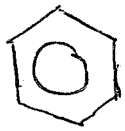
Benzene

- empirical formula CH
- molecular mass 78
- molecular formula C_6H_6
- structural formula (displayed formula)



- skeletal formula 

Naming of aromatic compounds



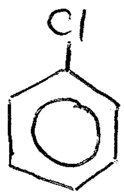
C_6H_6

benzene

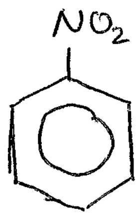
C_6H_5- phenyl

(always attached to something)

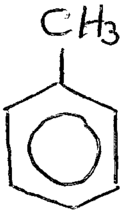
The name is base on benzene



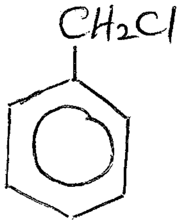
chlorobenzene



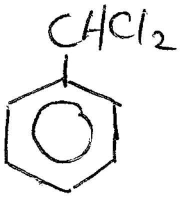
nitrobenzene



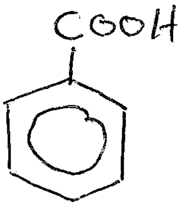
methylbenzene



(chloromethyl)benzene

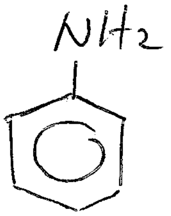


(dichloromethyl)benzene

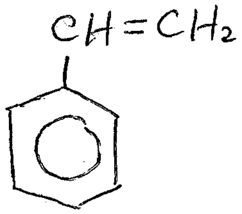


benzoic acid.

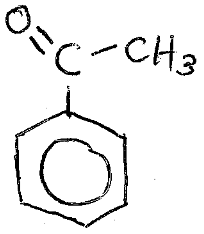
The name is based on phenyl



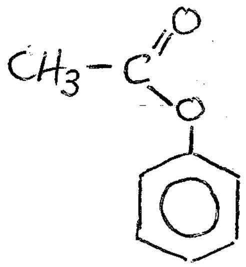
phenylamine



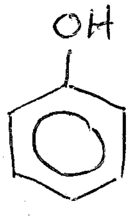
phenylethene



phenylethanone

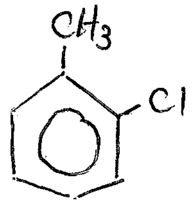


phenyl ethanoate

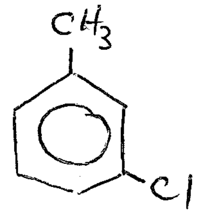


phenol

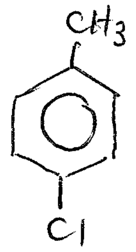
More than one group attached to the benzene ring



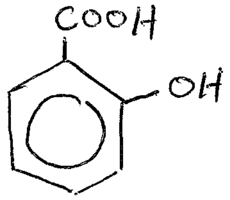
2-chloromethylbenzene



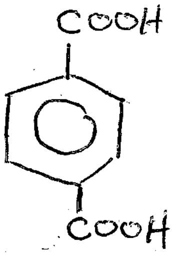
3-chloromethylbenzene



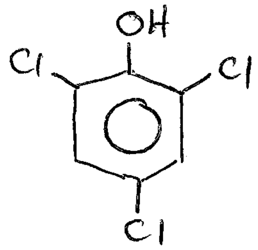
4chloromethyl-
benzene



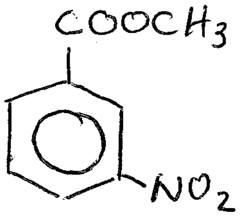
2-hydroxybenzoic acid



benzene-1,4-
dicarboxylic acid



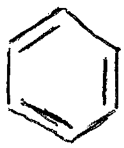
2,4,6-trichloro-
phenol.



methyl 3-nitrobenzoate

Kekulé's structure of benzene

A planar, cyclic structure with alternating double and single bonds.



