37. Analytical techniques

37.4 Proton (1H) NMR spectroscopy

Paper 4

Question Paper

1 **(e)** Complete Table 6.2 to predict the number of peaks in the proton (^1H) NMR spectrum for Dewar benzene, Ladenburg benzene and delocalised benzene.

Table 6.2

	number of peaks
Dewar benzene	
Ladenburg benzene	
delocalised benzene	

[1]

2 Four esters, **A**, **B**, **C** and **D**, with the molecular formula $C_6H_{12}O_2$ are shown in Fig. 7.1.

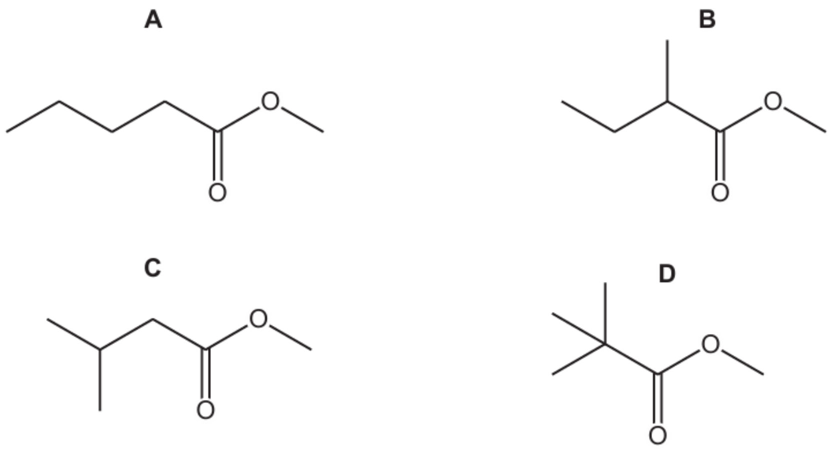


Fig. 7.1

(c) Separate samples of the esters, **A**, **B**, **C** and **D**, are analysed using proton (^1H) NMR and carbon-13 NMR spectroscopy.

(i) Complete Table 7.1 to show the number of peaks in each NMR spectrum for esters **B** and **C**.

Table 7.1

ester	number of peaks in proton (^1H) NMR spectrum	number of peaks in carbon-13 NMR spectrum
B		
C		

[2]

(ii) Identify **all** of the esters from **A**, **B**, **C** and **D** that have at least one triplet peak in their proton (^1H) NMR spectrum.

.... [1]

3 **(c)** Compound **H**, $C_6H_{10}O_3$, reacts with alkaline I_2(aq) to form yellow precipitate **J** but does **not** react with Na_2CO_3(aq).

The proton (^{1}H) NMR spectrum of **H** in $CDCl_3$ is shown in Fig. 9.2.

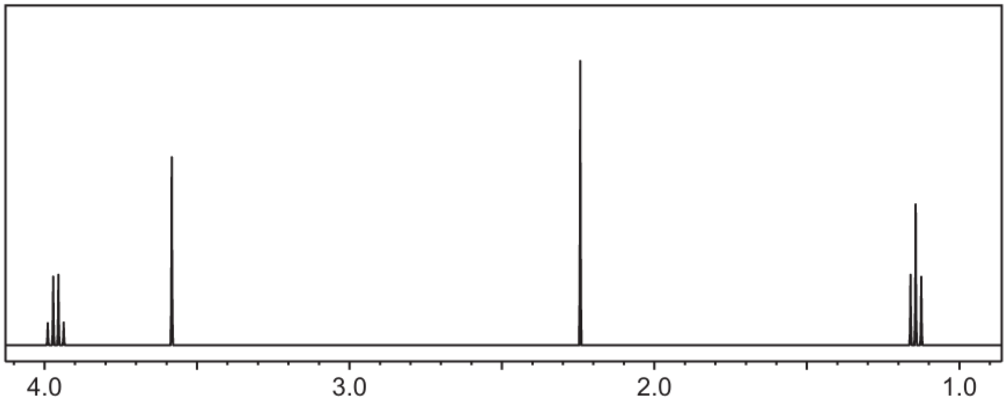


Fig. 9.2

Table 9.1

environment of proton	example	chemical shift range δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Identify yellow precipitate **J**.

.... [1]

(ii) Complete Table 9.2 for the proton (^1H) NMR spectrum of **H**, $C_6H_{10}O_3$.

Table 9.2

chemical shift δ/ppm	splitting pattern	number of ^1H atoms responsible for the peak	number of protons on adjacent carbon atoms
1.15			
2.25			
3.60			
3.95			

[4]

(iii) Suggest a structure for **H**, $C_6H_{10}O_3$.

[1]

4 The amino acid serine, $HOCH_2CH(NH_2)COOH$, exists in two optically active forms. These optical isomers, isomer **P** and isomer **Q**, are shown in Fig. 8.1.

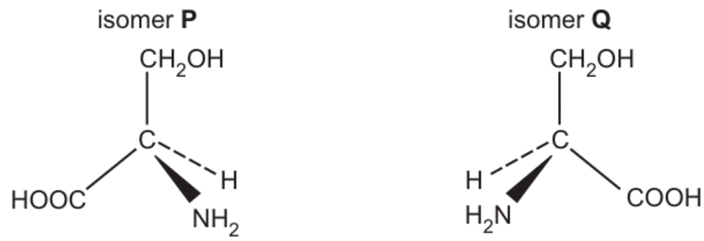


Fig. 8.1

(f) Complete Table 8.1 to describe the peaks seen in the proton (^1H) NMR spectrum of $HOCH_2CH(NH_2)COOH$ dissolved in D_2O.

Use as many rows in Table 8.1 as you need to, leaving the other rows blank.

