

Benzene : Aromatic Hydrocarbons / Arenes

There are two major classes of organic chemicals
aliphatic : straight or branched chain organic substances
aromatic or arene: includes one or more ring of six carbon atoms with delocalised bonding.

All of the organic substances we have looked at so far have been aliphatic

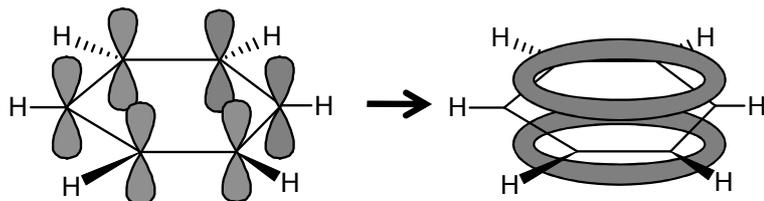
Benzene belongs to the aromatic class.

Benzene's Structure

The simplest arene is benzene. It has the molecular formula C_6H_6
Its basic structure is six C atoms in a hexagonal ring, with one H atom bonded to each C atom

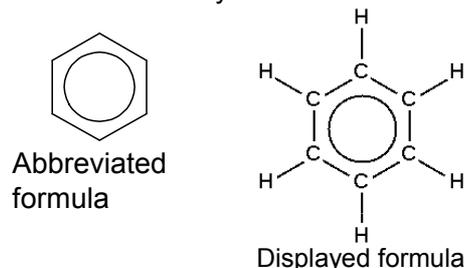
Each C atom is bonded to two other C atoms and one H atom by single covalent σ -bonds. This leaves one unused electron on each C atom in a p orbital, perpendicular to the plane of the ring.

The Six p electrons are delocalised in a ring structure above and below the plane of carbon atoms



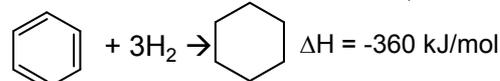
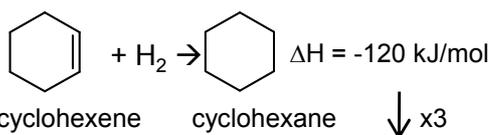
Benzene is a planar molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond

In formulae we draw a circle to show this delocalised system

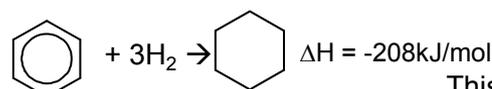


The six electrons in the pi bonds are delocalised and spread out over the whole ring. Delocalised means not attached to a particular atom.

Enthalpies of hydrogenation



Non delocalised structure

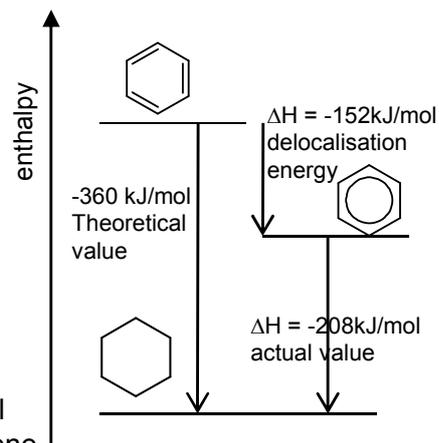


delocalised structure

Theoretically because there are 3 double bonds one might expect the amount of energy to be 3 times as much.

However, the real amount of energy is less. The 6 pi electrons are delocalised and not arranged in 3 double bonds

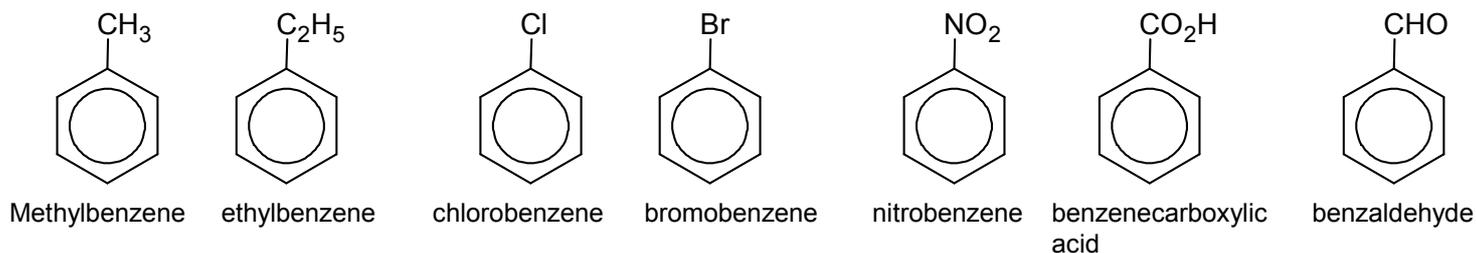
This when represented on an energy level diagram shows that the delocalised benzene is more thermodynamically stable.



