

AROMATIC CHEMISTRY

113 - Term 1

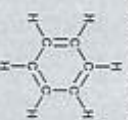
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BONDING

Benzene is a compound with a ring of six carbons, each with a hydrogen attached. It has the formula C_6H_6 .

KEKULÉ STRUCTURE

Kekulé proposed that the structure of benzene involved three double bonds, like this:

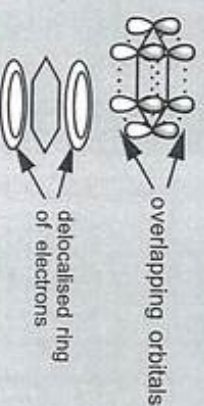


PLANAR STRUCTURE

You can see the structure is planar, with the delocalised electrons above and below the ring.

p-ORBITAL OVERLAP

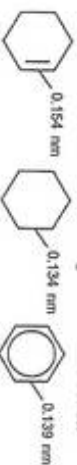
There are six delocalised electrons in the benzene π -system. This is formed when the six p-orbitals overlap, forming a ring above and below the ring of carbon atoms.



EVIDENCE FOR THE DELOCALISED STRUCTURE

BOND LENGTH

The bond lengths in benzene are all the same, and between the bond lengths of an alkane and an alkene. This suggests that the bonds are somewhere between single and double bonds.



RESISTANCE TO REACTION

Most molecules with carbon-carbon double bonds will react easily with molecules such as HBr and Br_2 , but benzene does not. Benzene's resistance to reaction is evidence that benzene has a delocalised structure, giving it extra stability. Benzene's low reactivity with electrophiles is due to the low electron density in the bonds compared to alkenes; electrons are more spread out and so electrophiles are not as attracted.

ELECTROPHILIC SUBSTITUTION

ENTHALPY OF HYDROGENATION

A second piece of evidence is that the delocalised model matches the enthalpy of hydrogenation data.

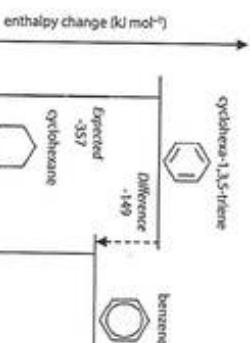
The enthalpy of hydrogenation of cyclohexene is -119 kJ mol^{-1} .



Chemists predicted that the enthalpy of hydrogenation would be $3 \times -119 = -357 \text{ kJ mol}^{-1}$.



The actual enthalpy of hydrogenation is -208 kJ mol^{-1} . Benzene is **149 kJ mol⁻¹ more stable than predicted**. This is due to the stability of the delocalised ring.

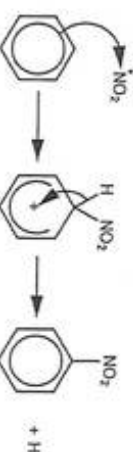


NITRATION

This reaction converts benzene into nitrobenzene, using concentrated nitric acid as a reagent and concentrated sulfuric acid as a catalyst.

1. The nitronium ion (NO_2^+) is formed from nitric acid and sulfuric acid:
 $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$

2. The nitronium ion attacks the benzene ring:



3. The catalyst is reformed:



AROMATIC

Aromatic nitro groups are reduced by tin and concentrated hydrochloric acid to form an aromatic amine group.

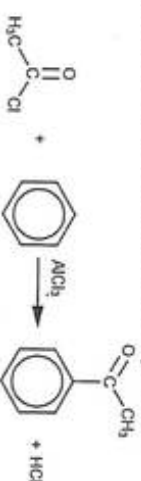


USES OF AROMATIC NITRO COMPOUNDS

Aromatic nitro compounds can be used to make explosives such as TNT, or reduced to make aromatic amines which are used to make dyes (azo dyes).

FRIEDEL-CRAFTS ACYLATION

These reactions add a carbonyl group to a benzene ring. These reactions are important because they involve forming a $C-C$ bond, which is used in synthesis of organic compounds. An aluminium catalyst is used.



SUBSTITUTION VS ADDITION

Benzene undergoes a substitution reaction rather than addition reactions, as addition reactions would break up the stable delocalised ring.

