OCR

RECOGNISING ACHIEVEMENT

OXFORD CAMBRIDGE AND RSA EXAMINATIONS

Advanced GCE

CHEMISTRY 2814

Chains, Rings and Spectroscopy

Friday **21 JANUARY 2005** Morning 1 hour 30 minutes

Candidates answer on the question paper.
Additional materials:
Data Sheet for Chemistry
Scientific calculator

Candidate Name	Centre Number	Candidate Number

TIME 1 hour 30 minutes

INSTRUCTIONS TO CANDIDATES

- Write your name in the space above.
- Write your Centre number and Candidate number in the boxes above.
- Answer **all** the questions.
- Write your answers in the spaces provided on the question paper.
- Read each question carefully and make sure you know what you have to do before starting your answer.

INFORMATION FOR CANDIDATES

- The number of marks is given in brackets [ ] at the end of each question or part question.
- You will be awarded marks for the quality of written communication where this is indicated in the question.
- You may use a scientific calculator.
- You may use the *Data Sheet for Chemistry*.
- You are advised to show all the steps in any calculations.

FOR EXAMINER'S USE		
Qu.	Max.	Mark
1	20	
2	17	
3	13	
4	16	
5	10	
6	14	
TOTAL	90	

This question paper consists of 15 printed pages and 1 blank page.

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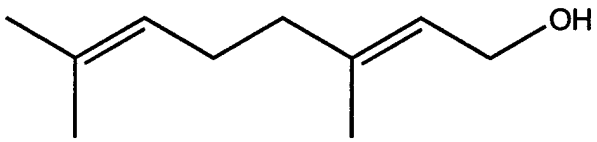
Answer **all** the questions.

1 Geraniol, $C_9H_{15}CH_2OH$, is a naturally occurring compound that contributes to the smell of roses. The skeletal formula of geraniol is shown below.



geraniol

(a) Name the two different functional groups in geraniol.

..... and ..... [1]

(b) Geraniol has stereoisomers due to one of the double bonds in the molecule.

(i) What is meant the term *stereoisomer*?

.....

.....

.....[1]

(ii) Name the type of stereoisomerism shown by geraniol.

.....[1]

(iii) State how this type of stereoisomerism arises in organic molecules.

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.....[1]

(iv) Explain why one of the double bonds in geraniol does **not** give rise to stereoisomerism.

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.....[1]

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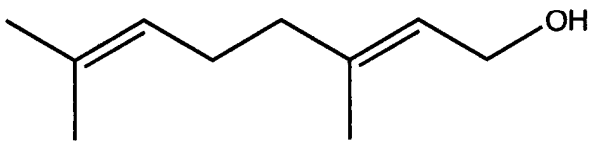
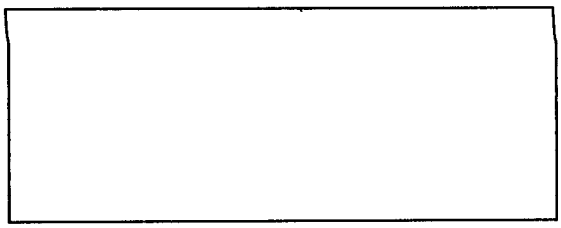


geraniol

(c) Mild oxidation of geraniol gives an aldehyde **Y**.

(i) Draw the skeletal formula of aldehyde **Y** below.



aldehyde **Y**

[2]

(ii) Complete the equation for the oxidation of geraniol to aldehyde **Y**.

$C_9H_{15}CH_2OH \quad + \quad [O] \quad \rightarrow$

[2]

(d) Reaction of geraniol with ethanoic acid can be used to make ester **Z**, which is used in chewing gum and desserts.

(i) Suggest why esters are used in the manufacture of foods.

.....[1]

(ii) State the conditions needed to make ester **Z** from geraniol and ethanoic acid.

.....

.....[2]

(iii) Complete the equation for the formation of ester **Z**.

$+ \quad C_9H_{15}CH_2OH \quad \rightarrow$

[3]

(e) Infra-red spectroscopy can be used to distinguish between geraniol, aldehyde **Y** and ester **Z**.