Table 8.1

group responsible for peak	name of splitting pattern shown by peak	explanation for splitting pattern

[3]

5 **(e)** Alanine, $H_2NCH(CH_3)COOH$, reacts with methanol to form the ester **G** under certain conditions.

The proton (^1H) NMR spectrum of **G** dissolved in D_2O is shown in Fig. 7.3.

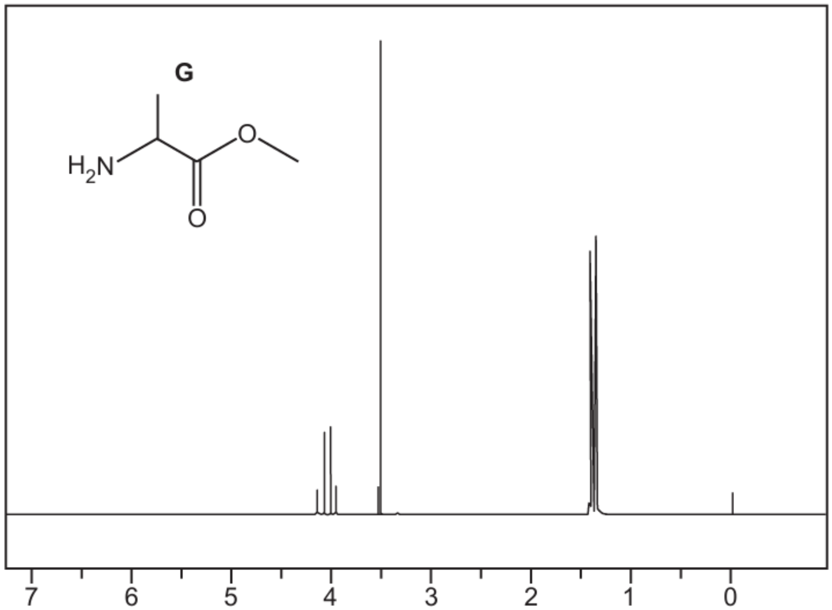


Fig. 7.3

Table 7.1

environment of proton	example	chemical shift range, δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Complete Table 7.2 for the proton (^1H) NMR spectrum of **G**.

Table 7.2

chemical shift (δ)	splitting pattern	number of ^1H atoms responsible for the peak	number of protons on adjacent carbon atoms
1.4			
3.5			
4.0			

[3]

(ii) The proton (^1H) NMR spectrum of **G** dissolved in $CDCl_3$ is obtained.

Describe the difference observed between this spectrum and the proton NMR spectrum in D_2O shown in Fig 7.3.

Explain your answer.

....

....

.... [1]

6 **(c)** The proton (^1H) NMR spectrum of compound **T**, $C_5H_9O_2Cl$, in $CDCl_3$ is shown in Fig. 8.2.

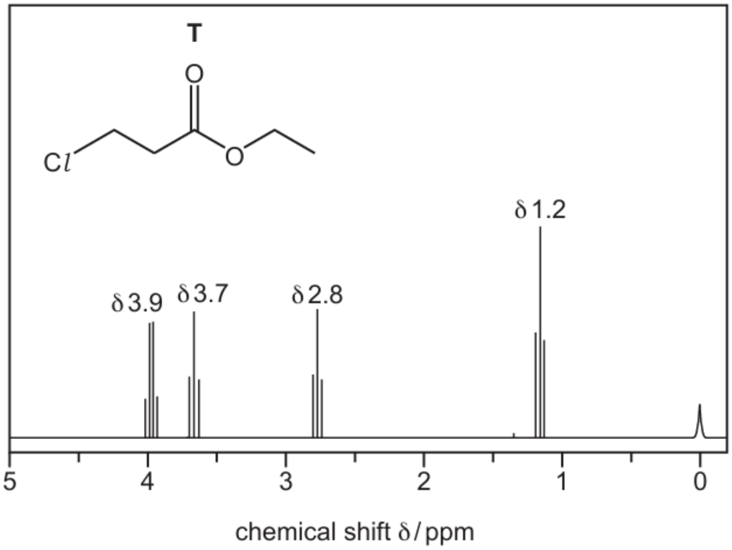


Fig. 8.2

Table 8.1

environment of proton	example	chemical shift range δ / ppm
alkane	$-CH_3$, $-CH_2-$, >CH–	0.9–1.7
alkyl next to C=O	CH_3–C=O, $-CH_2$–C=O, >CH–C=O	2.2–3.0
alkyl next to aromatic ring	CH_3–Ar, $-CH_2$–Ar, >CH–Ar	2.3–3.0
alkyl next to electronegative atom	CH_3–O, $-CH_2$–O, $-CH_2$–Cl	3.2–4.0
attached to alkene	=CHR	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Suggest why $CDCl_3$ is used as a solvent instead of $CHCl_3$ for the proton (^1H) NMR spectrum.

....

.... [1]

(ii) Complete Table 8.2 for the proton (^1H) NMR spectrum of **T**.

Table 8.2

chemical shift δ / ppm	environment of proton	splitting pattern	number of ^1H atoms responsible for the peak
1.2			
2.8			
3.7			
3.9			

[4]

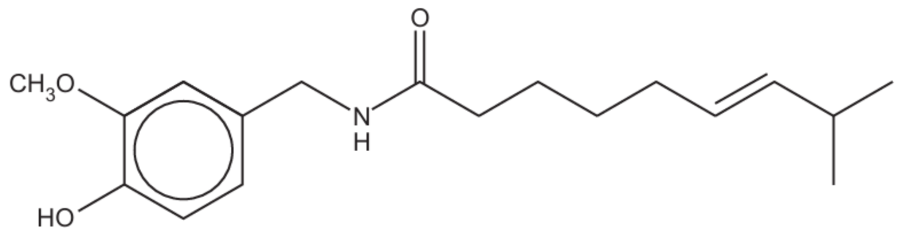
(iii) Explain the splitting pattern of the peak at δ 3.9 ppm.

