A-LEVEL CHEMISTRY • EXERCISE SHEET

29.3 Shape and bonding of benzene

Name: _____ Class: _____ Date: _____ **Total: 21 marks**

KEY WORDS delocalised 离域 • benzene 苯 • hybridisation 杂化 • enthalpy change of hydrogenation 氢化焓变

Objective

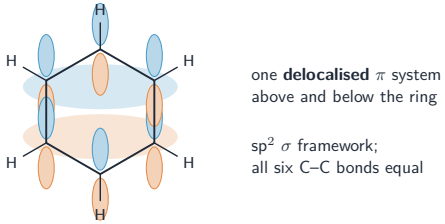
Build the skills to answer exam questions on the **shape and bonding of benzene** 苯的形状与成键 — **sp^2** hybridisation, σ and π bonds, **delocalisation** 离域, and the evidence for it.

You must be able to:

- describe benzene as a planar regular hexagon of sp^2 carbons
- explain the σ framework and the delocalised π system
- use enthalpy of hydrogenation as evidence for delocalisation

1 Worked examples

Bonding and stability



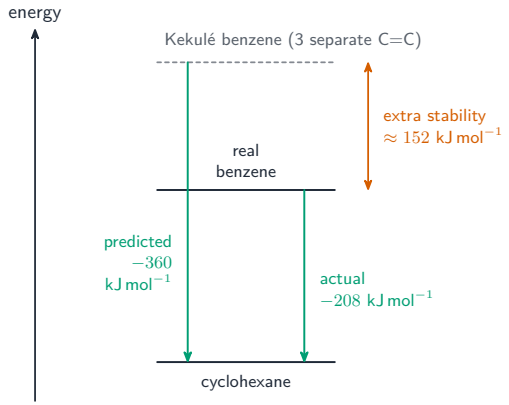
one **delocalised** π system above and below the ring

sp^2 σ framework; all six C–C bonds equal

Each carbon is sp^2: three σ bonds make the flat hexagon; the leftover p orbitals overlap into one delocalised π system

- each C is **sp^2**: three σ bonds (to 2 C + 1 H) in the plane.
- each C keeps one electron in a **p orbital**; these overlap sideways all round → one **delocalised** π ring above and below the plane.
- all six C–C bonds are **equal length** (between single and double); the ring is very stable.

Evidence: enthalpy of hydrogenation



Real benzene releases only 208 $kJ\,mol^{-1}$ vs the Kekulé prediction 360 = 3× cyclohexene → ~152 more stable

The shortfall ($360 - 208 = 152$ kJ mol^{-1}) is the extra stability from delocalisation.

2 Practice

2.1 State the hybridisation of each carbon atom in benzene. [1]

2.2 State what the equal C–C bond lengths in benzene tell you about its bonding. [1]

3 Exam-style questions

3.1 The π system in benzene is formed by the overlap of: [1]

- **A** sp^2 hybrid orbitals
- **B** s orbitals
- **C** p orbitals at right angles to the ring
- **D** sp^3 hybrid orbitals

3.2 Hydrogenation of cyclohexene releases 120 kJ mol^{-1}. The Kekulé model of benzene would predict a hydrogenation enthalpy of about: [1]

- **A** -120 kJ mol^{-1}
- **B** -208 kJ mol^{-1}
- **C** -240 kJ mol^{-1}
- **D** -360 kJ mol^{-1}

3.3 Describe the bonding in benzene, referring to sp^2 hybridisation, the σ framework and the delocalised π system. [3]

3.4 The real enthalpy of hydrogenation of benzene is -208 kJ mol^{-1}; the Kekulé prediction is -360 kJ mol^{-1}. State and explain what this difference shows. [2]

3.5 Benzene is a planar molecule with all six C–C bonds of the same length, 0.139 nm. (C–C in ethane is 0.154 nm; C=C in ethene is 0.134 nm.)

(a) Describe the bonding in benzene in terms of sp^2 hybridisation, σ bonds and π bonds. [4]

(b) Explain how the bond-length data support the delocalised model rather than the Kekulé structure. [2]

(c) The enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1}, and of benzene -208 kJ mol^{-1}. Explain what these values show, with a calculation. [3]

(d) Explain why benzene undergoes substitution rather than addition. [3]

Solutions

2.1 sp^2.

2.2 the bonding is delocalised / identical round the ring (not alternating single and double bonds).

3.1 C. The p orbitals at right angles to the ring overlap sideways to form the delocalised π system.

3.2 D. Three C=C $\times$ 120 = -360 kJ mol^{-1}.

3.3 each carbon is sp^2 hybridised, forming three σ bonds (to two C and one H) in a planar hexagon; each carbon has one electron in a p orbital perpendicular to the ring; these p orbitals overlap sideways all round to give one delocalised π system above and below the plane.

3.4 benzene is about 152 kJ mol^{-1} more stable than the Kekulé model predicts; this extra stability is due to delocalisation of the π electrons.

3.5 (a) Each carbon uses three sp^2 hybrid orbitals, in a plane at 120°; these overlap end-on to form σ bonds to two carbons and one hydrogen, giving the planar hexagonal ring; each carbon keeps one electron in an unhybridised p orbital perpendicular to the ring; these six p orbitals overlap sideways all round the ring, forming a π system **delocalised** above and below the plane.
(b) Kekulé's structure needs alternating single (0.154 nm) and double (0.134 nm) bonds; the measured 0.139 nm is the same for all six and lies **between** the two, which is what a delocalised, evenly shared π system predicts.
(c) Three isolated C=C bonds would give $3 \times (-120) = -360$ kJ mol^{-1}; benzene releases only -208, i.e. 152 kJ mol^{-1} **less**; so real benzene lies 152 kJ mol^{-1} lower in energy than the Kekulé model — the delocalisation (resonance) energy.
(d) Addition would destroy the delocalised π system and lose that stabilisation; substitution replaces a hydrogen and leaves the ring intact; so the substitution route is energetically far more favourable.