Describe how the infra-red spectra of these three compounds differ. Identify the wavenumber ranges at which you would expect to find the characteristic absorptions for each of the three compounds.

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[5]

[Total: 20]

2 The nitration of benzene is a very important industrial reaction.

(a) Name **two** types of commercially important material whose manufacture involves the nitration of benzene.

.....

.....[2]

(b) State the conditions required for the nitration of benzene using nitric acid and sulphuric acid.

.....

.....[2]

(c) Write a balanced equation for the nitration of benzene.

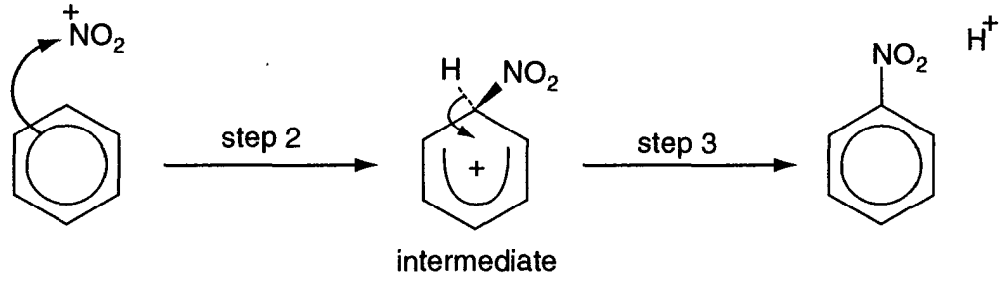
[2]

(d) The mechanism for the reaction is given below.

Step 1: formation of the electrophile, NO_2^+, from HNO_3 and H_2SO_4

$$HNO_3 + H_2SO_4 \longrightarrow H_2O + NO_2^+ + HSO_4^-$$

Steps 2 and 3: substitution of NO_2^+ into the benzene ring



intermediate

Step 4: protonation of the HSO_4^-

$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

(i) Explain what a curly arrow  represents in this type of mechanism.

.....

.....[2]

(ii) State why the NO_2^+ is described as an electrophile in this mechanism.

.....

.....[1]

(iii) State why this mechanism is described as substitution.

.....[1]

(iv) How does the mechanism show that the sulphuric acid is acting as a catalyst?

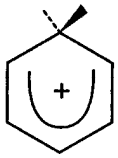
.....

.....[1]

(e) In this question, one mark is available for the quality of spelling, punctuation and grammar.

The benzene ring and the ring in the intermediate formed after **step 2** have different structures shown below. Both structures have π-bonds.

benzene ring



ring in the intermediate

Deduce how many electrons are involved in the π-bonding in each structure and describe how their arrangements are different.

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.....[5]

Quality of Written Communication [1]

[Total: 17]

3 E110 is a yellow colouring agent that is commonly added to a variety of foods.

E110 contains an azo dye made from an amine and a phenol.

(a) Describe how you would prepare a sample of an azo dye in the laboratory from an amine, a phenol and any other necessary reagents.

Include in your answer

- essential reagents and conditions for each stage
- names of any functional groups formed during the process.

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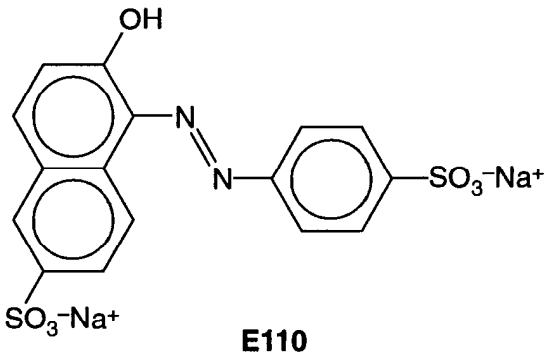
.....[7]

(b) The structure of E110 is shown below.



E110

(i) On the structure above, draw a circle around the functional group that identifies this molecule as an azo dye. [1]

(ii) Deduce how many carbon and hydrogen atoms are in a molecule of E110.

..... carbon atoms and ..... hydrogen atoms. [2]

(c) The solubility of E110 in water can be improved by converting the phenolic –OH group into a charged $-O^-$ group.

