

GCE

Chemistry A

Advanced GCE

Unit F324: Rings, Polymers and Analysis

Mark Scheme for June 2012

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All examiners are instructed that alternative correct answers and unexpected approaches in candidates' scripts must be given marks that fairly reflect the relevant knowledge and skills demonstrated.

Mark schemes should be read in conjunction with the published question papers and the report on the examination.

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Annotations

Annotation	Meaning
1.101	Benefit of doubt given
[4:1]	Contradiction
×	Incorrect response
[44]	Error carried forward
	Ignore
NAG	Not answered question
2.200	Benefit of doubt not given
Exit	Power of 10 error
A	Omission mark
NE.	Rounding error
SF	Error in number of significant figures
✓	Correct response

Annotation Meaning	
DO NOT ALLOW Answers which are not worthy of credit	
IGNORE Statements which are irrelevant	
ALLOW	Answers that can be accepted
()	Words which are not essential to gain credit
	Underlined words must be present in answer to score a mark
ECF	Error carried forward
AW	Alternative wording
ORA Or reverse argument	

The following questions should be annotated with ticks, etc. to show where marks have been awarded in the body of the text:

Q1(a), Q3(c)(iii), Q4(a), Q4(d)(i), Q5(b).

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C	uesti	on	Answer	Marks	Guidance
1	(a)		In benzene, electrons OR π-bond(s) are delocalised ✓		ANNOTATIONS MUST BE USED
					ALLOW diagram with (π-bond) electrons
					AND delocalised labelled
			QWC requires delocalised/delocalized spelled correctly		LONG DEL
			and used in correct context		IGNORE benzene has delocalised structure or ring
					ALLOW diagram with π-bond labelled
			In alkenes, Π -electrons are OR Π -bond is		ALLOW pi bond for π-bond
			AND		·
			localised OR between two carbons ✓		π-bond OR $π$ -electrons essential for this mark
					IGNORE charge density
			benzene has a lower electron density		DO NOT ALLOW electronegativity
			OR alkene/C=C has a higher electron density ✓		a contract of the contract of
			Comparison essential		
					ALLOW Br–Br for Br ₂
					ALLOW electrophile for Br ₂
					ALLOW benzene does NOT polarise bromine / Br ₂
			benzene polarises bromine / Br ₂ LESS		OR alkene/C=C polarises Br ₂
					2
			OR benzene attracts bromine / Br ₂ LESS		ALLOW benzene does NOT attract bromine / Br ₂
			ON Benzene attracts bromme / Br ₂ ELSO		OR alkene/C=C attracts Br ₂
					ALLOW benzene does NOT induce dipole in bromine / Br ₂
			OR benzene induces a weaker dipole in bromine / Br₂ ✓	4	OR alkene/C=C induces dipole in Br ₂
				_	

C	uest	ion	Answer	Marks	Guidance
1	(b)	(i)	Br Br H C C H H	1	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous
		(ii)	6 ✓	1	NO ECF from (i)
		(iii)	Two of the three structures below with 1 mark for each correct structure Br B	2	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous Structures must clearly show position of Br on benzene ring
			Br H H C C C H H C C C H		ALLOW ECF from (i) if BOTH Br atoms on same carbon on side chain DO NOT ALLOW ECF from (i) if EITHER bromine has been substituted onto the benzene ring
		(iv)	reaction 1: electrophilic addition ✓		ALLOW electrophile addition
			reaction 2: electrophilic substitution ✓	2	ALLOW electrophile substitution
					ALLOW other phonetic spellings for electrophilic, e.g. electrophylic, etc.
			Total	10	

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Q	uestic	on	Answer	Marks	Guidance
2	(a)	(i)	photodegradable OR light/sunlight/UV ✓	1	IGNORE IR/heat IGNORE bacteria DO NOT ALLOW burn/combustion
		(ii)	но Он 🗸	1	DO NOT ALLOW structure with any C shown (especially as part of C=O) DO NOT ALLOW OH—
	(b)	(i)	ammonia/NH₃ AND ethanol OR ethanolic ammonia ✓	1	ALLOW ammonia in a sealed tube IGNORE heat ALLOW dilute ethanolic ammonia /NH ₃ DO NOT ALLOW any reference to water or hydroxide ions, e.g. DO NOT ALLOW dilute ethanolic NH ₃ (aq) e.g. DO NOT ALLOW ethanolic NH ₃ + NaOH
		(ii)	Nitrogen electron pair/lone pair accepts a proton/H ⁺ ✓ Requires position of electron pair on N Cl⁻H₃N⁺(CH₂)₄N⁺H₃Cl⁻ OR ClH₃N(CH₂)₄NH₃Cl ✓	2	DO NOT ALLOW Nitrogen/N lone pair accepts hydrogen proton/H ⁺ required ALLOW nitrogen donates an electron pair IGNORE NH ₂ group donates electron pair ALLOW + charge (if shown) on N or H of NH ₃ e.g. Cl ⁻ H ₃ N ⁺ (CH ₂) ₄ NH ₃ ⁺ Cl ⁻ DO NOT ALLOW just H ₃ N ⁺ (CH ₂) ₄ NH ₃ ⁺ i.e. 2 x Cl ⁻ MUST be included