....

.... [1]

7 Capsaicin is found in chilli peppers.

capsaicin



You should assume the CH_3O group is unreactive in the reactions involved in this question.

(d) When capsaicin is treated with reagent **J** under suitable conditions one of the products is methylpropanoic acid, $CH_3CH(CH_3)COOH$.

(ii) There are three different peaks in the proton (^1H) NMR spectrum of $CH_3CH(CH_3)COOH$ in $CDCl_3$.

Table 8.1

environment of proton	example	chemical shift range δ/ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0

Use Table 8.1 to complete Table 8.2 and state:

- the typical proton (^{1}H) chemical shift values (δ) for the protons
- the splitting pattern (singlet, doublet, triplet, quartet or multiplet) shown by each peak
- the explanation for the splitting patterns of the CH_3 protons and the CH proton.

Table 8.2

environment	δ / ppm	splitting pattern	explanation for splitting pattern
CH_3			
CH			
COOH			

[3]

8 Lactic acid, $CH_3CH(OH)COOH$, is the only monomer needed to form the polymer polylactic acid, PLA.

(b) The proton (^{1}H) NMR spectrum of $CH_3CH(OH)COOH$ in $CDCl_3$ is shown in Fig. 8.1. The proton NMR chemical shift ranges are shown in Table 8.1.

Lactic acid

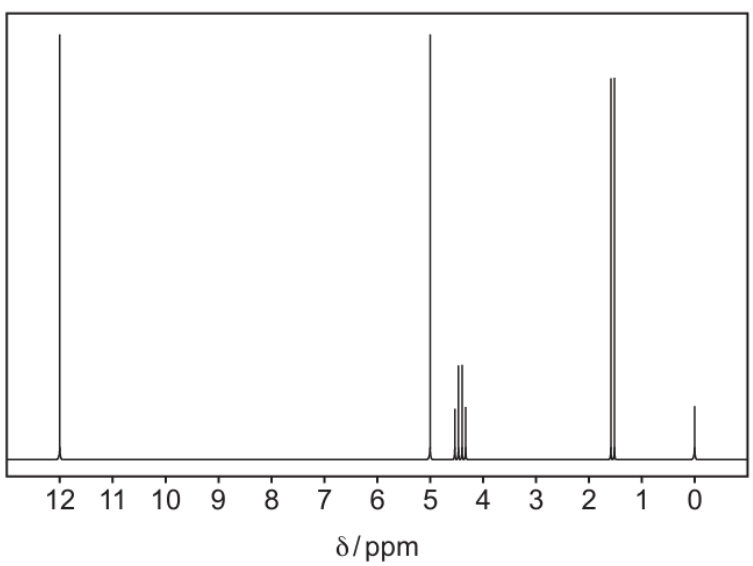


Fig. 8.1

Table 8.1

environment of proton	example	chemical shift range δ / ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to aromatic ring	C**H**$_3$–Ar, –C**H**$_2$–Ar, >C**H**–Ar	2.3–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–C*l*	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0

(i) Use Fig. 8.1 and Table 8.1 to complete Table 8.2.

Table 8.2

proton environment	chemical shift (δ)	name of splitting pattern
–COOH		
⋺CH		
–OH		
–CH$_3$		

[3]

(ii) Name the substance responsible for the peak at δ = 0.0.

.... [1]

(iii) Explain why CDCl_3 is a better solvent than CHCl_3 for use in proton NMR.

....

.... [1]

9 **(b)** Asparagine is an amino acid that contains a chiral carbon atom and displays stereoisomerism.

Separate samples of asparagine are dissolved in $CDCl_3$ and analysed using carbon-13 and proton (^1H) NMR spectroscopy.

asparagine

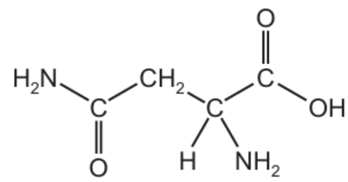


Fig. 6.1

Predict the number of peaks seen in the carbon-13 and proton (^1H) NMR spectra of asparagine.

	carbon-13 NMR	proton (^1H) NMR
number of peaks		

[1]

10 Procaine is used as an anaesthetic in medicine. It can be synthesised from methylbenzene in five steps as shown in Fig. 7.1.