Suggest a suitable reagent that will convert the –OH group in E110 into an $-O^-$ group.

.....[1]

(d) In the boxes below, draw the structures of a phenol and an amine that could be used to make E110 by the method in part **(a)**.

Assume that the SO_3^- Na^+ groups do not change during the process.

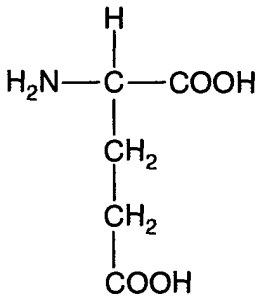
phenol

amine

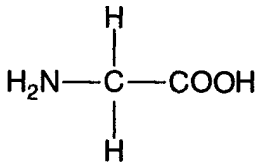
[2]

[Total: 13]

4 Glutamic acid and glycine are both α-amino acids that occur widely in living organisms. Their structures are shown below.



glutamic acid



glycine

(a) (i) State the general formula for an α-amino acid.

.....[1]

(ii) Explain how glutamic acid and glycine both fit the general formula given in part **(i)**

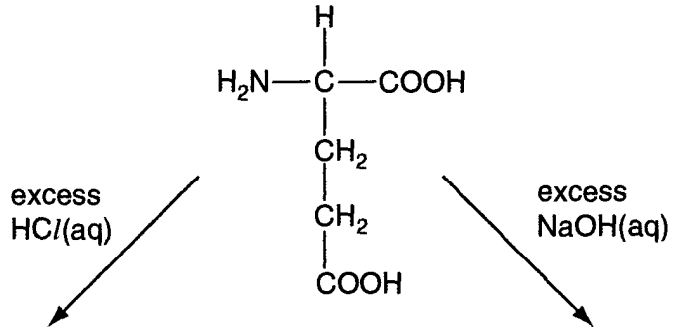
.....

.....

.....[2]

(b) Amino acids react with both acids and alkalis.

Draw structures below to show how the glutamic acid molecule is changed in the presence of excess acid and alkali.



glutamic acid

[5]

(c) In this question, one mark is available for the quality of use and organisation of scientific terms.

Glutamic acid exists as two optical isomers, but glycine does not.

Explain what structural feature causes optical isomerism in organic molecules. Include appropriate diagrams and use these two amino acids to illustrate your answer.

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[7]

Quality of Written Communication [1]

[Total: 16]

5 Poly(phenylethene) is one of the most versatile and successful polymers.

The 3-D skeletal formula of a section of atactic poly(phenylethene) is shown in **Fig 5.1** below.

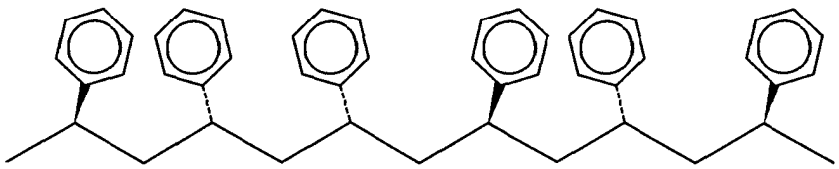

Fig. 5.1

(a) (i) State the type of polymerisation used to make poly(phenylethene).

.....[1]

(ii) Draw a skeletal or displayed formula to show the monomer used to make poly(phenylethene).

[1]

(iii) Outline how the polymer is formed from the monomer molecules. (You do **not** need to give any details of the catalyst or conditions involved.)

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.....[2]

(b) Poly(phenylethene) can also be made with a *syndiotactic* arrangement of its side chains.

Explain what is meant by the term *syndiotactic*. Illustrate your answer by completing the 3-D skeletal formula of a section of syndiotactic poly(phenylethene) below.

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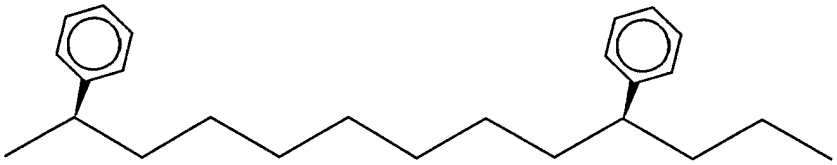

[3]

(c) Syndiotactic poly(phenylethene) has a high melting point and is particularly useful in situations in which the polymer might get hot.

