

Exercise walk-through

29.3

Shapes of aromatic organic molecules; σ and π bonds

A-Level Chemistry

Why chirality matters for drugs

Two enantiomers

A molecule with a **chiral centre** exists as two enantiomers, and they can behave very differently in the body – one may cure while the other does harm.

Separate them

One route: make the **racemic mixture** and then separate it into the two pure enantiomers – slow, and half the product is wasted.

Or make only one

The better route: a **chiral catalyst** builds just the single enantiomer wanted, so nothing has to be thrown away.

Same formula, same bonds, opposite handedness – and a receptor in the body only fits one of them.

New functional groups at A Level

A **functional group** is the reactive part that names the family and fixes how the molecule behaves. Two join the list:

amide

–CONH₂ – a carbonyl bonded straight to nitrogen; the link in proteins and nylon

aromatic

anything built on a benzene ring, with its delocalised electrons and its own chemistry

As before, name the parent chain, then the substituents – and number so the functional group gets the **lowest** locant.

Worked example – spotting a chiral centre

Explain why lactic acid $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ is optically active but propanoic acid is not.

- Look for one carbon carrying **four different groups**.
- In lactic acid the middle C has CH_3 , OH, COOH and H – all different $\Rightarrow$ a **chiral centre**.
- Its mirror image cannot be superimposed $\Rightarrow$ two **enantiomers**, rotating polarised light oppositely.
- $\text{CH}_3\text{CH}_2\text{COOH}$ has no such carbon (the middle C has two H) $\Rightarrow$ not chiral.

One carbon, **four different groups**. Enantiomers are identical in every physical and chemical property *except* optical rotation and reactions with other chiral molecules.

Exercises 2.1·2.2

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]

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- sp^2

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

2.2

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

Exercise 3.1

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

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3.1 C

- The p orbitals at right angles to the ring overlap sideways to form the delocalised π system

Exercises 3.2-3.3

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]

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3.2 D

- Three $\text{C}=\text{C} \times 120 = -360 \text{ kJ mol}^{-1}$

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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

Exercise 3.4

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]

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- 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

Exercise 3.5 (a)

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]

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- 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

Exercise 3.5 (b)

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.)

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

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- 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

Exercise 3.5 (c)

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(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]

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(c)

- Three isolated C=C bonds would give $3 \times (-120) = -360 \text{ kJ mol}^{-1}$; 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

Exercise 3.5 (d)

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(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