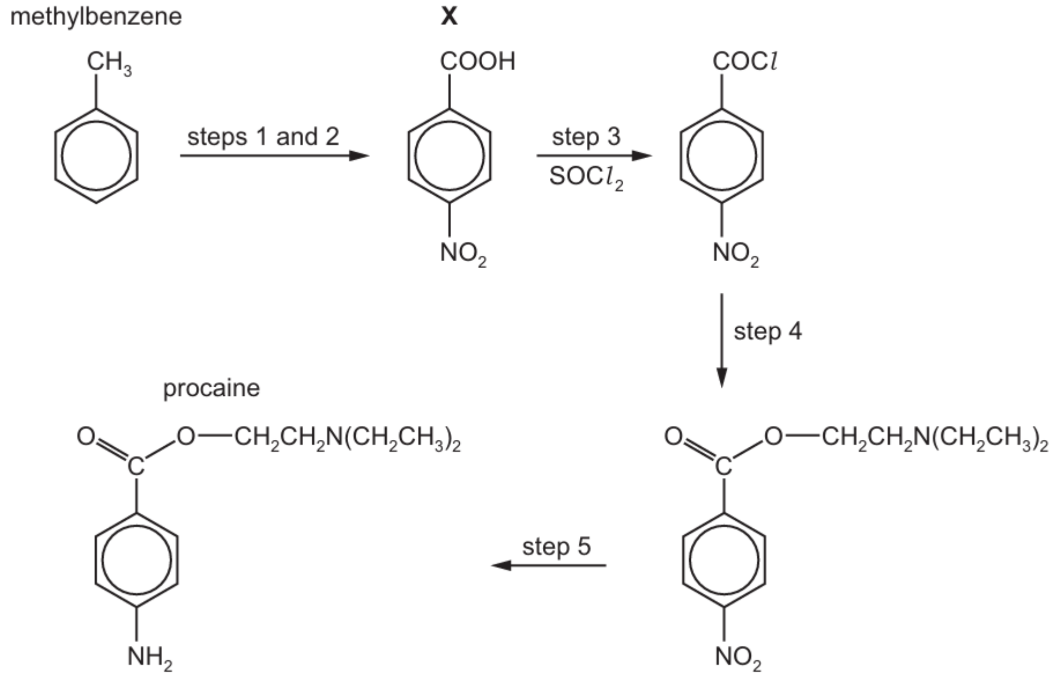


Fig. 7.1

(b) The proton (^{1}H) NMR spectrum of procaine dissolved in D_2O is recorded.

Predict the number of peaks observed.

.... [1]

11 **(a)** State the uses of TMS and D_2O in NMR spectroscopy.

TMS ....

D_2O ....
[1]

(b) The three isomeric ketones with molecular formula $C_5H_{10}O$ are:

- pentan-2-one
- pentan-3-one
- 3-methylbutanone.

(i) Complete Table 7.1 to show the number of peaks observed in the proton (^1H) NMR spectrum and in the carbon-13 NMR spectrum for each compound listed.

Table 7.1

ketone	number of peaks observed in the proton (^1H) NMR spectrum	number of peaks observed in the carbon-13 NMR spectrum
pentan-2-one		
pentan-3-one		
3-methylbutanone		

[2]

(ii) State **all** the ketones with molecular formula $C_5H_{10}O$ that have:

a doublet in their proton (^1H) NMR spectrum

....

a singlet in their proton (^1H) NMR spectrum.

....
[2]

12 **(c)** State the number of peaks that would be seen in the proton (^1H) NMR spectrum of methyl butanoate, $CH_3CH_2CH_2CO_2CH_3$. Name all the splitting patterns seen in this spectrum.

number of peaks ....

splitting patterns ....
[2]

(d) **D** and **E** are both esters with the molecular formula $C_5H_{10}O_2$. Their proton (^1H) NMR spectra are shown in Fig. 9.2 and Fig. 9.3.

D

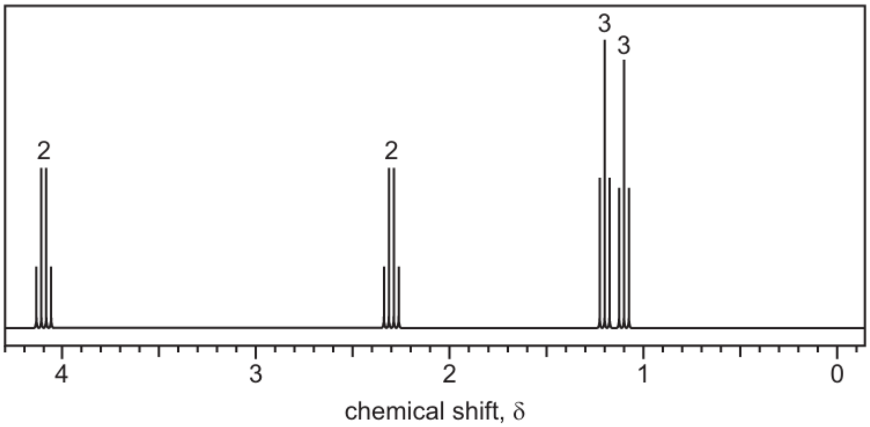


Fig. 9.2

E

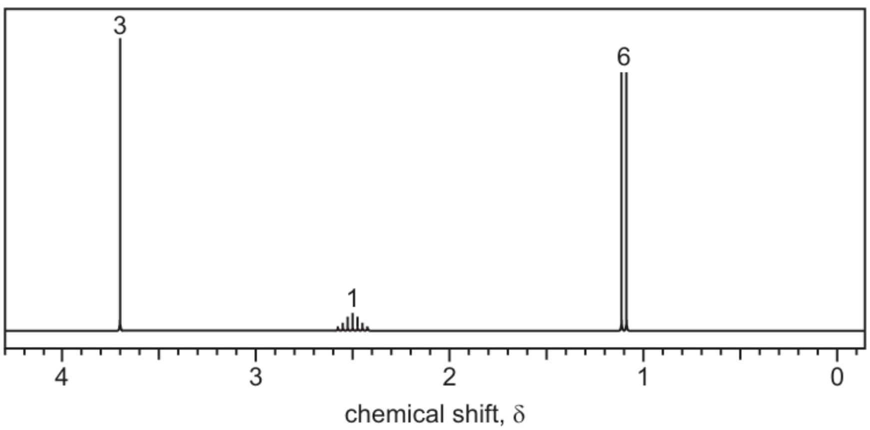


Fig. 9.3

Table 9.2

environment of proton	example	typical chemical shift range, δ/ppm
alkane	$–CH_3$, $–CH_2–$, >CH–	0.9–1.7
alkyl next to C=O	$CH_3–C=O$, $–CH_2–C=O$, >CH–C=O	2.2–3.0
alkyl next to aromatic ring	$CH_3–Ar$, $–CH_2–Ar$, >CH–Ar	2.3–3.0
alkyl next to electronegative atom	$CH_3–O$, $–CH_2–O$, $–CH_2–Cl$	3.2–4.0
attached to alkene	=CHR	4.5–6.0

(iii) The spectrum of **E** has a doublet at δ 1.1.