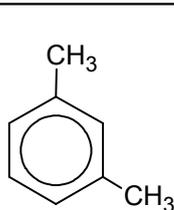
The increase in stability connected to delocalisation is called the **delocalisation energy**

Naming aromatic molecules

Naming aromatic compounds can be complicated. The simplest molecules are derivatives of benzene and have benzene at the root of the name



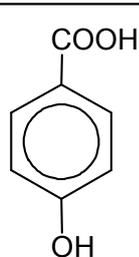
If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes should be used.



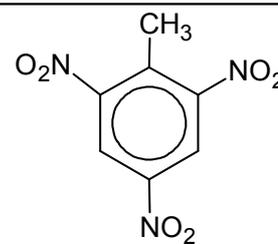
1,4-dimethylbenzene



1-chloro-4-methylbenzene

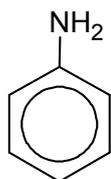


4-hydroxybenzenecarboxylic acid

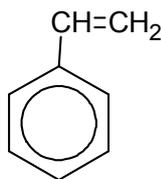


2,4,6-trinitrotoluene

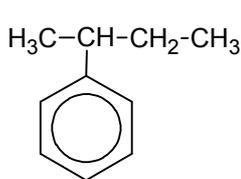
In other molecules the benzene ring can be regarded as a substituent side group on another molecule, like alkyl groups are. The C_6H_5- group is known as the **phenyl** group.



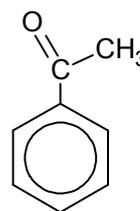
phenylamine



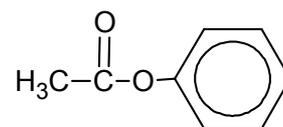
phenylethene



2-phenylbutane



phenylethanone



phenylethanoate

Reactions of Benzene

Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised system. Most of Benzene's reactions involve substituting one H for another atom or group of atoms. Benzene has a high electron density and so attracts electrophiles. Its reactions are usually **electrophilic substitutions**

Toxicity of Benzene

Benzene is a carcinogen (cancer causing molecule) and is banned for use in schools.

Methylbenzene is less toxic and also reacts more readily than benzene as the methyl side group releases electrons into the delocalised system making it more attractive to electrophiles

Nitration of Benzene

Change in functional group: benzene \rightarrow nitrobenzene

Reagents: conc nitric acid in the presence of concentrated sulphuric acid (catalyst)

Mechanism: Electrophilic Substitution

Electrophile: NO_2^+

Importance of this reaction

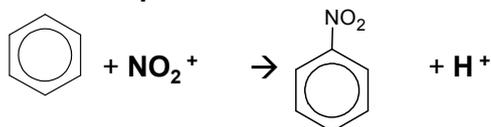
Nitration of benzene and other arenes is an important step in synthesising useful compounds

e.g. explosive manufacture (like TNT, trinitrotoluene/2,4,6-trinitrotoluene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

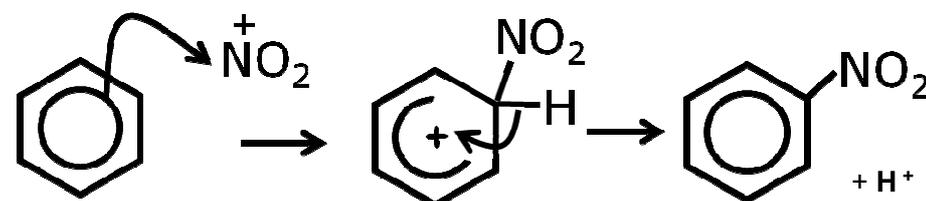
Equation for Formation of electrophile: (Learn!)



Overall Equation for reaction



Mechanism



The horseshoe shape of the intermediate must not extend beyond C's 2 to 6

The H^+ ion rejoins with the HSO_4^- to reform H_2SO_4 catalyst.

This reaction is done at $60^\circ C$. On using higher temperatures a second nitro group can be substituted.

Friedel Crafts acylation

Change in functional group: benzene → phenyl ketone

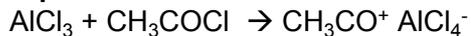
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst

Conditions: heat under reflux (50°C)

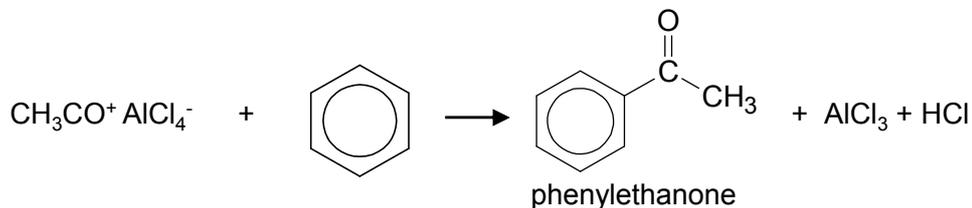
Mechanism: Electrophilic Substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. $-\text{CH}_3$, $-\text{C}_2\text{H}_5$. The electrophile is the RCO^+ .

Equation for Formation of the electrophile.



Overall Equation for reaction



These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism