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Q	uestion	Answer	Marks	Guidance
2	(iii	1 mark for amide/peptide link correctly displayed within an attempted repeat unit ✓		Minimum requirement is each end of a displayed amide group attached to a carbon atom (could be skeletal)
		1 mark for rest of structure correct including side links ✓	2	Brackets not required
				IF more than one repeat unit has been drawn a single repeat unit MUST be identified by brackets or clear label
		$ \begin{array}{c cccc} & \ddot{C} & (CH_2)_4 & \ddot{C} & N & (CH_2)_4 & N & \\ & & & & & & & \\ & & & & & & \\ & & & &$		DO NOT ALLOW 2nd mark if amide/peptide link wrong 1st mark requires amide group fully displayed For 2nd mark, ALLOW –CONH– in correct structure
				ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous e.g.
1				

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ALLOW COO- '-' charge must be on O of COO- but ALLOW + sign shown as +NH ₃ OR NH ₃ + BUT only one NH ₂ can be protonated in zwitterion 2 (ii) Zwitterion at pH 9.60/higher pH has one NH ₂ group OR ALLOW coo- '-' charge must be on O of COO- but ALLOW + sign shown as +NH ₃ OR NH ₃ + BUT only one NH ₂ can be protonated in zwitterion	Q	uestio	n	Answer	Marks	Guidance
OR Zwitterion OR amino acid at pH 9.60/higher pH has a side chain with an NH ₂ group ✓ Note: ALLOW amino acid at 9.60/higher pH has more NH ₂ group ✓ ALLOW amino for NH ₂	2	(c)	(i)	H_{3} N————————————————————————————————————	2	formula ALLOW combination of formulae as long as unambiguous ALLOW COO- '-' charge must be on O of COO- but ALLOW + sign shown as +NH3 OR NH3+
Total 10			(ii)	OR Zwitterion OR amino acid at pH 9.60/higher pH has a side chain with an NH₂ group ✓ Note: ASSUME that 'it' refers to zwitterion		

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C	uest	ion	Answer	Marks	Guidance
3	(a)	(i)	cis-isomer has Hs on same side OR cis-isomer has branches on same side OR cis-isomer has same groups on same side OR cis-isomer has lowest priority groups on same side OR cis-isomer has highest priority groups on same side ✓	2	ALLOW trans-isomer has Hs on opposite sides OR trans-isomer has branches on opposite sides OR trans-isomer has same groups on opposite sides DO NOT ALLOW 'similar groups' for 'same groups' OR trans-isomer has lowest priority groups on opposite sides OR trans-isomer has highest priority groups on opposite sides ✓ For explanation, ALLOW a clear diagram, ie: Cis ALLOW response in terms of packing, e.g. molecules/chains of trans-isomer pack close together OR molecules/chains of cis-isomer do not pack closely together DO NOT ALLOW 'carbon atoms' for 'molecules/chains'
		(ii)	heart disease/strokes ✓	1	ALLOW any named heart/circulatory complaint e.g. atheroma, atherosclerosis ALLOW increase in bad cholesterol/LDL ALLOW high in LDLs ALLOW fat lining arteries ALLOW high blood pressure ALLOW hypertension IGNORE reference to HDLs and cholesterol on its own

