

# Benzene

N Goalby  
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## Aromatic Hydrocarbons or Arenes: Benzene and Phenol

There are two major classes of organic chemicals

1. aliphatic : straight or branched chain organic substances
2. 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

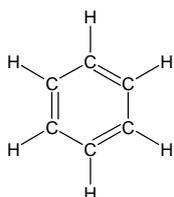
Benzene belongs to the second class.

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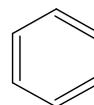
## The simplest arene is benzene

Benzene has the molecular formula  $C_6H_6$

In 1865 Kekule suggested the following structure for Benzene consisting of alternate single and double covalent bonds between the carbon atoms



Structural formula showing kekule structure



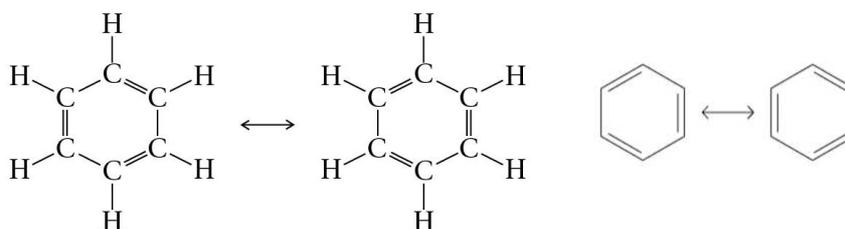
Abbreviated formula showing kekule structure

This structure is not correct. Evidence suggests that all the C-C bonds are the same.

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## Resonance hybrids of Benzene.

Resonance structures are one way of describing the bonding in Benzene



Resonance structures have the same atomic structure but different placement of double bonds, single bonds, and non-bonding electrons. **The structure does not switch back and forth between the two forms.** Rather, the true structure is a hybrid of the two forms: A *Resonance hybrid*.

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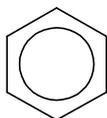
## Delocalised structure of Benzene

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

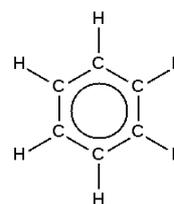
Explanation: Six Pi electrons are delocalised in a ring structure above and below the plane of carbon atoms

We draw a circle to show this delocalised system

Abbreviated formula showing delocalised bonding



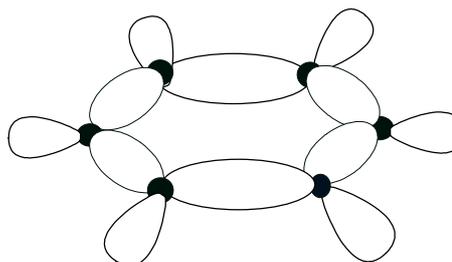
Structural formula showing delocalised bonding



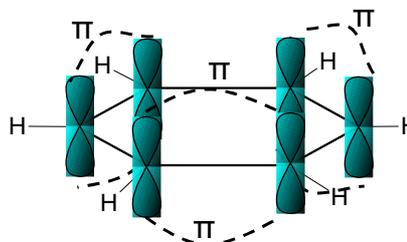
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## Orbitals in benzene: explaining its structure