Suggest why the syndiotactic poly(phenylethene) has a higher melting point than the atactic poly(phenylethene) shown in **Fig. 5.1**.

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.....[3]

[Total: 10]

For Examiner's Use

6 Forest fires release a large number of organic compounds into the atmosphere. These include alcohols and carboxylic acids. An environmental chemist is trying to identify one of these compounds in a sample of air.

The unknown compound **X** is thought to be a carboxylic acid with empirical formula $C_2H_3O_2$.

(a) Mass spectrometry is used to help deduce the molecular formula of compound **X**.

(i) Describe how the mass spectrum of compound **X** is used to determine its relative molecular mass.

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.....[2]

(ii) The relative molecular mass of compound **X** is shown to be 118.

Explain how this relative molecular mass and the empirical formula are used to deduce that the molecular formula of compound **X** is $C_4H_6O_4$. Show any working.

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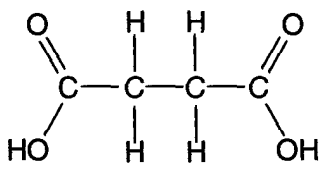
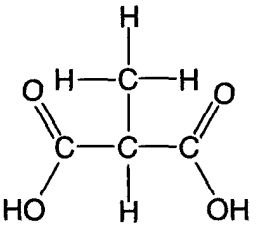
.....[2]

(b) The two dicarboxylic acids with molecular formula $C_4H_6O_4$ are shown below.





N.m.r. spectroscopy is used to deduce which of these is the unknown compound.

The environmental chemist obtains an n.m.r. spectrum of compound **X** and then adds some D_2O and obtains a second n.m.r. spectrum.

(i) What difference would you expect between these two n.m.r. spectra?

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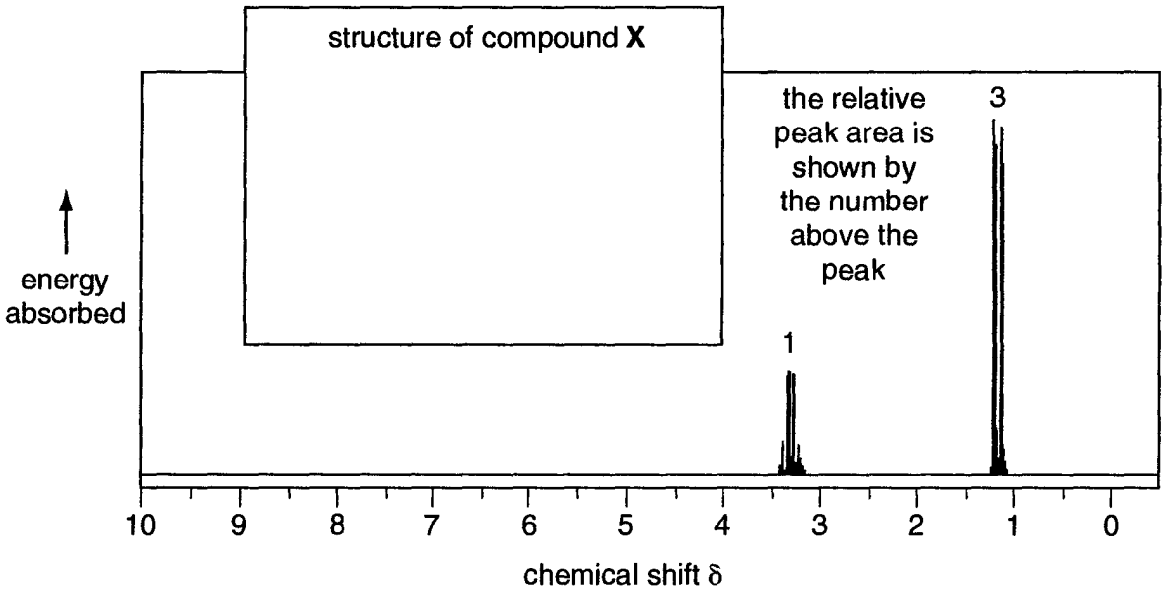
.....[1]

(ii) The n.m.r. spectrum of compound **X** in D_2O is shown below.



