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Level: CIE AS and A Level (9701)
Subject: Chemistry
Topic: CIE Chemistry
Type: Topic Question

Chemistry CIE AS & A Level
To be used for all exam preparation for 2025+

CHEMISTRY AS and A

This to be used by all students studying CIE AS and A level Chemistry (9701) But students of other boards may find it useful

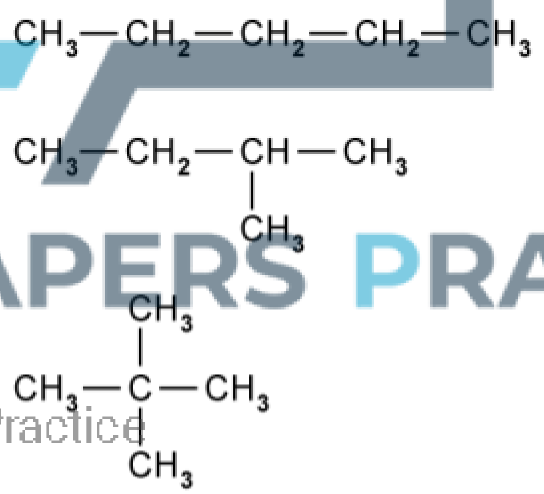
Question 1.

(a) This question is about the NMR analysis of various organic compounds.

Name and draw the structure of the chemical that is commonly used as a standard in NMR spectroscopy.

(2 marks)

(b) Fig. 1.1 shows the structures of compounds **A**, **B** and **C**.



A $CH_3-CH_2-CH_2-CH_2-CH_3$

B $CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

C $CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$

Fig. 1.1

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Compound **A** is pentane, with the chemical formula C_5H_{12}. Compound **B** is 2-methylbutane and compound **C** is 2,2-dimethylpropane, which are both isomers of pentane.

State the number of hydrogen peaks that would be expected in low resolution ^{1}H-NMR spectrum of each isomer.

(3 marks)

(c) More structural details can be deduced using high resolution ^1H NMR.

Explain why the methyl groups in 2-methylbutane, compound **B**, give a doublet splitting pattern while the methyl groups in 2,2-dimethylpropane, compound **C**, give a singlet splitting pattern.

(3 marks)

(d) Carbon-13 NMR is also commonly used to distinguish chemicals.

Predict the number of peaks in the carbon-13 NMR spectra of compounds **A**, **B** and **C**.

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(3 marks)

Question 2.

(a) Compound **X** is a carbohydrate.

Compound **X** contains 62.1% C, 10.3% H and 27.6% O by mass.

i) Show that the empirical formula of compound **X** is C_3H_6O.

[2]

ii) The empirical formula of compound **X** is C_3H_6O and the M_r is 58.0.

Deduce the molecular formula of compound **X**. You **must** explain your reasoning.

molecular formula ....

....

[1]

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(3 marks)

(b) There are several possible isomers of compound **X**.

Draw the structures of **two** isomers of compound **X** that contain a carbonyl group.

isomer 1	**isomer 2**

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(2 marks)

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(c) A sample of a different isomer of compound **X** is cyclopropanol, which was analysed by NMR spectroscopy.

i) Predict the number of peaks in the carbon-13 NMR spectrum of cyclopropanol.

[1]

ii) Cyclopropanol was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded as shown in Fig. 2.1.

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Fig. 2.1

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Suggest **one** change that can be made to the solvent used for the proton NMR and how this will affect the spectrum produced.

[2]

………

………

………

(3 marks)

Question 3.

(a) Methyl cinnamate, $C_{10}H_{10}O_2$, is a white crystalline solid used in the perfume industry.

The proton NMR spectrum of methyl cinnamate in the solvent $CDCl_3$ is shown in Fig. 1.1.