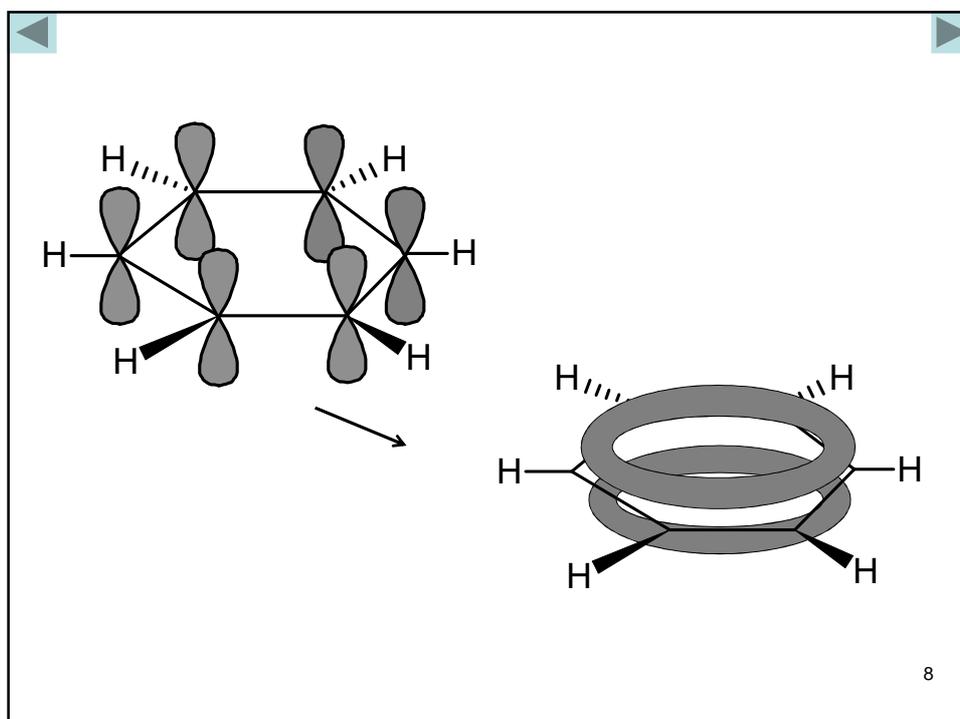
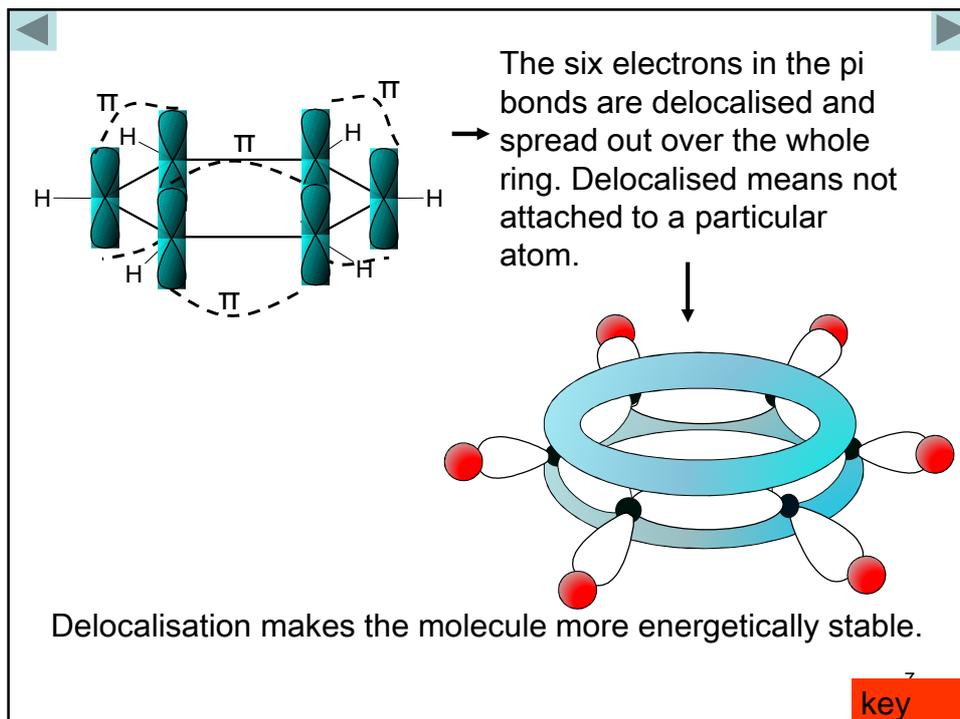
The  $\sigma$  electrons are arranged hexagonally in the same plane



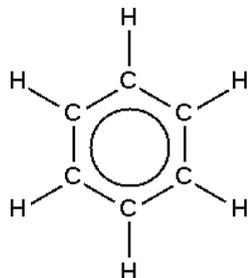
The six  $\pi$  electrons are arranged in orbitals above and below this plane



background



## Effect of delocalisation on bond length



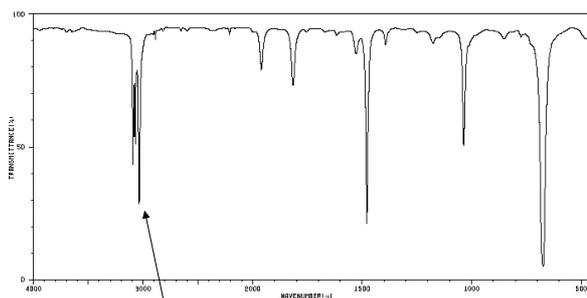
Kekule's structure shows alternate double and single bonds. In theory the bonds would have different lengths. (Double bonds would be shorter than single bonds)

In delocalised bonding, the bonds length are all the same at 0.14nm (half way between C-C and C=C).

