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ANSWER BOOK

Benzene: its structure and the evidence for delocalisation

Aromatic chemistry and amines · Unit C21

AQA 3.3.10.1 · OCR A 6.1.1 (a) to (c), 6.1.1 (h)

18 questions · 61 marks

NAVY EDITION

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SECTION A · Short, 1 to 2 marks

A1 BSE-Q2

B1 cyclohexa-1,3,5-triene, a six-membered ring of alternating single and double bonds; allow cyclohexatriene. **B1** six delocalised electrons, one from the p orbital of each carbon atom. [2]

A2 BSE-Q4

B1 the six p electrons are delocalised evenly around the ring, so every pair of neighbouring carbons shares the same electron density. **B1** there are no separate single and double bonds, so every bond has the same length, between single and double. [2]

SECTION B · Standard, 3 to 5 marks

B1 BSE-Q1

B1 all twelve atoms lie in one plane, the carbons forming a regular hexagon with every bond angle 120°. **B1** all six carbon–carbon bonds are the same length, 140 pm; accept any value from 139 to 140 pm. **B1** the Kekulé structure predicts two lengths in turn, C–C 154 pm and C=C 134 pm, so an uneven hexagon. **B1** 140 pm lies between the single and double bond lengths, so every bond is the same and none is a double bond. [4]

B2 BSE-Q3

B1 each carbon forms σ bonds to two neighbouring carbons and one hydrogen, so the ring is planar with bond angles of 120°. **B1** each carbon has one electron in a p orbital at right angles to the plane of the ring. **B1** each p orbital overlaps sideways with the p orbitals on both neighbouring carbons, giving rings of electron density above and below the plane. **B1** six electrons are delocalised around the whole ring rather than held in three separate double bonds; ignore 'resonance' unless the delocalisation is described. [4]

B3 BSE-Q9

B1 $C_6H_5CH_3$ is named methylbenzene, a methyl group on the ring. **B1** C_6H_5COOH keeps its own name, benzoic acid. **B1** $C_6H_5NH_2$ is named phenylamine, the ring as a phenyl group; allow aminobenzene. **B1** the ring with two chlorines on opposite carbons is 1,4-dichlorobenzene; reject para-dichlorobenzene alone. [4]

B4 BSE-Q14

B1 cyclohexene adds bromine at room temperature, decolourising it, whereas benzene does not react with bromine water. **B1** benzene reacts with bromine only with a halogen carrier, and then by substitution, giving bromobenzene and HBr. **B1** both add hydrogen to give cyclohexane, but benzene releases 208 kJ mol^{-1}, far less than three times cyclohexene's 120 kJ mol^{-1}. **B1** the differences arise because benzene's delocalised ring makes it more stable, and addition would destroy that ring. [4]

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B5 BSE-Q18 **B1** each acid loses a proton from an O–H group, and the more stable the anion formed, the stronger the acid. **B1** in the phenoxide ion a lone pair on oxygen overlaps with the ring, so the negative charge is delocalised over the ring and the ion is stabilised. **B1** in the ethoxide ion the charge stays on one oxygen and the ethyl group releases electron density onto it, so the ion is least stable and ethanol is the weakest acid. **B1** in the ethanoate ion the charge is shared between two electronegative oxygen atoms, which stabilise it more than the ring does, so ethanoic acid is the strongest. [4]

B6 BSE-Q22 **B1** benzene needs pure bromine and a halogen carrier such as $FeBr_3$, whereas phenol reacts with bromine water at room temperature. **B1** benzene gives bromobenzene, one bromine atom substituted, whereas phenol gives a white precipitate of 2,4,6-tribromophenol. **B1** a lone pair on phenol's oxygen is partly delocalised into the ring, raising its electron density above benzene's. **B1** phenol's ring can therefore polarise a bromine molecule itself, whereas benzene needs the carrier to make Br^+. [4]

B7 BSE-Q5 **B1** the C=C bond in cyclohexene is a region of high electron density that polarises Br_2, which adds across the double bond. **B1** in benzene the π electron density is delocalised over six carbons, so it is too low to polarise a bromine molecule. **B1** addition to benzene would destroy the delocalised ring and lose its stability, so no addition takes place; reject 'benzene's double bonds are stronger'. [3]