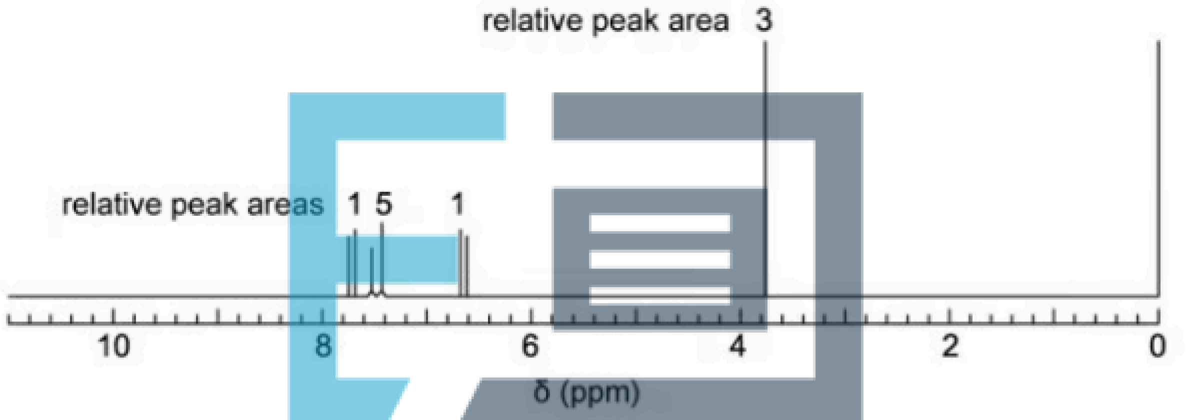

Fig. 1.1

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

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[1]

ii) Explain why TMS is added to give the small peak at chemical shift $\delta = 0$.

[1]

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(2 marks)

(b) The structure of methyl cinnamate is shown in Fig. 1.2.

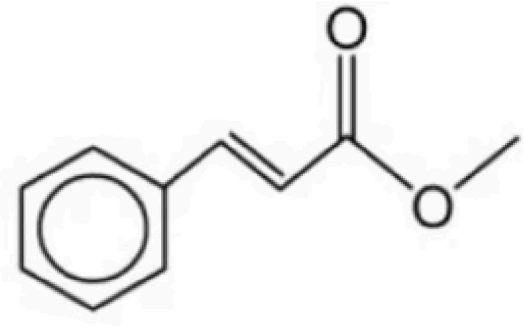

Fig. 1.2

The data in Table 1.1 should be used in answering this question.

Identify the proton environment that gives rise to the peak at a chemical shift of 3.8 ppm in Fig. 1.1. Explain your answer.

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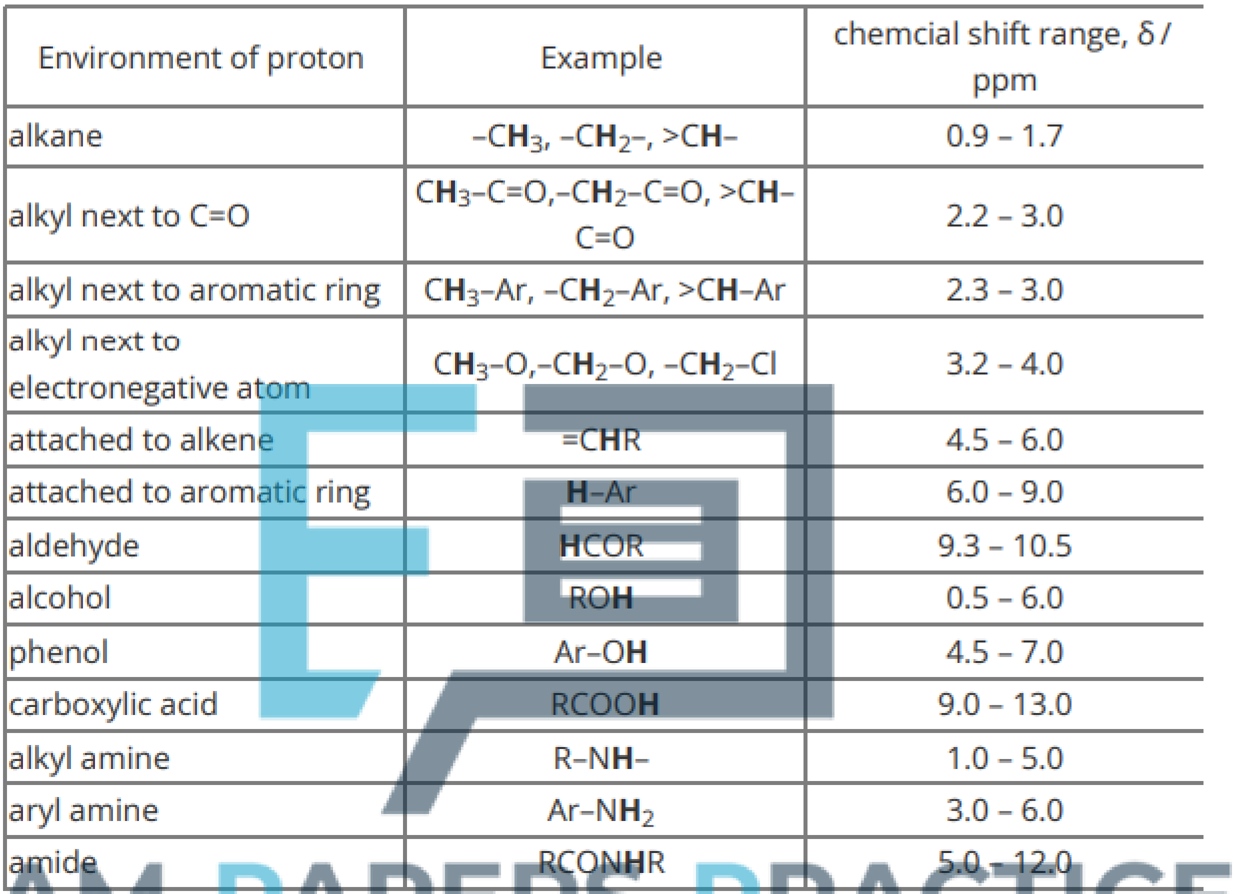
Table 1.1