Use this spectrum to identify which of the two carboxylic acids is compound **X**.

- Draw the correct structure in the box above the spectrum.
- Use labels to show which protons on the structure are responsible for each peak on the spectrum.
- Explain your reasoning by referring to the relative peak areas and the spin-spin splitting patterns of the peaks.

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.....[6]

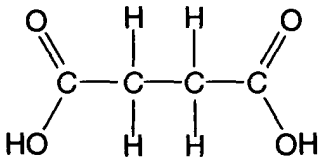
TURN OVER FOR Q6 PART (b)(iii)

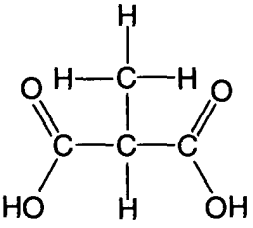
For Examiner's Use

(iii) Predict the number of peaks and any spin-spin splitting expected on the n.m.r. spectrum of a solution in D_2O of the **other** acid with formula $C_4H_6O_4$.

Explain your reasoning.

(The two possible structures of compound **X** are shown again below.)





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.....[3]

[Total: 14]

END OF QUESTION PAPER

Subject: Chains, Rings and Spectroscopy **Code:** 2814

Session: Jan **Year:** 2005

Mark Scheme

MAXIMUM MARK	90

ADVICE TO EXAMINERS ON THE ANNOTATION OF SCRIPTS

1. Please ensure that you use the **final** version of the Mark Scheme.
   You are advised to destroy all draft versions.

2. Please mark all post-standardisation scripts in red ink. A tick (✓) should be used for each answer judged worthy of a mark. Ticks should be placed as close as possible to the point in the answer where the mark has been awarded. The number of ticks should be the same as the number of marks awarded. If two (or more) responses are required for one mark, use only one tick. Half marks should never be used.

3. The following annotations may be used in when marking. No comments should be written on scripts unless they relate directly to the mark scheme. Remember that scripts may be returned to centres.

✘	=	incorrect response (errors may also be underlined)
^	=	omission of the correct response
bod	=	"benefit of the doubt" (where professional judgement has been used in deciding a response is worthy of a mark)
ecf	=	"error carried forward" (in consequential marking)
con	=	contradiction (in cases where candidates contradict themselves in the same response). No mark awarded, even if one response was correct. [1]
sf	=	error in the number of significant figures (only penalised once on the paper).

4. The marks awarded for each part question should be indicated in the margin provided on the right hand side of the page. The mark total for each question should be ringed at the end of the question, on the right hand side. These totals should be added up to give the final total on the front of the paper.

5. In cases where candidates are required to give a specific number of answers, (e.g. 'give three reasons …'), mark the first answer(s) given up to the total number required. Strike through the remainder. In specific cases where this rule cannot be applied, the exact procedure to be used is given in the mark scheme

6. Correct answers to calculations should gain full credit even if no working is shown, unless otherwise indicated on the mark scheme. (An instruction to 'Show your working' is to help candidates, who may then gain partial credit even if their final answer is not correct.)

7. Strike through all blank spaces and/or pages in order to give clear indication that the whole of the script has been considered.

8. An element of professional judgement is required in the marking of any written paper, and candidates may not use the exact words that appear in the mark scheme. If the science is correct and answers the question, then the mark(s) should normally be credited. If you are in doubt about the validity of any answer, contact your Team Leader/Principal Examiner for guidance.

[1] Note that in organic chemistry a candidate may identify a compound by name and formula. If one of these is wrong then the mark is not awarded as this is a contradictory answer.

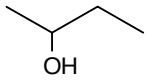
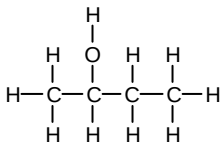
Abbreviations, annotations and conventions used in the mark scheme

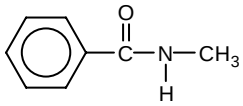
/ = alternative and acceptable answers for the same marking point
; = separates marking points
NOT = answers not worthy of credit
( ) = words which are not essential to gain credit
___ (underlining) = key words which must be used
ecf = allow error carried forward in consequential marking
AW = alternative wording
ora = or reverse argument

Marking structures in organic chemistry

When a structure is asked for, there must be sufficient detail using conventional carbon skeleton and functional group formulae (e.g. CH_3, C_2H_5, OH, COOH, $COOCH_3$) to unambiguously define the arrangement of the atoms. (E.g. C_3H_7 would not be sufficient).