Identify the protons responsible for this doublet on your structure in **(i)** by labelling these protons with the letter **G**.

Explain why this peak has a chemical shift of 1.1.

....

.... [1]

(i) Deduce the structures of the two esters **D** and **E** and draw their displayed formulae in the boxes below.

D $C_5H_{10}O_2$	**E** $C_5H_{10}O_2$

[2]

(ii) The spectrum of **D** includes a quartet at δ 4.1.

Identify the protons responsible for this quartet on your structure in **(i)** by labelling these protons with the letter **F**.

Explain why this peak is split into a quartet.

....

.... [1]

13 When answering this question it should be assumed that together all the hydrogen atoms in a benzene ring result in a single unsplit peak at δ = 7.2 in a proton ([1]H) NMR spectrum.
The structures of five isomeric ketones, **P**, **Q**, **R**, **S** and **T** are given.

P $C_6H_5COCH(CH_3)_2$

Q $C_6H_5COCH_2CH_2CH_3$

R $C_6H_5CH_2COCH_2CH_3$

S $C_6H_5CH_2CH_2COCH_3$

T $C_6H_5CH(CH_3)COCH_3$

(a) Identify all the chiral carbon atoms on the structures above. Label each chiral carbon atom with an asterisk (*). [1]

(b) The proton ([1]H) NMR spectrum of one of the five isomers, **P**, **Q**, **R**, **S** or **T**, is shown in Fig. 8.1.

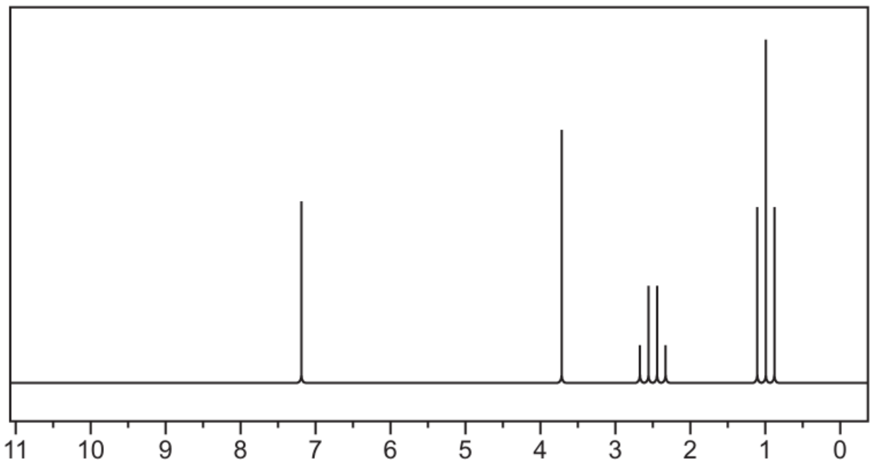


Fig. 8.1

(i) Identify which of the compounds **P**, **Q**, **R**, **S** or **T** gives this spectrum.
Draw the displayed formula of the compound you have identified. Identify the protons responsible for the peaks at δ = 3.7, δ = 2.5 and δ = 1.0 on the structure you have drawn.

[2]

(ii) Name the splitting pattern of the peak at δ = 3.7. Explain why it has this splitting pattern.

....

.... [1]

(c) Choose from the letters **P**, **Q**, **R**, **S** and **T** to identify:

(i) the **two** compounds that each have a doublet peak in the proton (^1H) NMR spectrum

.... [1]

(ii) the compound with only three peaks in its proton (^1H) NMR spectrum.

.... [1]

(d) Suggest a suitable solvent that should be used for obtaining the spectrum shown in Fig. 8.1.

.... [1]

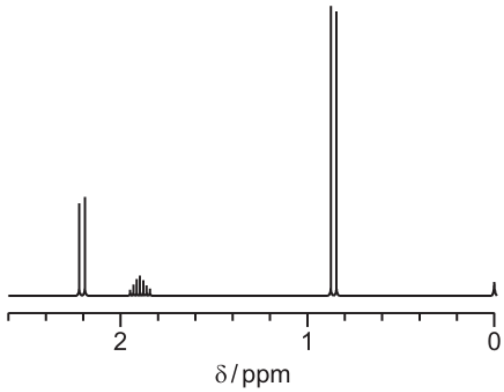
(e) The proton (^1H) NMR spectrum of compound **T** is compared in the presence of D_2O and in the absence of D_2O.

Describe any difference between the two spectra. Explain your answer.

....

.... [1]

14 **(c)** Compound **Y**, $C_5H_{10}O_2$, reacts with Na_2CO_3(aq) to evolve bubbles of gas. The proton (^1H) NMR spectrum of compound **Y** in D_2O is shown.



(i) Use this information to suggest a structure for **Y**.

[1]

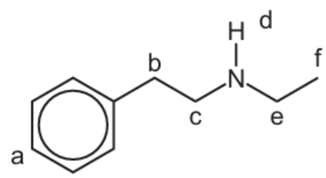
(ii) Use the *Data Booklet*, the proton (^1H) NMR spectrum and your answer to **(c)(i)** to complete the table.

chemical shift (δ)	environment of proton	splitting pattern	number of ^1H atoms responsible for the peak
0.95			
1.90			
2.20			

[3]

15 Compound **T** is made by a three-stage synthesis.

(e) The proton (^{1}H) NMR spectrum of compound **T** shows hydrogen atoms in different environments. Six of these environments are shown on the structure using letters a, b, c, d, e and f.



Use the letters a, b, c, d, e and f to answer the questions that follow. The questions relate to the proton (^{1}H) NMR spectrum of **T**.