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(Quest	ion	Answer	Marks	Guidance
3	(b)	(i)	27	1	
		(ii)	8	1	
	(c)	(i)	alcohol ✓		IGNORE OH OR hydroxyl OR hydroxy
					DO NOT ALLOW phenol OR hydroxide
			ester ✓	2	IGNORE COOR
					IF there is a list with more than two responses, mark wrong responses first, e.g. alcohol, ketone X, ether X zero marks alcohol ✓, ester, methyl X 1 mark ester, hydroxide X, ketone X zero marks ester ✓, hydroxyl I, ketone X 1 mark
		(ii)	ensures correct chirality ✓	1	ALLOW enantiomer for optical isomer
					ALLOW produces only one optical isomer ALLOW stops need/cost/difficulty of separating optical isomers ALLOW stops formation of the optical isomer which may have (harmful) side effects DO NOT ALLOW lower doses/dosage needed DO NOT ALLOW forms one stereoisomer (could be E/Z) DO NOT ALLOW stereoselectivity

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Q	uestion		Answer	Marks	Guidance
3	(iii)				ANNOTATIONS MUST BE USED
		1st step			
		reagent.	NaBH₄ ✓		ALLOW H ₂ /Ni (catalyst) DO NOT ALLOW LiAIH ₄ (because LiAIH ₄ reduces COOH)
		functional groups:	aldehyde forms an alcohol ✓ names required		IGNORE type of reaction or conditions IGNORE CHO OR OH IGNORE carbonyl OR hydroxyl OR hydroxy DO NOT ALLOW phenol OR hydroxide
		2nd step Marks ONLY availab formed in 1st step	le from correct hydroxycarboxylic acid		
		reagent.	Acid OR H⁺ (catalyst) ✓	4	ALLOW named acid/correct formula IGNORE dilute/concentrated
		functional groups:	alcohol and carboxylic acid / carboxyl group form an ester ✓ names required	4	IGNORE OH, COOH, COO, IGNORE hydroxyl OR hydroxy DO NOT ALLOW phenol OR hydroxide
			Total	12	

Question	Answer	Marks	Guidance
	curly arrow from ring curly arrow from ring to NO ₂ * NOte: ALLOW M1, M2 AND M3 for benzene OR ANY substituted benzene compound For M4, credit ONLY the correct products HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR HNO ₃ + 2H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR HNO ₃ + H ₂ SO ₄ \longrightarrow H ₂ SO ₄ \checkmark OR	6	Mark 1 (M1) ALLOW curly arrow from the ring OR from within the ring Mark 2 (M2) – intermediate showing delocalisation over less than 6 carbons with the correct orientation BUT DO NOT ALLOW intermediate with π system less than halfway up: H NO2 Mark 3 (M3) curly arrow from C–H bond reforming π-delocalised ring in benzene ALLOW Kekulé mechanism: NO2 ALLOW double bonds shown in other Kekulé arrangement Mark 4 (M4) BOTH correct products: 3-nitrobenzaldehyde AND H ⁺

	Answer	Marks	Guidance
)	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous
	1 mark for C ₆ H ₅ CH ₂ OH ✓		ALLOW use of NaOH instead of KOH throughout, i.e. $2 C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$
	1 mark for C ₆ H ₅ COOK OR C ₆ H ₅ COOH OR C ₆ H ₅ COO ⁻ ✓		ALLOW C ₆ H ₅ COO ⁻ K ⁺
	1 mark for complete fully correct balanced equation (i.e. as above) ✓	3	
)	С=N—ОН Н		ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous
	С=с-соон		e.g. ALLOW C ₆ H ₅ ——C=—N——OH
			С ₆ H ₅ ——С——СООН Н Н
			C ₆ H ₅ —C—C—C—C—C—C ₆ I
		OR $2 C_6H_5CHO + OH^- \longrightarrow C_6H_5CH_2OH + C_6H_5COO^-$ $1 \text{ mark for } C_6H_5CH_2OH \checkmark$ $1 \text{ mark for } C_6H_5COOK \text{ OR } C_6H_5COOH \text{ OR } C_6H_5COO^- \checkmark$ $1 \text{ mark for complete fully correct balanced equation (i.e. as above)} \checkmark$	OR $2 C_6H_5CHO + OH^- \longrightarrow C_6H_5CH_2OH + C_6H_5COO^-$ $1 \text{ mark for } C_6H_5CH_2OH \checkmark$ $1 \text{ mark for complete fully correct balanced equation (i.e. as above)} \checkmark$ 3