Each carbon atom has a hydrogen attached to it.

Problems with the Kekulé structure

Kekulé structure was a good attempt in its time.

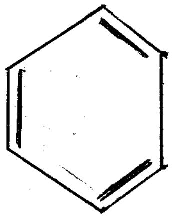
1. Problems with the chemistry

The 3 double bonds should allow addition reactions like ethene.

Not the case, benzene rarely does this. Instead, it usually undegoes substitution reactions in which one of the hydrogen atoms is replaced by some substituent group/atom.

2. Problems with the shape

Kekulé structure would be irregular hexagon due to C-C single and double bonds are different lengths.



C − C 0.154 nm

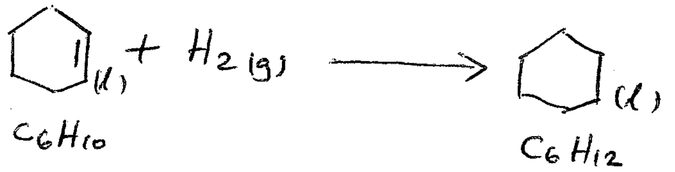
C = C 0.134 nm

In real benzene, all the bonds are exactly the same - intermediate in length between C-C and C=C at 0.139 nm. Real benzene is a perfectly regular hexagon.

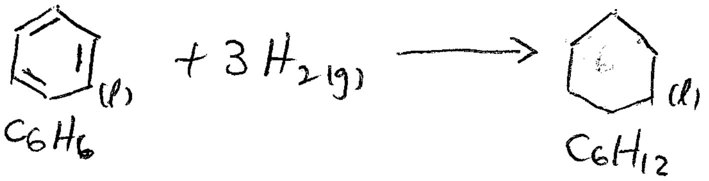
3. Problems with the stability of benzene

Real benzene is a lot more stable than the Kekulē structure. Based on the Kekulē structure, themochemistry calculation is always 15 kJ mol^{-1} more than the actual benzene structure.

When cyclohexene (one C=C bond) is reduced to cyclohexane, 120 kJ of energy is released per mole.



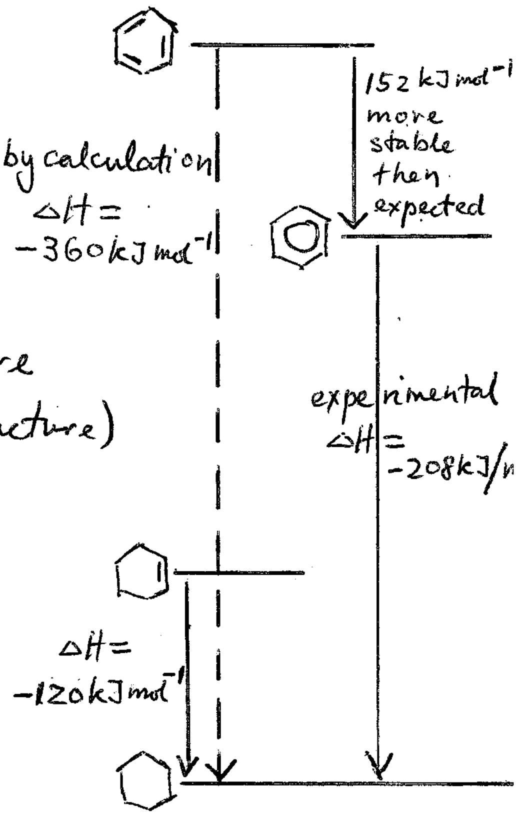
By direct calculation, if benzene (based on Kekulē structure) contained 3 seperate C=C bonds, it would release 360 kJ per mole when reduced to cyclohexane



Actual benzene releases 208 kJ mol^{-1} when fully reduced to cyclohexane, putting it lower down the energy scale.