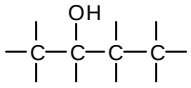
If not specified by the question, this may be given as either:

- a **structural formula** – e.g. $CH_3CH(OH)C_2H_5$,
- a **skeletal formula** – e.g.  ,
- a **displayed formula** – e.g. 

or as a hybrid of these – e.g. 

The following errors should be penalised – although each one only loses a maximum of one mark on the paper:

- clearly connecting a functional group by the wrong atom
- showing only 'sticks' instead of hydrogen atoms –

  e.g. 

Benzene rings may be represented as  *as well as*  *in any of the types of formula above.*

Qu. **Expected answers:** **Marks:**

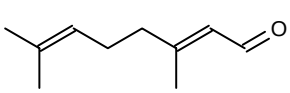
1 (a) (i) alkene / C=C double bond
(primary) alcohol / hydroxy(l) ✓ **[1]**

(b) (i) molecules with the same structure / order of bonds … but different arrangements in space / 3-D arrangment ✓ **[1]**

(ii) cis-trans / geometric ✓ **[1]**

(iii) the double bond does not rotate ✓ **[1]**

(iv) same groups at one end / need different groups at both ends of the C=C ✓ **AW** **[1]**

(c) (i) 

a correct skeletal aldehyde is shown on C_1 ✓

rest of the skeletal structure (C_2-C_{10})correct ✓ **[2]**

(ii) $C_9H_{15}CH_2OH + [O] \longrightarrow C_9H_{15}CHO$ ✓ $+ H_2O$ ✓

NOT COH, allow $C_{10}H_{16}O$ **[2]**

(d) (i) flavouring / fruity smell etc

NOT perfume or sweetener **[1]**

(ii) conc H_2SO_4 ✓
reflux/ distil ✓ **[2]**

(iii) $CH_3COOH + C_9H_{15}CH_2OH \longrightarrow CH_3COOCH_2C_9H_{15} + H_2O$
✓ ✓ ✓

allow $C_2H_4O_2$ and $C_{12}H_{20}O_2$ but **NOT** wrong structures
allow ecf on the wrong acid **[3]**

(e)

wavenumber range (cm^{-1})	3230-3550 (for *OH*)	1680-1750 (for *C=O*)	1000-1300 (for *C-O*)
geraniol	present ✓	(absent)	present ✓
aldehyde Y	(absent)	present ✓	(absent)
ester Z	(absent)	present ✓	present ✓

[5]

[Total: 20]

Qu.	Expected answers:		Marks:
2 (a)	any two of … fibres / dyes / explosives / pharmaceuticals etc ✓✓	allow any specific examples as long as they do involve aromatic nitro or amine groups – eg **NOT** nylon, fertiliser etc	**[2]**
(b)	temp 50-60° ✓ concentrated (acids) ✓	allow abbreviations for concentrated	**[2]**
(c)	$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$ reactants ✓ products ✓	allow a balanced equation for multiple nitration at any positions	**[2]**
(d) (i)	a pair of electrons … ✓ … (electrons) move / transferred / a (covalent) bond breaks/forms ✓		**[2]**
(ii)	it accepts a pair of electrons (from the benzene) ✓	**NOT** a 'lone' pair	**[1]**
(iii)	$H(^+)$ (on the ring) is replaced by $NO_2(^+)$ ✓	allow 'substitutes' ignore $^+$ charges	**[1]**
(iv)	it is not used up / reformed at the end **AW** ✓		**[1]**
(e)	π-bonding electrons are <u>delocalised</u> ✓ **six** π-electrons in benzene ✓ **four** π-electrons in the intermediate ✓		
	π-electrons are not over one carbon atom / over **five** carbon atoms / p-orbitals in the intermediate ✓ π-electrons are over the **complete** ring / **all around** the ring **all six** carbon atoms/ p-orbitals overlapping ✓	this must be stated in words to compare benzene and the intermediate	
	Quality of written communication for at least two sentences/statements with legible text and correct spelling, punctuation and grammar ✓		**[6]**
			[Total: 17]