B8 BSE-Q6 **M1** the Kekulé structure is expected to give 3 × (-120) = -360 kJ mol^{-1}. **M1** difference = -208 - (-360), the measured value minus the expected value. **A1** delocalisation energy = 152 kJ mol^{-1}, benzene being 152 kJ mol^{-1} more stable; allow -152 kJ mol^{-1} if the stabilisation is stated. [3]

B9 BSE-Q12 **B1** the two bond lengths show it has localised single and double bonds, so its electrons are not delocalised round the ring. **B1** each C=C bond is a region of high electron density that can polarise bromine, so it reacts like an alkene. **B1** it reacts by addition, because it has no delocalisation stability to lose when a double bond is used up. [3]

B10 BSE-Q13 **B1** the Kekulé structure predicts two different 1,2-isomers, one with the chlorines across a C=C bond and one across a C–C bond, so four isomers in all. **B1** in the delocalised model every bond is the same, so there is only one 1,2-isomer. **B1** the delocalised model predicts three isomers, 1,2, 1,3 and 1,4, which matches the three found. [3]

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B11 BSE-Q15

B1 the p electrons in benzene are delocalised over six atoms instead of being held in three separate π bonds. **B1** delocalisation lowers the energy of the electrons and so of the molecule. **B1** benzene's enthalpy of hydrogenation is 152 kJ mol^{-1} less exothermic than three times cyclohexene's, showing it starts 152 kJ mol^{-1} lower in energy. [3]

B12 BSE-Q17

B1 the claim explains why only one 1,2-disubstituted isomer is found, which is what it was proposed for. **B1** it cannot explain the 152 kJ mol^{-1} of extra stability, because a molecule with three C=C bonds at any moment would be hydrogenated as three alkenes. **B1** X-ray diffraction shows six equal bonds at all times, so benzene has one delocalised structure and the claim is wrong. [3]

B13 BSE-Q19

B1 a lone pair on the chlorine of chlorobenzene overlaps with the delocalised π system of the ring. **B1** this gives the C–Cl bond partial double-bond character, so it is shorter and stronger than the C–Cl bond in 1-chlorobutane. **B1** the delocalised electrons of the ring also repel the hydroxide ion as it approaches the carbon, so nucleophilic substitution does not happen. [3]

B14 BSE-Q20

B1 add sodium carbonate solution, or solid sodium hydrogencarbonate, to each compound. **B1** benzoic acid fizzes, giving carbon dioxide, because it is strong enough an acid to react with carbonate. **B1** phenol gives no effervescence, because it is too weak an acid to release carbon dioxide; ignore whether it dissolves. [3]

B15 BSE-Q21

M1 $K_a = 10^{-10.0} = 1.0 \times 10^{-10}$ mol dm^{-3}. **M1** $[H^+] = \sqrt{(1.0 \times 10^{-10} \times 0.0250)} = 1.58 \times 10^{-6}$ mol dm^{-3}. **A1** $pH = -\log(1.58 \times 10^{-6}) = 5.80$, to two decimal places; error carried forward from an incorrect $[H^+]$. [3]

SECTION C · Long, 6 marks or more

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C1 BSE-Q7 **Indicative content** [6]

B1 X-ray diffraction shows all six carbon–carbon bonds are 140 pm, whereas Kekulé predicts alternating bonds of 154 pm and 134 pm. **B1** in the delocalised model every pair of neighbouring carbons shares the same electron density, so every bond has one length between single and double. **B1** benzene does not decolourise bromine water at room temperature, whereas a compound with C=C bonds would add bromine at once. **B1** the delocalised electron density is spread over six carbons, too low to polarise bromine, and addition would lose the stability of the ring. **B1** the enthalpy of hydrogenation of benzene is -208 kJ mol^{-1}, far less exothermic than the -360 kJ mol^{-1} expected for three C=C bonds. **B1** delocalising six electrons over the ring lowers the energy of the molecule, so benzene starts about 152 kJ mol^{-1} lower than the Kekulé structure would.

Levels

Level 3 (5–6 marks) all three pieces of evidence are given with the values, bond length, lack of addition with bromine and the enthalpy of hydrogenation, and each is matched to what the delocalised model predicts and the Kekulé structure does not.

Level 2 (3–4 marks) two pieces of evidence are given with values and explained by delocalisation, or all three are named and one is left unconnected to the model.

Level 1 (1–2 marks) one piece of evidence is named, often with benzene said to have stronger double bonds than an alkene, which is offered as the reason it resists addition.

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