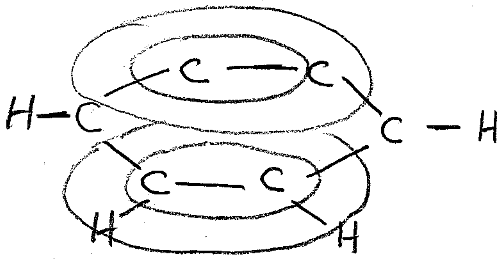
Actual benzene is 152 kJ mol^{-1} more stable than expected (Kekulē structure)

This value (152 kJ mol^{-1}) is known as the <u>delocalisation energy</u> or <u>resonance energy</u>.



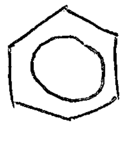
Structure of Benzene

- Benzene is a planar molecule containing a ring of six carbon atoms, each with a hydrogen atom attached.
- The 6 carbon atoms form a perfectly regular hexagon. All the carbon-carbon bonds have exactly the same lengths – somewhere between single and double bonds
- There are delocalised electrons above and below the plane of the ring.



Delocalised electrons cloud is formed by overlapping of the 6 p orbitals from the 6 carbon atoms

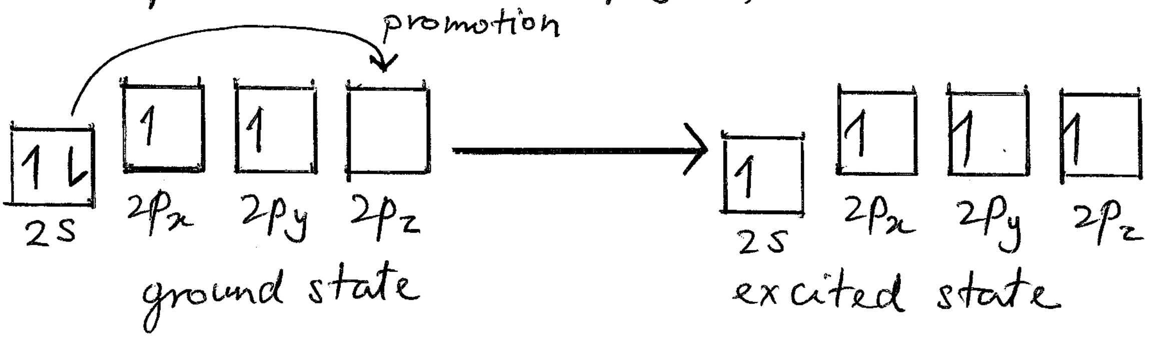
- The presence of the delocalised electrons makes benzene particularly stable.
- Benzene resists addition reactions because that would involve breaking the delocalisation and losing that stability.
- Benzene is represented by the symbol, where the circle represents the delocalised electrons, and each corner of the hexagon has a carbon atom with a hydrogen attached.



Bonding in Benzene

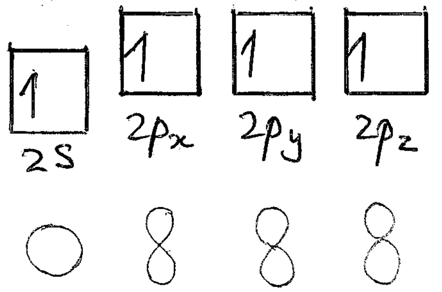
The electronic configuration of a carbon atom is $1S^2 2S^2 2p_x^1 2p_y^1$.

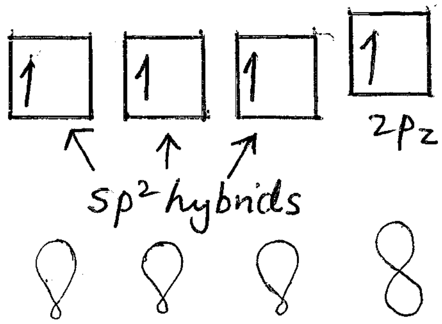
Each carbon atom has to join to three other atoms (one hydrogen and two carbons) and doesnt have enough unpaired electrons to form the required number of bonds, so it needsto promote one of the $2s^2$ pair into the empty $2p_z$ orbital.