Proton d does not cause splitting of the peaks for protons c or e under the conditions used.

Each answer may be one, or more than one, of the letters a, b, c, d, e and f.

(i) Identify the proton or protons with a chemical shift (δ) in the range 6.0 to 9.0.

.... [1]

(ii) Identify the proton or protons whose peak will disappear if D_2O is added.

.... [1]

(iii) Identify the proton or protons whose peak is a triplet.

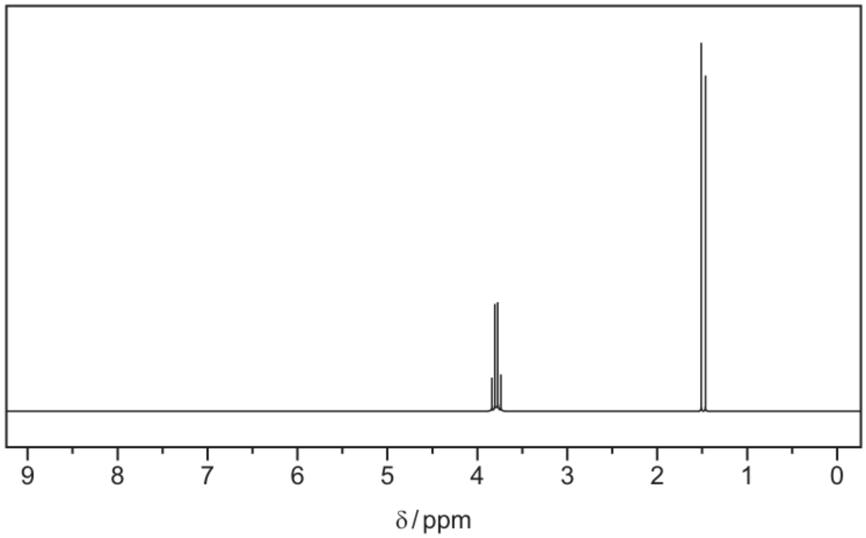
.... [1]

(iv) Identify the proton or protons with the lowest chemical shift (δ).

.... [1]

16 Alanine, $H_2NCH(CH_3)CO_2H$, and glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, are two naturally occurring amino acids.

(b) The proton (^1H) NMR spectrum of **either** alanine in D_2O or glutamic acid in D_2O is shown.



State whether this is the spectrum of alanine in D_2O or the spectrum of glutamic acid in D_2O. Explain your answer by reference to the number of peaks and splitting patterns.

....

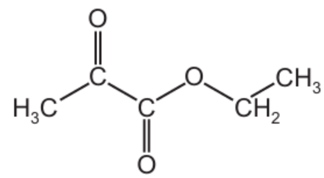
....

....

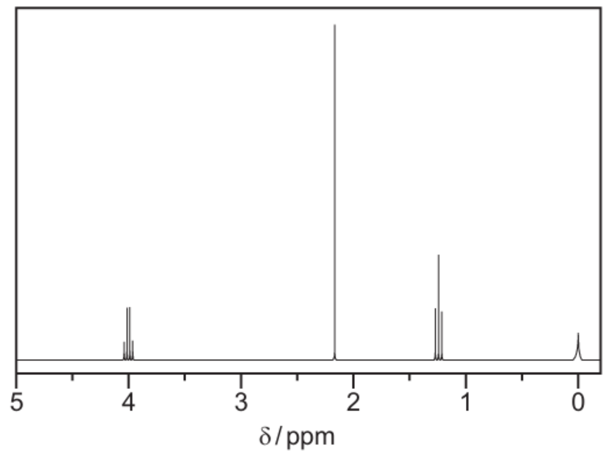
.... [3]

17 **(e)** An ester of pyruvic acid, **F**, is dissolved in $CDCl_3$ and analysed by proton NMR spectroscopy.

F



The proton NMR spectrum of **F** is shown.



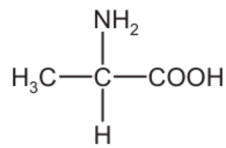
Use the proton NMR spectrum of **F** to complete the table.

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3			
2.2			
4.0			

[3]

(f) Deuterium oxide, D_2O, where D is ^2H, can be used as a solvent in proton NMR spectroscopy.
The proton NMR spectrum of alanine in $CDCl_3$ has 4 peaks.
The proton NMR spectrum of alanine in D_2O has 2 peaks.

alanine



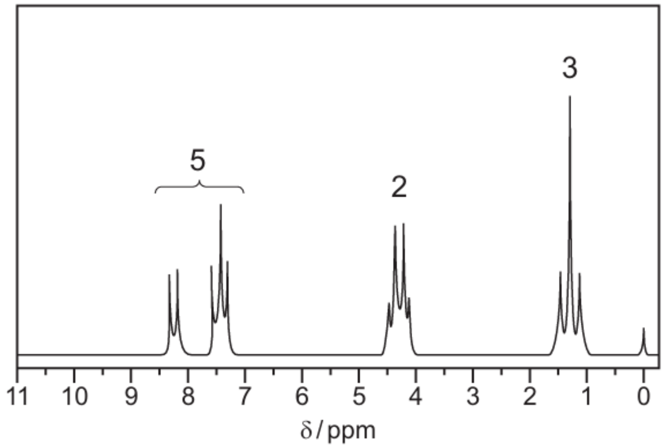
On the diagram of alanine, circle the protons that show peaks in **both** NMR spectra.
Explain your answer.

....

....

.... [2]

18 The proton NMR spectrum of compound **E** in the solvent $CDCl_3$ is shown. The molecular formula of compound **E** is $C_9H_{10}O_2$.



(a) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

.... [1]

(b) Explain why TMS is added to give the small peak at chemical shift δ = 0.

