29.3 SHAPE OF AROMATIC MOLECULES

Learning outcomes

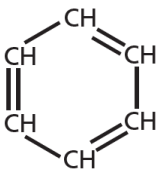
Candidates should be able to:

1. Describe and explain the shape of benzene and other aromatic molecules, including sp^2 hybridisation, in terms of σ bonds and a delocalised π system

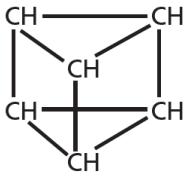
Introduction

Structure of Benzene

Arenes are hydrocarbons that contain one or more benzene rings. Benzene was first isolated and identified by the English chemist Michael Faraday in 1825. Its structure posed a problem for nineteenth-century chemists. Comparing its molecular formula, C_6H_6, with that of the alkane hexane, C_6H_{14}, it can be seen that benzene is highly deficient in hydrogen. Other compounds with very low hydrogen-to-carbon ratios were all known to be highly unsaturated, containing many C=C double bonds: they readily decolourise $KMnO_4(aq)$ and $Br_2(aq)$, and react with HBr, and with H_2O in the presence of acids. Benzene showed none of these reactions. Furthermore, it was apparent that all six hydrogen atoms in benzene were equivalent to each other, in that only one isomer of chlorobenzene, C_6H_5Cl, could be made. There were three isomers of dichlorobenzene, $C_6H_4Cl_2$, however. No open-chain structure would show these properties, but several structures containing rings were suggested in the 1860s. Those proposed by the German chemists August Kekulé and Albert Ladenburg are shown in Figure

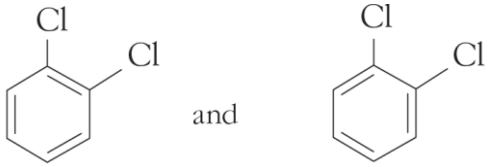


Kekule's structure
(1865)



Ladenburg's structure
(1869)

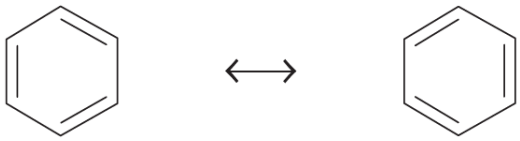
If two hydrogens are replaced by chlorines, to form dichlorobenzene, it is found that three (and only three) isomers of $C_6H_4Cl_2$ can be made. Although this fitted with Ladenburg's structure, Kekulé's structure did not quite account for this observation; his proposed structure implied that there should be two isomers of 1,2-dichlorobenzene:



In fact, there is only one 1,2-dichlorobenzene. To overcome this disagreement with his structure, Kekulé proposed that the bonding in the benzene ring alternated between two equivalent structures:

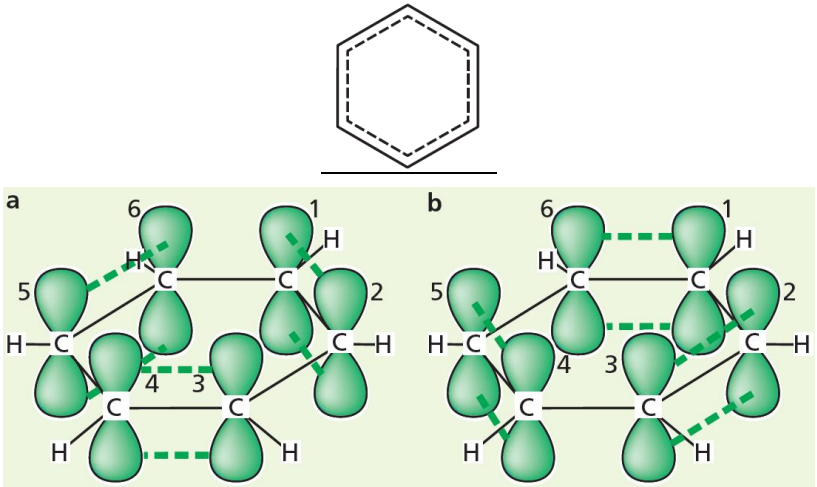
Now that we accept that p electrons can become delocalised in many-atom p orbitals, formed by the overlapping of p orbitals on adjacent atoms, we have no need to postulate this alternation between the two Kekulé forms. The true bonding in benzene has sometimes been described as being in between the two extremes represented by the two Kekulé forms.

