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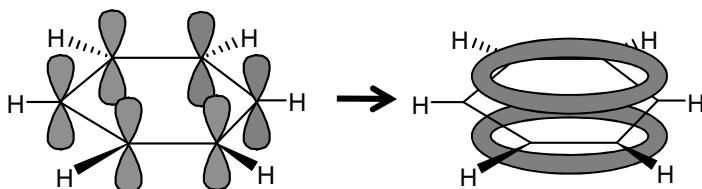
Benzene is a **planar** molecule. The evidence suggests all the C-C bonds are the same and have a length and bond energy between a C-C single and C=C double bond.

In formulae draw a circle to show the delocalised system.


Abbreviated formula
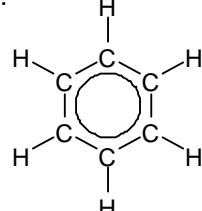
Displayed formula

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

The H-C-C bond angle is 120° in benzene

Using enthalpies of hydrogenation to show thermodynamic stability

cyclohexene   cyclohexane   ↓ x3

ΔH = -120 kJ/mol

ΔH = -360 kJ/mol

Non delocalised structure

ΔH = -208kJ/mol

delocalised structure
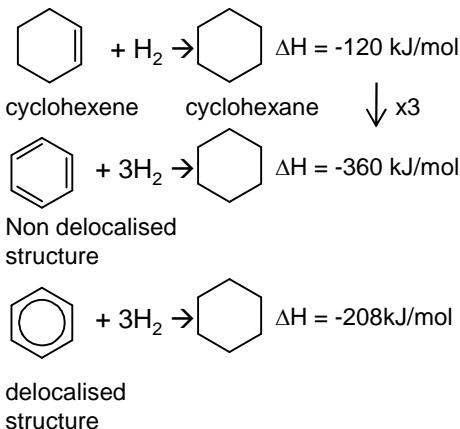
Theoretically because there are 3 double bonds in the theoretical cyclohexa-1,3,5-triene one might expect the amount of energy to be 3 times as much as cyclohexene.

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


enthalpy

ΔH = -152kJ/mol delocalisation energy

-360 kJ/mol Theoretical value

ΔH = -208kJ/mol actual value

The increase in stability connected to delocalisation is called the **delocalisation energy.**
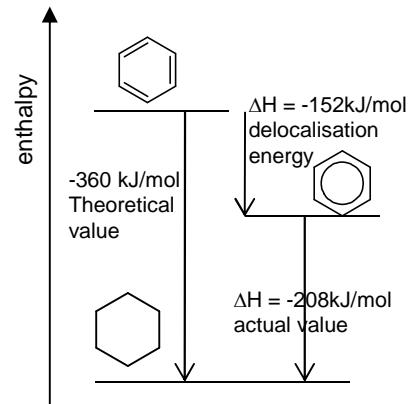
This when represented on an energy level diagram shows that the delocalised benzene is more thermodynamically stable than the theoretical structure.
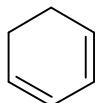

In cyclohexa-1,3-diene, there would be some delocalisation and extra stability as the pi electrons are close together and so overlap. The hydrogenation value would be less negative than -240 kJ mol⁻¹ (showing more stable)
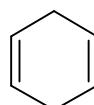
In cyclohexa-1,4-diene, there would not be delocalisation as the pi electrons are too far apart and so don't overlap. The hydrogenation value would be -240 kJ mol⁻¹

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
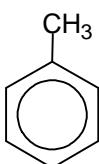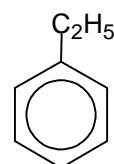
CH_3	C_2H_5	Cl	Br	NO_2	CO_2H	CHO
Methylbenzene	ethylbenzene	chlorobenzene	bromobenzene	nitrobenzene	benzenecarboxylic acid	benzaldehyde
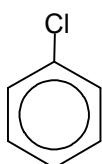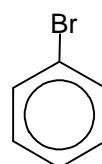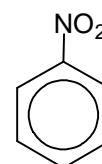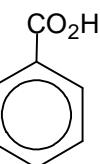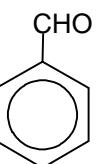
If two or more substituents are present on the benzene ring, their positions must be indicated by the use of numbers. This should be done to give the lowest possible numbers to the substituents. When two or more different substituents are present, they are listed in alphabetical order and di, tri prefixes should be used.
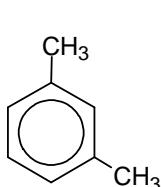
1,3-dimethylbenzene
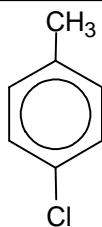
1-chloro- 4-methylbenzene
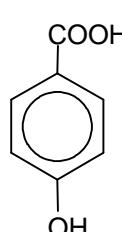
4-hydroxybenzenecarboxylic acid
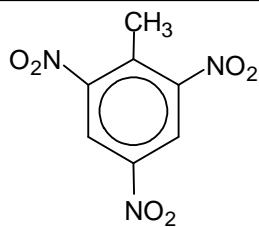
2-methyl-1,3,5-trinitrobenzene