.... [1]

(c) Compound **E** is hydrolysed by hot NaOH(aq), giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq).

.... [1]

(d) (i) Describe and explain the splitting patterns of the peaks at δ = 1.4 and δ = 4.3.

splitting pattern at δ = 1.4 ....

reason for splitting pattern at δ = 1.4 ....

splitting pattern at δ = 4.3 ....

reason for splitting pattern at δ = 4.3 ....
[2]

(ii) Each molecule of compound **E** contains five protons which give rise to the peaks between δ = 7.0 and δ = 8.5.

Identify the functional group in compound **E** which contains these protons.

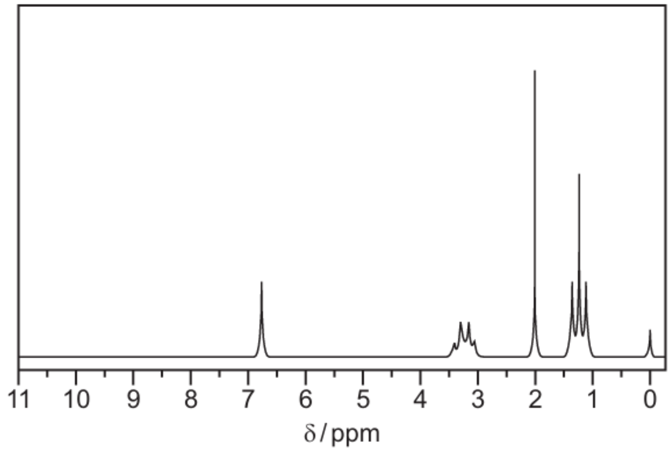
.... [1]

(iii) Give the structural formula of compound **E**.

[1]

19 **(d)** Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.

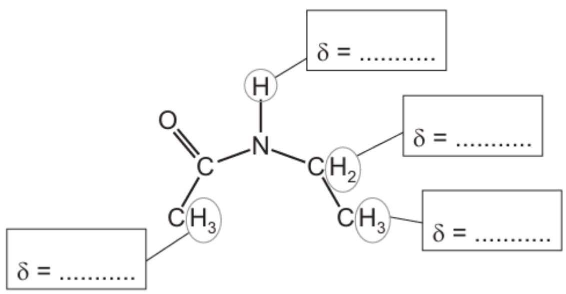
The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(i) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

.... [1]

(ii) Complete the diagram with the chemical shifts, δ, of the protons labelled in the $CH_3CONHC_2H_5$ molecule.



[2]

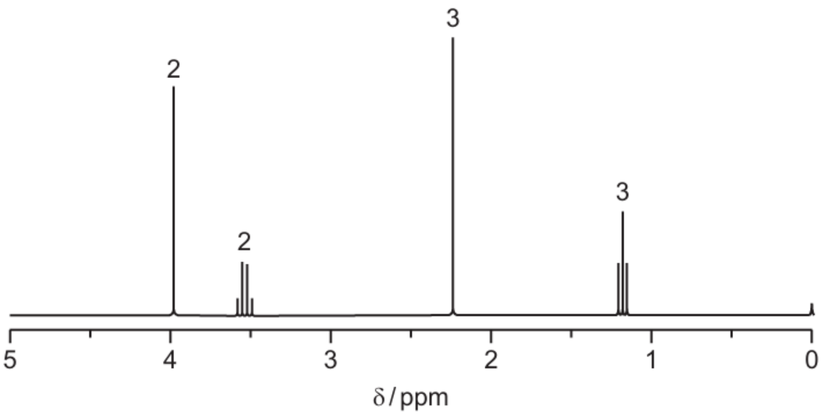
(iii) State and explain how the proton NMR spectrum of the amide $CH_3CONHC_2H_5$ differs when dissolved in D_2O rather than $CDCl_3$.

....

....

.... [2]

20 **(c)** The proton NMR spectrum of compound **X**, $C_5H_{10}O_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at δ 2.2,

....

- deduce the part of the molecule that produces the peaks at δ 1.2 and δ 3.5,

....

- deduce the part of the molecule that produces the peak at δ 4.0.

....

[3]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

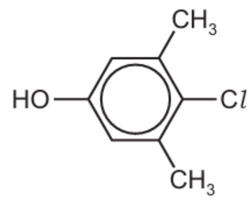
The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

21 Compound **R** is shown.

R



(b) (i) **R** is dissolved in $CDCl_3$ and analysed using carbon-13 and proton NMR spectroscopy.

- Predict the number of peaks that are seen in the carbon-13 NMR spectrum of **R**.

....

- Predict the number of peaks that are seen in the proton NMR spectrum of **R**.

....

[2]

(ii) A separate sample of **R** is dissolved in D_2O. The proton NMR spectrum of this solution shows **one less** peak than is obtained in $CDCl_3$.

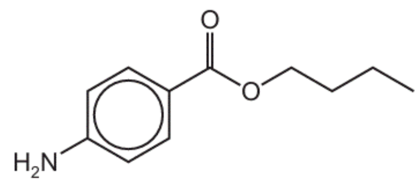
Explain why.

....

.... [1]

22 The structure of butamben is shown.

butamben

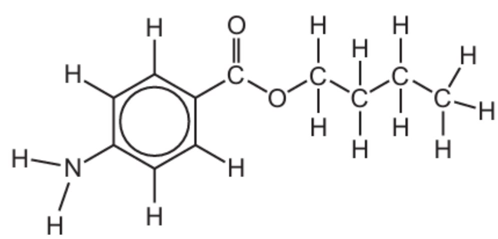


(c) The proton NMR spectrum of butamben in $CDCl_3$ contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

.... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in **(c)(i)**.