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## IR Spectrum

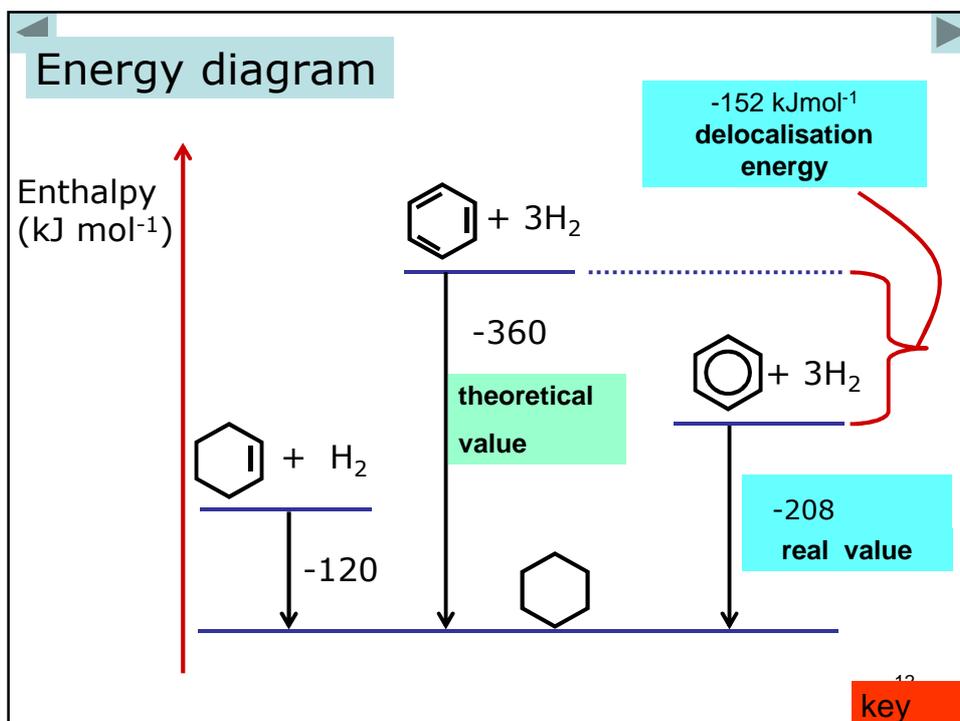
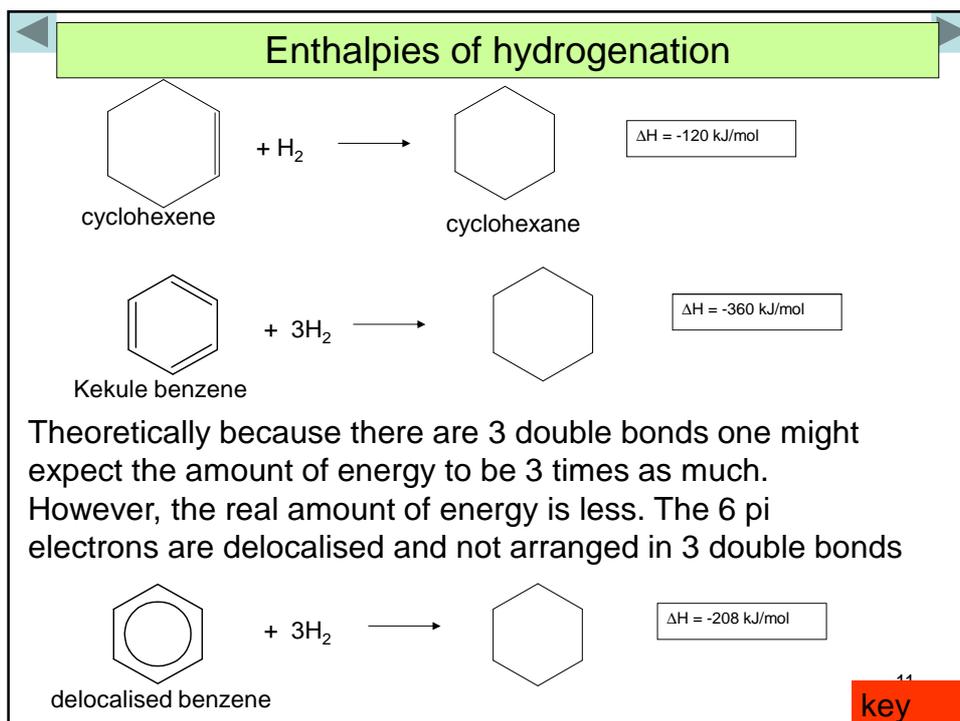
The IR spectrum for benzene also suggests that the molecule is delocalised.