Qu.	Expected answers:	Marks:

3 (a) **1st stage**

aromatic amine / named aromatic amine / structure ✓
sodium nitrite / nitrous acid ✓
HCl/H_2SO_4 (but not conc) $/H^+$ ✓
at <10°C ✓

which forms a diazonium salt / ion ✓

2nd stage

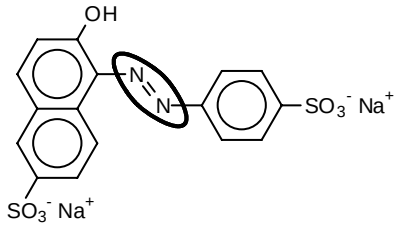
the product from the first stage mixed with the phenol **AW** ✓
(in excess) hydroxide / alkali ✓

if more than four are given, mark any wrong reagents, conditions first

allow correct formulae for the reagents

[7]

(b) (i)



✓

allow any benzene rings as well as N=N circled, as long as no other groups are

[1]

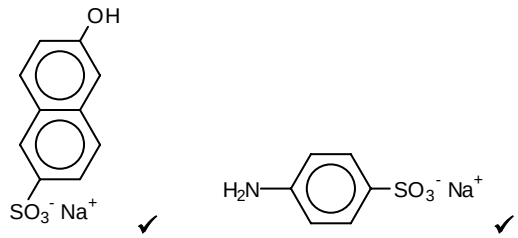
(ii) …16… carbon and ……10….. hydrogen atoms
✓ ✓

[2]

(c) Na / NaOH / OH^- etc ✓

[1]

(d)



✓ ✓

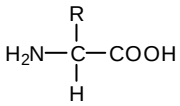
allow 1 mark if they are both correct, but in the wrong boxes

only penalise a slip with SO_3^- Na^+ once

[2]

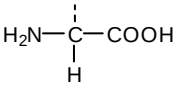
[Total: 13]

Qu. **Expected answers:** **Marks:**

4 (a) (i) $H_2NCHRCOOH$ /  ✓

allow R CH NH_2 and COOH in any order

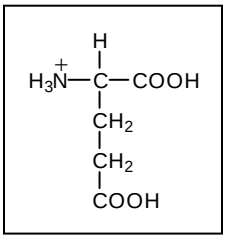
[1]

(ii) they both have the  group / or in words ✓

NOT just "they both have NH_2 and COOH"

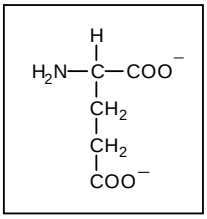
R group is H in glycine and CH_2CH_2COOH in glutamic acid ✓

[2]

(b) 

$-NH_3^+$ ✓

-COOH and side chain unaffected ✓



one $-COO^-$ ✓

both $-COO^-$ ✓

H_2N- and rest of molecule ✓

[5]

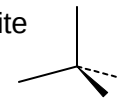
(c) **glutamic acid/molecule with optical isomers …**

… is <u>chiral</u> ✓

… has four different / distinguishable groups attached to a carbon ✓

… the mirror images/isomers cannot be superimposed **AW** ✓

NOT just "different atoms"

one diagram showing **two** 3-D bonds not opposite each other, and not with angles looking like 90°  ✓

3-D diagram of the other isomer (allow ecf on one 3-D error) ✓

all groups correctly connected for glutamic acid in both diagrams ✓

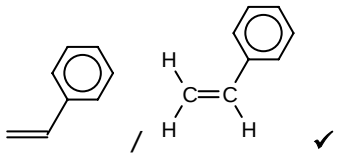
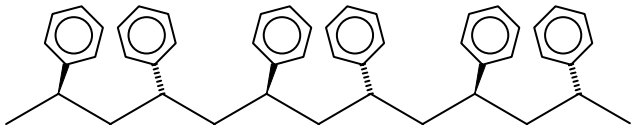
glycine
only has three different groups / two groups are the same / 3-D diagram used to show symmetry ✓

