



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
L.T.C.D.	Benefit of doubt given
[H=]]	Contradiction
×	Incorrect response
[-{+}_	Error carried forward
	Ignore
	Not answered question
2.162	Benefit of doubt not given
l de su	Power of 10 error
	Omission mark
	Rounding error
SP .	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).

Question	Answer	Marks	Guidance
1 (a)	In benzene, electrons OR π -bond(s) are delocalised \checkmark		ANNOTATIONS MUST BE USED
			ALLOW diagram with (π-bond) electrons
			AND delocalised labelled
	QWC requires delocalised/delocalized spelled correctly		
	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 ✓ Comparison essential		
	Companson essentia		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
			ALLOW benzene does NOT attract bromine / Br ₂
	OR benzene attracts bromine / Br ₂ LESS		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 / $Br_2 \checkmark$	4	OR alkene/C=C induces dipole in Br ₂
			· -
I			

4

1 (b) (i) Br Br Br Br Br ALLOW correct structural OR displayed OR skeletal formula. 4 (ii) 6 1 NO ECF from (i) 1 (iii) 6 1 NO ECF from (i) 2 (iii) 6 1 NO ECF from (i) 3 (iii) 6 1 NO ECF from (i) 4 Image: Structure of the three structures below with 1 mark for each correct structure / 2 ALLOW correct structural OR displayed OR skeletal formula as long as unambiguous 8 Image: Structure structure / Structures must clearly show position of Br on benzene ring in relation to side chain Structures must clearly show position of Br on benzene ring in relation to side chain 9 (iv) reaction 1: electrophilic addition / 2 ALLOW electrophile addition 10 V reaction 2: electrophilic substitution / 2 ALLOW electrophile addition 2 (iv) reaction 2: electrophilic substitution / 2 ALLOW electrophile addition 2 (iv) reaction 2: electrophilic substitution / 2 ALLOW electrophile addition 2 (iv) reaction 2: electrophilic subst	Q	Question		Answer		Guidance
(iii) Two of the three structures below with 1 mark for each correct structure v 2 ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous Br Br Br Br Br Br Br Br Br H C C H C C ALLOW combination of formulae as long as unambiguous Structures must clearly show position of Br on benzene ring in relation to side chain ALLOW ECF from (i) if BOTH Br atoms on same carbon on side chain Br H <t< th=""><th>1</th><th>(b)</th><th>(i)</th><th>нсн</th><th>1</th><th></th></t<>	1	(b)	(i)	нсн	1	
ALLOW combination of formulae as long as unambiguous Br Br H H H H Br H H			(ii)	6 ✓	1	NO ECF from (i)
Image: Structures first clearly show position of bit of benzene fing in relation to side chain $H \rightarrow C \rightarrow C \rightarrow H$ $H \rightarrow C \rightarrow H$ $H \rightarrow C \rightarrow C \rightarrow H$ $H \rightarrow C \rightarrow C \rightarrow H$ $H \rightarrow C \rightarrow H$ $H \rightarrow C \rightarrow H$ $H \rightarrow H \rightarrow H \rightarrow H$ $H \rightarrow H \rightarrow$			(iii)		2	
reaction 2: electrophilic substitution ✓ 2 ALLOW electrophile substitution ALLOW other phonetic spellings for electrophilic, e.g. electrophylic, etc. 2				$H = C = C = H \qquad H = C = C = H \qquad H = C = C = H$		in relation to side chain 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
ALLOW other phonetic spellings for electrophilic, e.g. electrophylic, etc.			(iv)	reaction 1 : electrophilic addition ✓		ALLOW electrophile addition
				reaction 2 : electrophilic substitution ✓	2	ALLOW other phonetic spellings for electrophilic,
				IstaT	10	
				TOLA	10	