We represent this 'in-between' state by a double-headed arrow joining the two formulae:

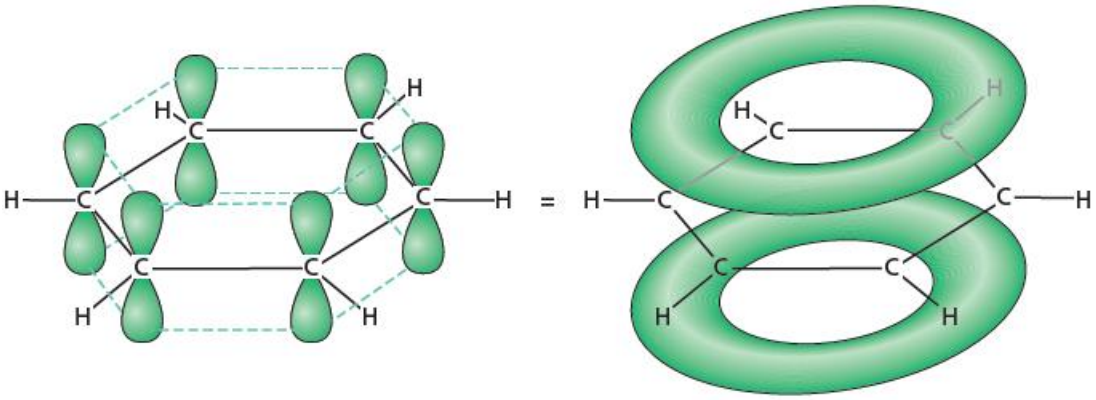


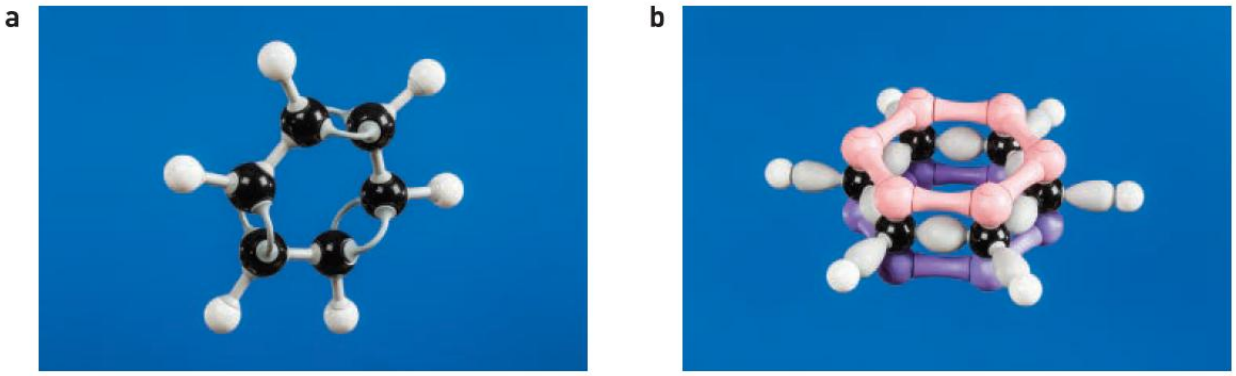
It is important to understand the meaning of the double-headed arrow, ↔. This states that there is *only one* structure, which is in between the two 'classical' structures drawn either side of the arrow. The existence of a structure which cannot be represented by a single 'classical' structure, but which is intermediate between several of them, is known as **mesomerism** (from the Latin/Greek work *meso*, meaning 'middle'). The classical structures are called **mesomers**.

An early representation of the mesomeric structure of benzene was proposed by the German chemist Johannes Thiele in 1899; this is very similar to the delocalised structure we draw today.



▲ **Figure 27.4** Alternative views of bonding between carbon pairs in benzene





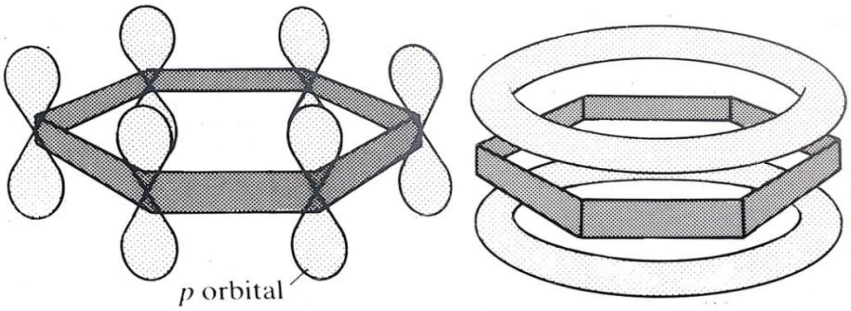
[Benzene structure explained for OCR A level Chemistry]

[Resonance in Chemistry Explained in Simple Words with Examples]

Electron Delocalization in Benzene

The extra stability of benzene and the fact that its C-C bonds are all of equal length can be explained using the following model, which is currently accepted by most chemists.