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Q	Question		Answer	Marks	Guidance
4	(d)	(i)			ANNOTATIONS MUST BE USED
			$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		IGNORE connectivity on OH of product
			R		
			1 mark for curly arrow from R ⁻ to C of C=O (lone pair not necessary) ✓		Curly arrow MUST start from – sign of R ⁻ OR from lone pair on R ⁻ lone pair does not need to be shown on R ⁻
			1 mark for correct dipoles on C=O AND curly arrow from double bond to O ^{δ−} ✓		
			1 mark for correct intermediate with – charge on O ✓		IGNORE any curly arrows shown for stage 2 i.e. in intermediate
			1 mark for correct product ✓	4	
		(ii)	Li Li ⁺		ALLOW correct structural OR displayed OR skeletal formula
			CH CH3 OR CH CH3		ALLOW combination of formulae as long as unambiguous
			H_3C CH_2 H_3C CH_2	1	IGNORE C ₄ H ₉ Li OR C ₄ H ₉ ⁻ Li ⁻
			Total	17	

Q	uestic	on	Answer	Marks	Guidance
5	(a)	(i)	(number of esters) from number of peaks/retention times AND		BOTH points for 1 mark
			(proportions) from (relative) peak areas ✓	1	ALLOW peak heights OR sizes of peaks
		(ii)	(Some esters may have) same retention time ✓	1	ALLOW (very) similar retention times ALLOW some esters come out at same time
	(b)		Ester structure 3 marks		ANNOTATIONS MUST BE USED
	(6)		CH ₂ —CH ₂ —O—C—CH ₃ STICKS		ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous NO ECF for structure
			IF there are sticks are shown in CH ₂ CH ₂ OR in CH ₃ DO NOT AWARD when first seen DO NOT ALLOW sticks on the benzene ring, Sticks on benzene ring must be interpreted as methyl groups	3	IF the structure is NOT fully correct, award the following marks: IF ESTER shown AND contains ONE of the following:
			e.g. X O C C C C C C C C C		C_6H_5 OR $CH_3C=O$ OR CH_2CH_2 1 mark ✓ IF ESTER shown AND contains TWO of the following: C_6H_5 OR $CH_3C=O$ OR CH_2CH_2 2 marks ✓ IF ESTER contains C_6H_5 AND CH_2CH_2 BUT ester link is reversed 2 marks ✓ $CH_2-CH_2-CH_2-C-O-CH_3$
			X		DO NOT ALLOW CH ₂ CH ₂ with H on any adjacent Cs e.g. DO NOT ALLOW CH ₂ CH ₂ CH ₃ , CH ₂ CH ₂ CH ₂ , etc. IGNORE any name

Question	Answer	Marks	Guidance
	Mass spectrum		Check back for any responses added to spectrum
	164 linked directly to molecular formula of $C_{10}H_{12}O_2$ OR an ester structure with formula $C_{10}H_{12}O_2 \checkmark$ This direct link could be seen anywhere in the response e.g. 164 is $C_{10}H_{12}O_2$ e.g. $C_{10}H_{12}O_2 = 120 + 12 + 32 = 164$ e.g. $(164 - 44/COO) = 120$; $120 = C_9H_{12}$	1	Credit responses throughout provided that it is clear which peaks are being referred to
	NMR analysis		ALLOW tolerance on δ values: \pm 0.2 ppm Throughout, ALLOW for H: proton OR H ⁺
	QWC Triplet must be spelled correctly and used in correct context Triplet at 2.8 ppm shows an adjacent CH ₂		For adjacent CH ₂ , ALLOW (C) adjacent to 2 Hs
	Triplet at 4.4 ppm shows an adjacent CH₂ ✓		ALLOW There are 2 triplets AND triplet shows an adjacent CH ₂
	Peak at 2.2 shows CH ₃ –C=O OR Peak at 2.2 shows HC–C=O AND 3 Hs of this type OR Peak at 2.2 shows HC–C=O AND adjacent to (C with) no Hs✓		For peak at (δ =) 2.2 ALLOW singlet OR peak labelled 3
	Peak at 7.3 shows 5 aromatic Hs OR shows C ₆ H ₅ ✓ 5Hs required		For peak at $(\delta =)$ 7.3 ALLOW peak labelled 5 OR multiplet OR quintet OR hextet OR heptet
	Peak at 2.8 shows C ₆ H ₅ –C H OR C ₆ H ₅ –C H₂ ✓ Just require C ₆ H ₅ –CH as testing environment here		For peak at (δ =) 2.8 ALLOW triplet at 2.8
	Peak at 4.4 due to HC–O OR H₂C–O ✓ Just require HC–O as testing environment here	5	For peak at (δ =) 4.4 ALLOW triplet at 4.4
	Total	11	

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