Marks

Answer

Question

Guidance

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 и	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 /NH₃ DO NOT ALLOW any reference to water or hydroxide ions, e.g. DO NOT ALLOW dilute ethanolic NH₃(aq) e.g. DO NOT ALLOW ethanolic NH₃ + NaOH
		(ii)	Nitrogen electron pair/lone pair accepts a proton/H ⁺ ✓ Requires position of electron pair on N CI ⁻ H ₃ N ⁺ (CH ₂) ₄ N ⁺ H ₃ CI ⁻ OR CIH ₃ N(CH ₂) ₄ NH ₃ CI ✓	2	 DO NOT ALLOW Nitrogen/N lone pair accepts hydrogen proton/H⁺ required ALLOW nitrogen donates an electron pair IGNORE NH₂ group donates electron pair ALLOW + charge (if shown) on N or H of NH₃ e.g. Cl⁻H₃N⁺(CH₂)₄NH₃⁺Cl⁻ DO NOT ALLOW just H₃N⁺(CH₂)₄NH₃⁺ i.e. 2 x Cl⁻ MUST be included

Q	uestic	on	Answer	Marks	Guidance
Q 2	uestic	on (iii)	Answer 1 mark for amide/peptide link correctly displayed within an attempted repeat unit \checkmark 1 mark for rest of structure correct including side links \checkmark $\stackrel{O}{=}$ <	Marks 2	 Minimum requirement is each end of a displayed amide group attached to a carbon atom (could be skeletal) Brackets not required IF more than one repeat unit has been drawn a single repeat unit MUST be identified by brackets or clear label 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. C C C C H H

Question	Answer	Marks	Guidance
2 (c) (i)	One mark for each correct structure $ \begin{array}{c} & & & \\ H_{3}N - CH - C - O^{-} \\ & & \\ H_{3}N - CH - C - O^{-} \\ & & \\ H_{3}N - CH - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-} \\ & & \\ H_{2}N - C - C - O^{-$	2	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous 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
(ii)	Zwitterion at pH 9.60/higher pH has one NH ₂ group OR Zwitterion OR amino acid at pH 9.60/higher pH has a side chain with an NH ₂ group ✓ Note: ASSUME that 'it' refers to zwitterion	1	ALLOW amino acid at 9.60/higher pH has two NH ₂ groups ALLOW amino acid at 9.60/higher pH has more NH ₂ groups ALLOW amine OR amino for NH ₂ IGNORE CHOH slightly acidic
	Total	10	

Question	Answer	Marks	Guidance
3 (a) (i)	<i>cis</i> -isomer has Hs on same side OR <i>cis</i> -isomer has branches on same side OR <i>cis</i> -isomer has same groups on same side OR <i>cis</i> -isomer has lowest priority groups on same side OR <i>cis</i> -isomer has highest priority groups on same side ✓	2	ALLOW <i>trans</i> -isomer has Hs on opposite sides OR <i>trans</i> -isomer has branches on opposite sides OR <i>trans</i> -isomer has same groups on opposite sides DO NOT ALLOW 'similar groups' for 'same groups' OR <i>trans</i> -isomer has lowest priority groups on opposite sides OR <i>trans</i> -isomer has highest priority groups on opposite sides ✓ For explanation, ALLOW a clear diagram, <i>ie</i> : ALLOW response in terms of packing, e.g. molecules/chains of <i>trans</i> -isomer pack close together OR molecules/chains of <i>cis</i> -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

C	Questi	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 <i>E</i>/<i>Z</i>) DO NOT ALLOW stereoselectivity

Q	uest	ion		Answer	Marks	Guidance
3		(iii)				ANNOTATIONS MUST BE USED
			1st step			
			reagent.	NaBH₄ ✓		ALLOW H ₂ /Ni (catalyst) DO NOT ALLOW LiAIH ₄ (<i>because LiAIH₄ reduces</i> <i>COOH</i>)
			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		IGNORE OH, COOH, COO, IGNORE hydroxyl OR hydroxy DO NOT ALLOW phenol OR hydroxide
				Total	12	