C-H absorption in alkenes occurs at about  $3100\text{cm}^{-1}$  whilst C-H absorption in alkanes occurs just under  $3000\text{cm}^{-1}$ .

In benzene, C-H absorption occurs at  $3030\text{cm}^{-1}$

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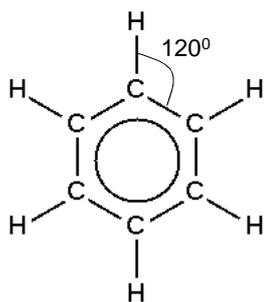
- The C-C bond lengths are all the same in benzene. If it was not delocalised one would expect the 3 C=C bond lengths to be shorter than the 3 C-C bond lengths.
- When benzene reacts the ring of delocalised electrons stays intact and does not get broken up because this would result in the loss of the stability.
- Benzene does not generally undergo addition reactions because these would involve breaking up the delocalised pi bonds. Most of Benzene's reactions involve substituting one H for another atom or group of atoms.

Most reactions of benzene are electrophilic substitutions

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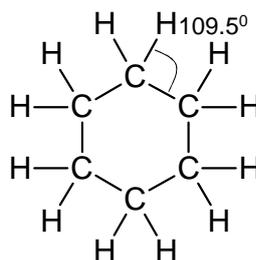
## Bond Angles

What is the H-C-C bond angle in Benzene  $C_6H_6$  and cyclohexane  $C_6H_{12}$ ?



Benzene  $C_6H_6$

$120^\circ$



cyclohexane  $C_6H_{12}$

$109.5^\circ$

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## Hazards of Benzene

We do not use benzene in the laboratory because : it is carcinogenic (causes cancer), and chemicals like methyl benzene react more readily (and are not carcinogenic).

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## Nitration of Benzene

**Change in functional group:** benzene → nitrobenzene

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

**(Conditions:** 60°C with constant agitation since the reactants are immiscible.)

**Mechanism:** Electrophilic Substitution

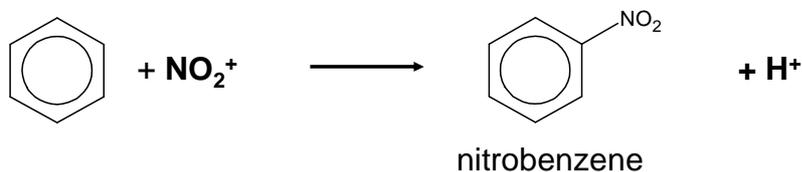
**Electrophile:**  $\text{NO}_2^+$

**Formation of electrophile:**



(When adding two concentrated acids together the reaction is highly exothermic and the mixture should be cooled and one acid should be added dropwise to the other.)

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On using higher temperatures than 60°C a second nitro group can be substituted. key

The H<sup>+</sup> ion rejoins with the HSO<sub>4</sub><sup>-</sup> to reform H<sub>2</sub>SO<sub>4</sub> catalyst.

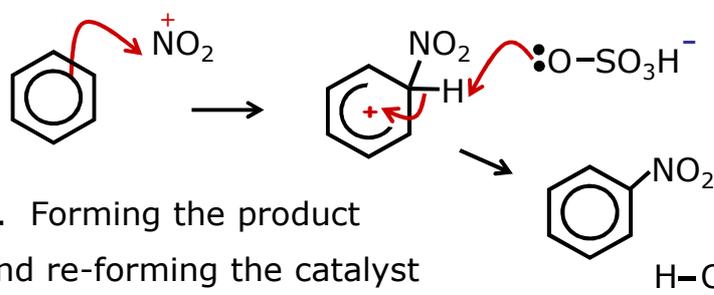
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### electrophilic substitution mechanism (nitration)