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.
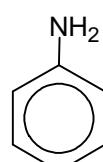
phenylamine
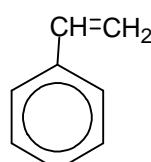
phenylethene
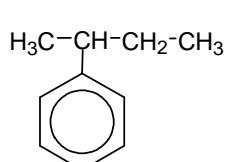
2-phenylbutane
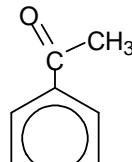
phenylethanone
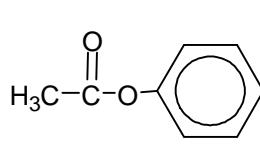
phenylethanoate
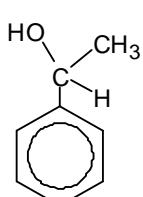
1-phenyl ethan-1-ol
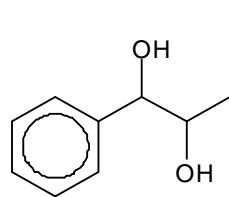
1-phenyl propane-1,2-diol
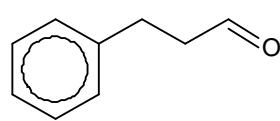
3-phenylpropanal

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 hydrogen for another atom or group of atoms. Benzene has a high electron density and so attracts electrophiles. It reactions are usually **electrophilic substitutions.**

Toxicity of benzene
Benzene is a carcinogen (cancers 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 → nitrobenzene
Reagents: conc nitric acid in the presence of concentrated sulfuric 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-methyl-1,3,5-trinitrobenzene) and formation of amines from which dyestuffs are manufactured. (The reaction for this is covered in the amines section.)

Overall equation for reaction
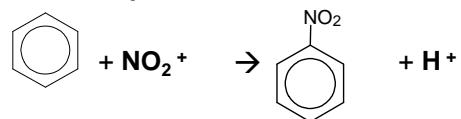
Formation of the electrophile

Overall equation for formation of the electrophile:
$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
This is an acid base reaction.

The mechanism for the formation of the electrophile occurs in two steps.

In the first step the HNO_3 acts as a base and accepts a proton (hydrogen ion) from the sulfuric acid

The intermediate then loses a water molecule leaving the electrophile $^+NO_2$
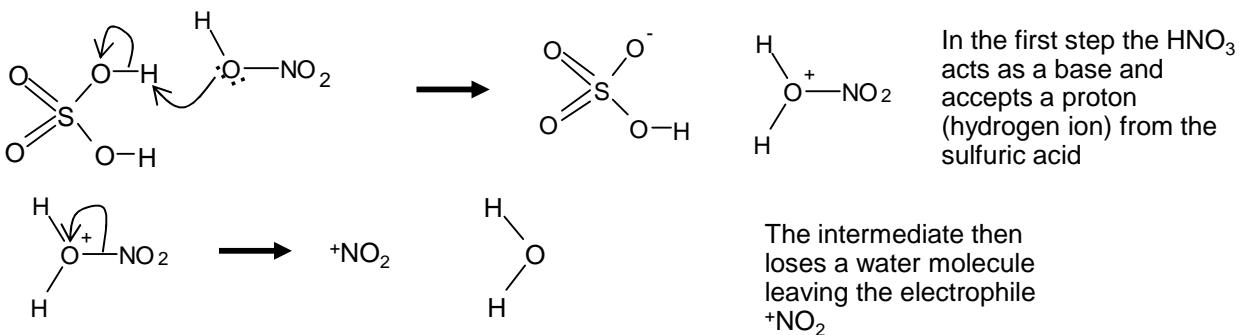
Mechanism
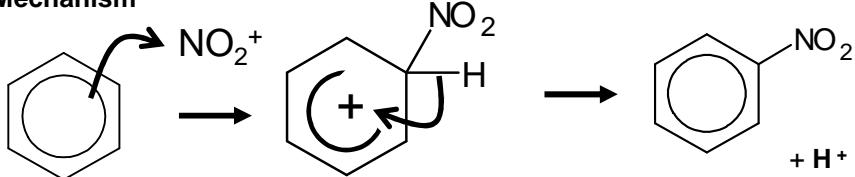
The horseshoe shape of the intermediate must not extend beyond C's 2 to 6