7 marks

quality of written communication
for correct use and organisation of at least **one** technical term:
*(in the correct place), non-superimposable, enantiomer, stereoisomer(ism), tetrahedral, assymetric ✓

[8]

[Total: 16]

Qu.	Expected answers:		Marks:
5 (a) (i)	addition (polymerisation) ✓	**NOT** additional	[1]
(ii)	 ✓		[1]
(iii)	π-bond breaks ✓ **many** molecules join / a **long** chain forms / equation to show this using 'n' ✓		[2]
(b)	alternating ✓  all four side groups placed above the chain with an alternating arrangement clearly shown by use of 3-D bonds ✓✓ where 1 mark is for an incorrect diagram, but "(alternating) 3-D /spacial arrangement of side chains" stated in words		[3]
(c)	atactic has side chains irregular / random(ly arranged in space/3-D) ✓ **ora** atactic has weaker intermolecular / Van der Waals' forces between the chains ✓ **ora** chemically sensible suggestion why irregular side chains could give weaker forces – eg because chains can't get as close / less surface contact ✓ **AW ora**	**NOT** just "weaker bonds"	[3]
			[Total: 10]

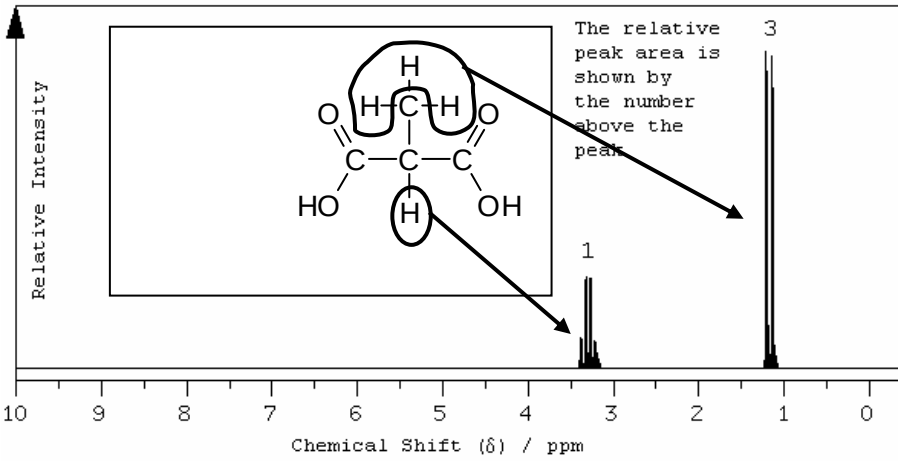
Qu.	Expected answers:	Marks:

6 (a) (i) Find the m /e of …. ✓
... the peak furthest to the right / with highest m /e or mass ✓
allow attempts to cater for the ^{13}C peak **[2]**

$C_2H_3O_2$ /empirical formula has $M_r = 59$ ✓
so M_r of molecular formula is $^{118}/_{59}$= 2 /twice the empirical formula ✓ **[2]**

(b) (i) OH peak disappears (with D_2O / on the second spectrum) **[1]**

(ii)



peak at 3.3ppm identifed as due to the CH ✓
assignment must be for this structure (not just R-CH_3 etc)

peak at 1.2ppm identified as due to the CH_3 ✓

protons (and not the carbon) on the groups are identified ✓
can be by Ha, Hb etc

relative peak areas / numbers above the peaks show …
the number of (equivalent) protons in each group / three protons on one carbon and one on the other carbon ✓ **AW**

quadruplet / 1:3:3:1 splitting (of the peak at 3.3ppm) shows…
three protons on the neighbouring/adjacent carbon ✓

doublet / 1:1 splitting (of the peak at 1.2ppm) shows …
one proton on the neighbouring /adjacent carbon ✓ **[6]**

(iii) no of peaks: one ✓
if the wrong structure is chosen allow ecf for:
two peaks ✓,
splitting ✓✓ (as last 2 marks for part **(ii)**) **[3]**

splitting: none ✓

all four protons equivalent / in the same environment ✓

[Total: 14]