1. Formation of NO<sub>2</sub><sup>+</sup> The **nitronium ion**



2. Electrophilic attack on benzene



3. Forming the product and re-forming the catalyst



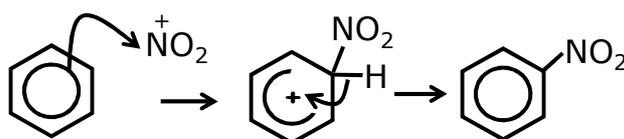
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### electrophilic substitution mechanism (nitration)

1. Formation of  $\text{NO}_2^+$  the **nitronium ion**



2. Electrophilic attack on benzene



3. Forming the product

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

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### Uses of aromatic nitro compounds

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

e.g. explosive manufacture (like TNT, trinitrotoluene/ 2,4,6-tri nitro methyl benzene)

and formation of amines from which dyestuffs are manufactured.  
(The reaction for this is covered in the amines section.)

## Effect of side groups on reactivity

Side groups can either withdraw or push electrons into the ring of electrons.

This can affect the reactivity of benzene (and change the position that the attacking species add on to the benzene ring). Electron rich side groups eg  $\text{CH}_3$  and  $\text{OCH}_3$  and  $\text{OH}$  add electrons to the ring of electrons.

The oxygen has a lone pair of electrons which joins in with delocalised electrons in the benzene ring. Benzene then becomes more reactive to electrophilic substitution reactions.

Therefore methoxy benzene undergoes the substitution reactions of benzene with less severe conditions than pure benzene (lower temps, less concentrated reagents)

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## Friedel Crafts Acylation

**Change in functional group:** benzene  $\rightarrow$  phenyl ketone

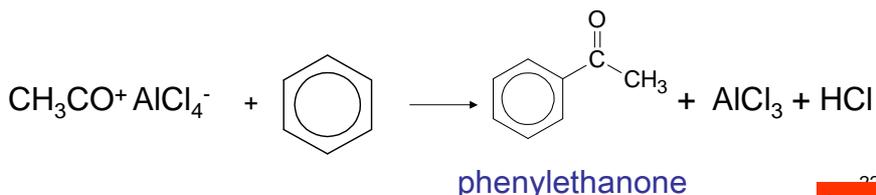
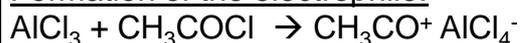
**Reagents:** acyl chloride in the presence of anhydrous aluminium chloride catalyst

**Conditions:** heat under reflux ( $50^\circ\text{C}$ )

**Mechanism:** Electrophilic Substitution

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

Formation of the electrophile.



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**Acylation electrophilic substitution mechanism**

1. Formation of the electrophile.  
 $\text{AlCl}_3 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO}^+ \text{AlCl}_4^-$
2. Electrophilic attack on benzene

3. Forming the product and re-forming the catalyst

phenylethanone

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**Acylation electrophilic substitution mechanism**

1. Formation of the electrophile.  
 $\text{AlCl}_3 + \text{CH}_3\text{COCl} \rightarrow \text{CH}_3\text{CO}^+ \text{AlCl}_4^-$
2. Electrophilic attack on benzene

3. Forming the product

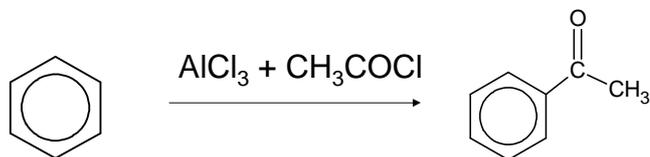
phenylethanone

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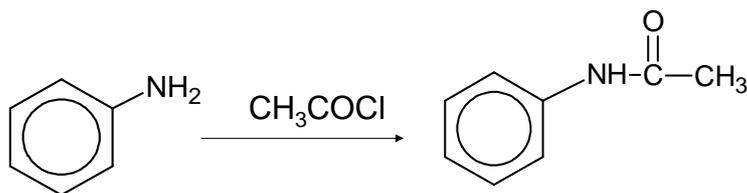
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## Acylation



This is Friedel-Crafts acylation. It is a reaction of the benzene ring



This is acylation but NOT Friedel-Crafts acylation. It is a not reaction of the benzene ring but of the amine group