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

This reaction with benzene is done at 60°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 ($50^{O}C$)
Mechanism: Electrophilic substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. $-CH_3$, $-C_2H_5$. The electrophile is the RCO^+.

Equation for formation of the electrophile.
$AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ AlCl_4^-$

Overall equation for reaction

$CH_3CO^+ AlCl_4^-$ + [benzene] $\longrightarrow$ [phenylethanone structure] C—CH_3 + $AlCl_3$ + HCl

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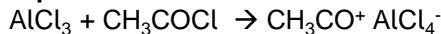
These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring

Mechanism
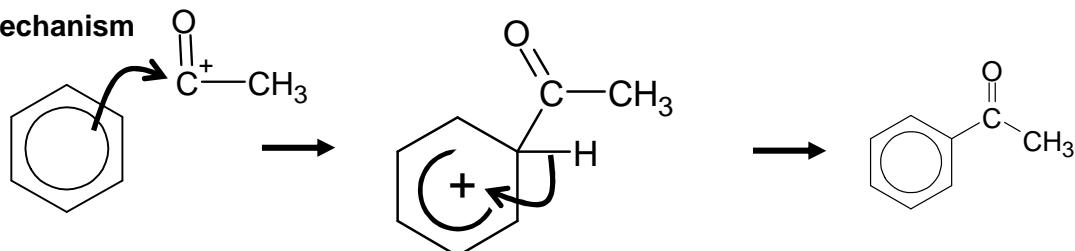
The H^+ ion reacts with the $AlCl_4^-$ to reform $AlCl_3$ catalyst and HCl.

$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Reducing a nitroarene to aromatic amines

The nitro group on an arene can be reduced an amine group as follows

Reagent: Sn and HCl or Fe and HCl
Conditions: Heating
Mechanism: reduction

[nitrobenzene structure] NO_2 + 6[H] $\Rightarrow$ [phenylamine structure] NH_2 + $2H_2O$

nitrobenzene   phenylamine
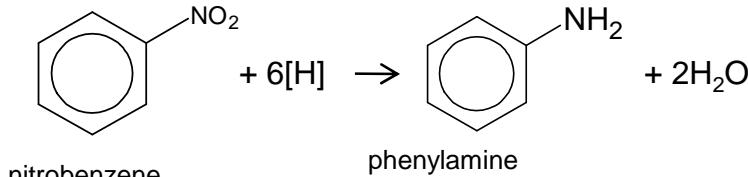
This reduction reaction can also be done with catalytic hydrogenation (H_2 using a Ni catalyst)

As the reaction is carried out in HCl, the ionic salt $C_6H_5NH_3^+Cl^-$ will be formed, which is soluble in water. Reacting this salt with NaOH will give the insoluble phenylamine.

Effect of delocalisation on side groups with lone pairs

If a –OH group, a Cl atom or an NH_2 group is directly attached to a benzene ring the delocalisation in the benzene ring will extend to include the lone pairs on the N,O and Cl. This changes the properties and reactions of the side group.

Cl

chlorobenzene

OH

phenol

NH_2

phenylamine
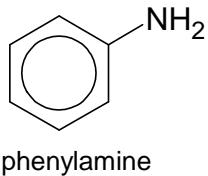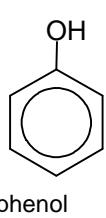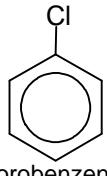
The C-Cl bond is made stronger. Typical halogenoalkane substitution and elimination reactions do not occur. Also the electron rich benzene ring will repel nucleophiles.

Delocalisation makes the C-O bond stronger and the O-H bond weaker. Phenol does not act like an alcohol- it is more acidic and does not oxidise.

Less basic than aliphatic amines as lone pair is delocalised and less available for accepting a proton.

Aromatic Synthetic Routes

Remember that many questions about aromatic compounds will actually be about normal aliphatic reactions of the side chains and not about the benzene ring.