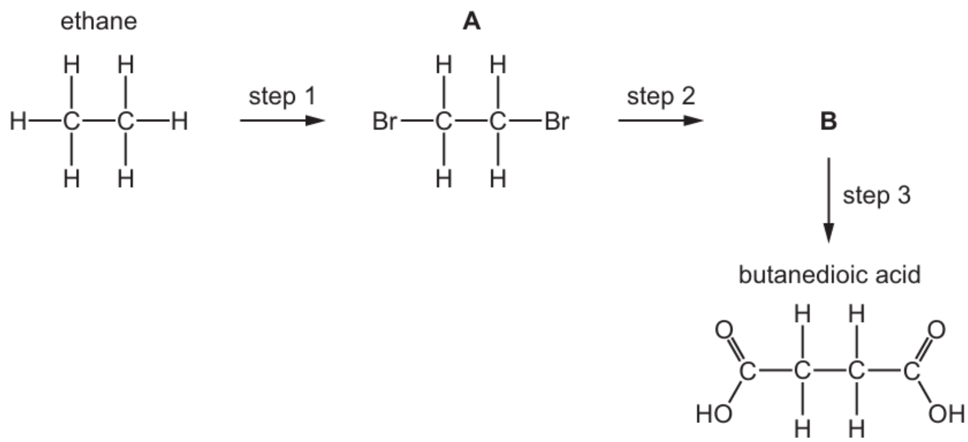
[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in $CDCl_3$.

....

.... [2]

23 Butanedioic acid can be made in a three-step synthesis using ethane as the starting material.



(f) Compare and explain the relative acidities of hexanoic acid, hexan-1-ol and phenol.

....

....

....

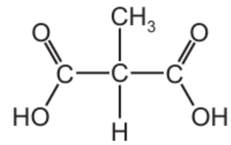
....

....

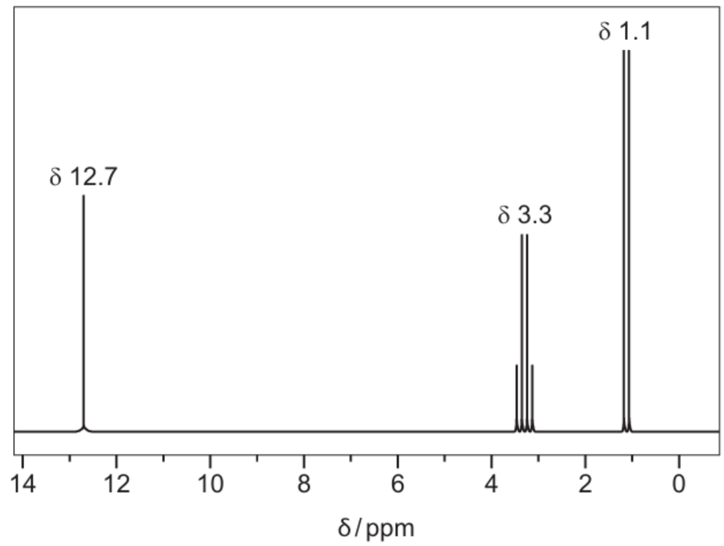
.... [3]

(g) Methylpropanedioic acid is an isomer of butanedioic acid.

methylpropanedioic acid



The proton NMR spectrum of methylpropanedioic acid in CCl_4 is shown.



(i) Identify the protons in the methylpropanedioic acid molecule that are responsible for each area of the proton NMR spectrum.

δ 12.7 ....

δ 3.3 ....

δ 1.1 ....

[2]

(ii) Name the splitting pattern shown at δ 3.3 and explain how it arises.

....

.... [1]

The carbon-13 NMR spectra of butanedioic acid, $HO_2CCH_2CH_2CO_2H$, and methylpropanedioic acid, $HO_2CCH(CH_3)CO_2H$ are different.

(iii) State the number of peaks

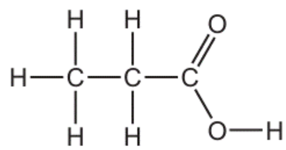
- in the carbon-13 NMR spectrum of butanedioic acid

....

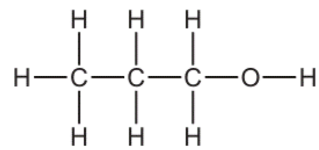
- in the carbon-13 NMR spectrum of methylpropanedioic acid.

....
[1]

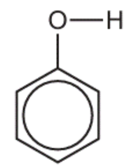
24 The three substances shown all have some acidic properties.



propanoic acid

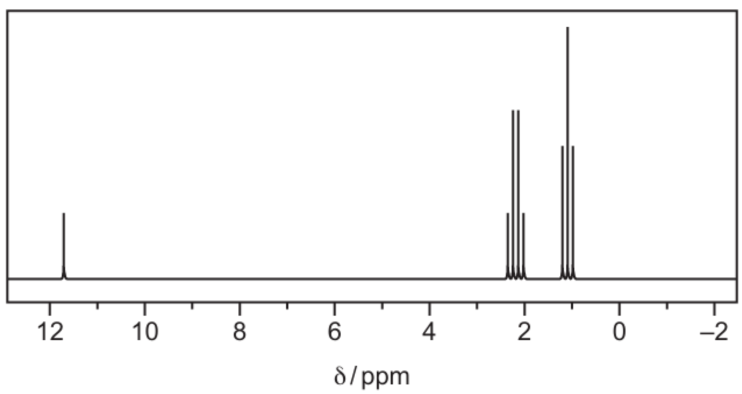


propan-1-ol



phenol

(e) An unknown compound, **Z**, is propan-1-ol, propanal or propanoic acid. The proton NMR spectrum of **Z** dissolved in $CDCl_3$ is shown.



(i) From the proton NMR spectrum, identify **Z**.

.... [1]

(ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

....

....

....

.... [2]