The carbon atoms in the ring are bonded to one another and their hydrogen atoms by σ-bonds. This leaves one unused p orbital on each carbon, each containing a single electron. The p orbitals are perpendicular to the plane of the ring, with one lobe above and one below this plane (Figure -1). Each p orbital overlaps sideways with the two neighbouring orbitals to form a single π-bond that extends as a ring of the charge above and below the plane of the molecule (Fig.-2)



a: σ-bonded skeleton (C & H Atoms omitted for clarity)

b: σ- skeleton with π- bonds

Fig 1: Bonding in benzene (Plane of the molecules is Perpendicular to the paper)

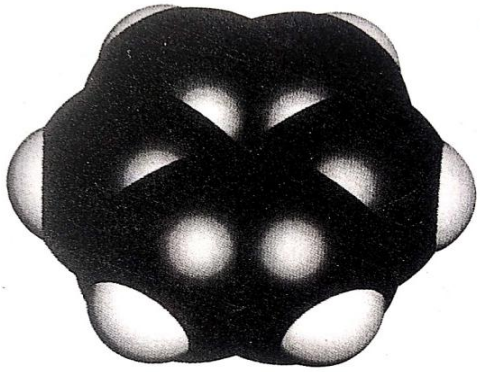


Fig 2: Computer-generated model of the benzene molecule (Planar symmetrical shape)

The electrons in the π-bond cannot be said to 'belong to' any particular carbon atom. Each electron is free to move throughout the entire π-system, so the electrons are said to be ***delocalized.*** *It is this delocalization that gives benzene its extra stability; any system in which electron delocalization can occur is stabilized. The reason for this is not hard to see. Electrons tend to repel one another, so a system in which they are as far apart as possible will involve minimum repulsion and will therefore be stabilized.*

To conform with this model, the structural formula of benzene is nowadays often written as  *rather than*  *.*
The delocalization of π-electrons has a profound effect on the chemical properties of benzene.

The word aromatic is used to describe any system that is stabilized by a ring of delocalized π- electrons. Non-aromatic compounds (such as alkanes and alkenes) are called aliphatic.

The structure described above means that the benzene molecule is planar, symmetrical, and nonpolar. Its lack of polarity results in benzene being a liquid at room temperature and makes it immiscible in water. Its boiling point is 80 °C and its melting point 6^{0}C. The surprisingly high melting point is due to the ease with which highly symmetrical benzene rings can pack into a crystal lattice. Compare it with that of the structurally similar but less symmetrical compound methyl benzene $C_6H_5CH_3$, which melts at -95^{0}C.

1. Benzene, C_6H_6, is an aromatic molecule.
   (a) State the C–C–C bond angle and the hybridisation shown by the carbon atoms in benzene.

   bond angle .....

   hybridisation ..... [1]

2. Cumene is an aromatic hydrocarbon used in the synthesis of other useful chemicals.

cumene

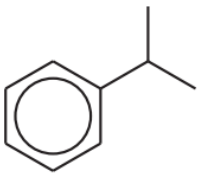


Fig. 5.1

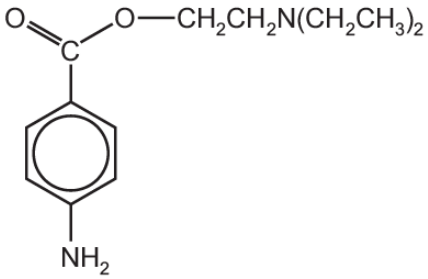
Complete Table 5.1 to show the number of sp2 and sp3 hybridised carbon atoms that are present in a molecule of cumene. [1]

Table 5.1

type of hybridisation	sp^2	sp3
number of carbon atoms		

3. A molecule of procaine has 13 carbon atoms.

procaine



State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in procaine.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ... [1]