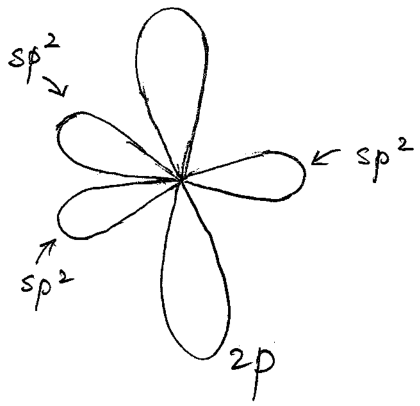


Hybridisation

Because each carbon is only joining to three other atoms, when the carbon atoms hybridise their outer orbitals before forming bonds, they only need to hybridise three of the orbitals. They use the 2s electron and two of the 2p electrons, but leave the other 2p electron unchanged.

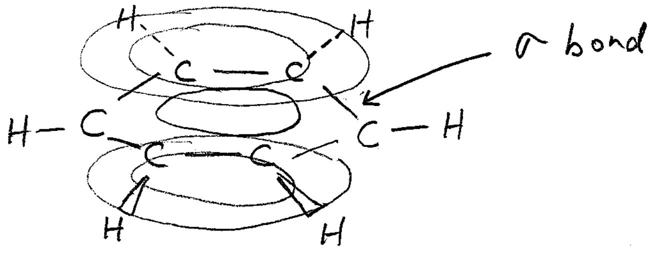






In benzene, each carbon atom is joined to two other similar carbon atoms. Each carbon atom uses the sp^2 hybrids to form sigma (σ) bonds with two other carbons and one hydrogen atom.

The p electron on each carbon is overlapping with those on both sides of it. This extensive sideways overlap produces a system of pi (π) bonds which are spread out over the whole carbon ring. The electrons are spread over the whole ring and the electrons are said to be delocalised. The six electrons make up the delocalised pi electron system in benzene.



The structure was particularly stable and resisted any attempt to break it down through normal electrophilic addition. However, overall subsitution of any of the hydrogen atoms would not affect the delocalised system.

The shape of benzene

Benzene is a planar regular hexagon, with bond angles of 120°. It is a regular hexagon because all the bonds are identical. The delocalisation of the electrons means that there aren't alternating double and single bonds. It is planar because that is the only way that the p orbitals can overlap sideways to give the delocalised pi system

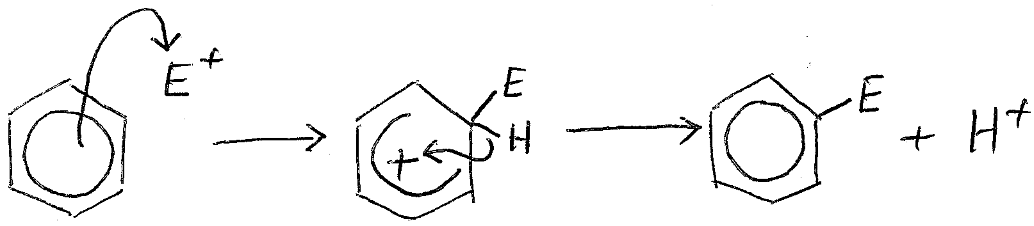
Electrophilic Substitution of Benzene Ring.

The high electron density of the ring makes it open to attack by electrophiles.

Substitution of hydrogen atoms on the ring does not affect the delocalisation.

Because the mechanism involves an initial disruption to the ring, electrophiles must be more powerful than those which react with alkenes.

Mechanism of Electrophilic Substitution



- a pair of electrons leaves the delocalised system to form a bond to the electrophile.
- this disrupts the stable delocalised system and forms an unstable intermediate.
- to restore stability, the pair of electrons in the C-H bond moves back into the ring.
- overall there is substitution of hydrogen.