Q	uestion	Answer	Marks	Guidance
4	(b)	$2 C_{6}H_{5}CHO + KOH \longrightarrow C_{6}H_{5}CH_{2}OH + C_{6}H_{5}COOK$ OR $2 C_{6}H_{5}CHO + OH^{-} \longrightarrow C_{6}H_{5}CH_{2}OH + C_{6}H_{5}COO^{-}$		ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous ALLOW use of NaOH instead of KOH throughout, i.e.
		1 mark for $C_6H_5CH_2OH \checkmark$		$2 C_6 H_5 CHO + NaOH \rightarrow C_6 H_5 CH_2 OH + C_6 H_5 COONa$
		1 mark for C_6H_5COOK OR C_6H_5COOH OR $C_6H_5COO^- \checkmark$		ALLOW C ₆ H ₅ COO ⁻ K ⁺
		1 mark for complete fully correct balanced equation (i.e. as above) ✓	3	
	(C)			ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous e.g. ALLOW C_6H_5 —C===N==OH H C_6H_5 —C===C==COOH
			3	н н О С ₆ H₅—СС_С_С_С_С_С ₆ H₅ H H H H

Q	Question		Answer	Marks	Guidance
4	(d)	(i)	$C_6H_5 \xrightarrow{\delta} C_6H_5 \xrightarrow{O^-} C_6 \xrightarrow{O^-} C_6H_5 \xrightarrow{O^-} C_6 O$		ANNOTATIONS MUST BE USED
			$C_6 \Pi_5 \longrightarrow C_6 \square_5 \longrightarrow C_6 \square_6 \longrightarrow C_6 $		IGNORE connectivity on OH of product
			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 $O^{\delta-} \checkmark$		
			1 mark for correct intermediate with – charge on O \checkmark		IGNORE any curly arrows shown for stage 2 i.e. in intermediate
			1 mark for correct product ✓	4	
		(ii)	Li Li ⁺ _CHCH3 OR CHCH3		ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous
			H_3C CH_2 H_3C CH_2 \checkmark	1	IGNORE C₄H ₉ Li OR C₄H ₉ [−] Li [−]
			Total	17	

Qu	Question		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	
	(D)		Ester structure 3 marks $\downarrow \downarrow $	3	ALLOW correct structural OR displayed OR skeletal formula ALLOW combination of formulae as long as unambiguous NO ECF for structure IF the structure is NOT fully correct, award the following marks: IF ESTER shown AND contains ONE of the following: C_6H_5 OR $CH_3C=0$ OR CH_2CH_2 1 mark \checkmark IF ESTER shown AND contains TWO of the following:	
			$\mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} \mathbf{x} $		$C_{6}H_{5} \text{ OR } CH_{3}C=O \text{ OR } CH_{2}CH_{2} \qquad 2 \text{ marks } \checkmark \checkmark$ IF ESTER contains $C_{6}H_{5} \text{ AND } CH_{2}CH_{2}$ BUT ester link is reversed $2 \text{ marks } \checkmark \checkmark$ $O = O = O + O + O + O + O + O + O + O + $	

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 $C_{10}H_{12}O_2 \checkmark$ <i>This direct link could be seen anywhere in the response</i> 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: ± 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 AND		For adjacent CH ₂ , ALLOW (C) adjacent to 2 Hs
	Triplet at 4.4 ppm shows an adjacent $CH_2 \checkmark$		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 (δ =) 7.3 ALLOW peak labelled 5 OR multiplet OR quintet OR hextet OR heptet
	Peak at 2.8 shows C_6H_5 –C H OR C_6H_5 –C H₂ \checkmark Just require C_6H_5 –CH as testing environment here		For peak at (δ =) 2.8 ALLOW triplet at 2.8
	Peak at 4.4 due to H C–O OR H ₂ C–O \checkmark 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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