4. The compound C_6H_6 has many structural isomers. Four suggested structures of C_6H_6 are shown in Fig. 6.1.

Kekulé benzene Dewar benzene Ladenburg benzene delocalised benzene

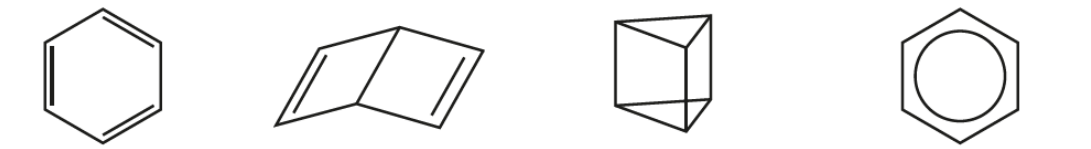


Fig. 6.1

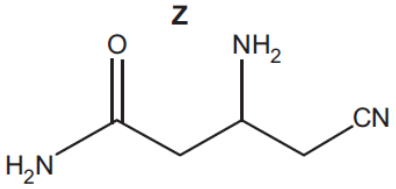
Using Fig. 6.1, complete Table 6.1 to predict the number of carbon atoms that have sp, sp^2 and sp^3 hybridisation in Kekulé benzene, Dewar benzene, and Ladenburg benzene. [2]

Table 6.1

C_6H_6 structure	sp hybridised	sp^2 hybridised	sp^3 hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

5. Compound Z is used in organic synthesis.

Z



Complete Table 6.1 to show the number of sp, sp^2 and sp^3 hybridised carbon atoms present in one molecule of Z.
Table 6.1

Table 6.1

type of hybridisation	sp	sp^2	sp^3
number of carbon atoms			

6. State the bond angles in benzene and cyclohexane.

bond angle in benzene ..... bond angle in cyclohexane .....
Explain your answers.

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..... [2]

7. (i) Describe the shape of delocalised benzene.
Include the geometry of each carbon, the C-C-H bond angle, and the type of bond(s) between the carbon atoms and between the carbon and hydrogen atoms.

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..... [2]

(ii) Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C_6H_6.

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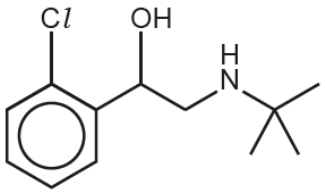
..... [1]

8. Tulobuterol is used in some medicines.

tulobuterol



Tulobuterol contains a benzene ring in its structure.
Describe and explain the shape of benzene.
In your answer, include:
• the bond angle between carbon atoms
• the hybridisation of the carbon atoms
• how orbital overlap forms σ and π bonds between the carbon atoms.

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..... [3]

9. State the hybridisation of the carbon atoms and the C–C–H bond angle in benzene, C_6H_6.
Explain how orbital overlap leads to the formation of σ and π bonds in benzene.

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..... [3]

10. Describe the structure of a benzene molecule, C_6H_6.
Your answer should include:
● the shape of the molecule
● the relative lengths of the C–C bonds
● bond angles
● the hybridisation of the carbon atoms
● the overlap between orbitals that produces each type of bond present.

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..... [4]

11. Describe the bonding in benzene, C_6H_6.
Your answer should include:
• the hybridisation of the six carbon atoms
• the types of bond between the carbon atoms
• the orbitals that overlap to produce the bonds between the carbon atoms
• the type of bond between the carbon atoms and the hydrogen atoms
• the orbitals that overlap to produce the bonds between the carbon atoms and the hydrogen atoms.

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..... [3]

12. Describe and explain the shape of benzene.
In your answer, include:
• the shape and bond angle in the ring
• the hybridisation of the carbon atoms
• how orbital overlap forms σ and π bonds between the carbon atoms in the ring.

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..... [4]

13. The ligand bipyridine consists of two pyridine rings.
Pyridine, C_5H_5N, and benzene, C_6H_6, have similar planar, cyclic structures.

pyridine

Fig. 4.2

By reference to the hybridisation of the carbon atoms and the nitrogen atom, and orbital overlap, suggest how the σ and π bonds are formed in a pyridine molecule.

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..... [3]

14. Pyrazine is an aromatic compound. The bonding and structure of pyrazine is similar to that of benzene.
Describe and explain the shape of pyrazine.
In your answer, include:
- the hybridisation of the nitrogen and carbon atoms
- how orbital overlap forms ***π*** bonds between the atoms in the ring.

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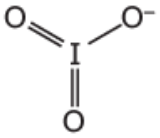
..... [2]

15. Iodates are compounds that contain the IO_3^- anion.
(a) The IO_3– anion is shown.



Explain, with reference to the qualitative model of electron-pair repulsion, why the IO_3^- anion has a pyramidal shape.

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..... [1]

(b) The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate, $NaIO_3$, is formed as one of the products.
Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

..... [1]