Environment of proton	Example	chemcial 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**$_2$–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
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

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(3 marks)

(c) Proton NMR spectroscopy can be used to distinguish between isomers of $C_6H_{12}O_2$.

Draw the two esters with formula $C_6H_{12}O_2$ that each have only two peaks, both singlets, in their ^1H NMR spectra. The relative peak areas are 3:1 for both esters.

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(2 marks)

(d) The proton NMR spectrum of another isomer of $C_6H_{12}O_2$ is shown in Fig. 1.3.

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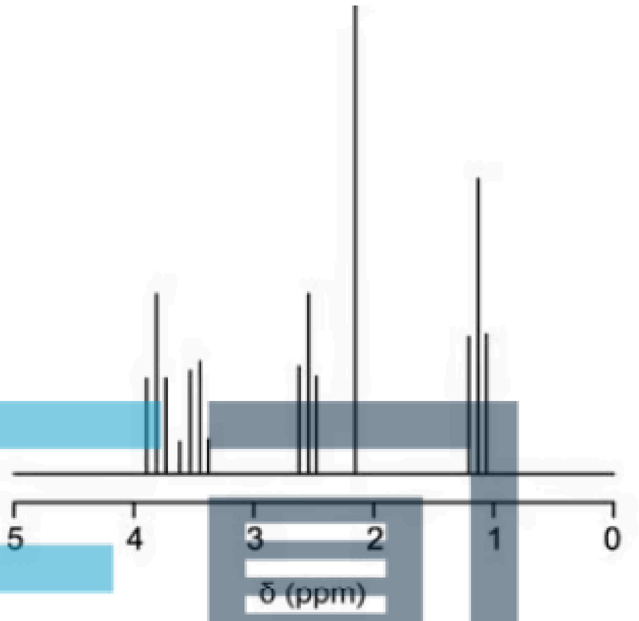

Fig. 1.3

The integration values for the peaks in the proton NMR spectrum of this isomer are given in Table 1.2.

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Table 1.2

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Chemical shift, δ/ppm	3.8	3.5	2.6	2.2	1.2
Integration value	0.6	0.6	0.6	0.9	0.9
Splitting pattern	triplet	quartet	triplet	singlet	triplet

i) Deduce the simplest ratio of the relative numbers of protons in each environment in the isomer.

[1]

ii) The data in Table 1.1 should be used in answering this question.

Describe and explain the splitting patterns of the peaks at δ = 3.5 and δ = 1.2.

splitting pattern at δ = 3.5 ....

reason for splitting pattern at δ = 3.5 ....

splitting pattern at δ = 1.2 ....

reason for splitting pattern at δ = 1.2 ....

[4]

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(5 marks)

(e) Four isomers of $C_6H_{12}O_2$, **A**, **B**, **C** and **D**, are shown in Fig. 6.4.

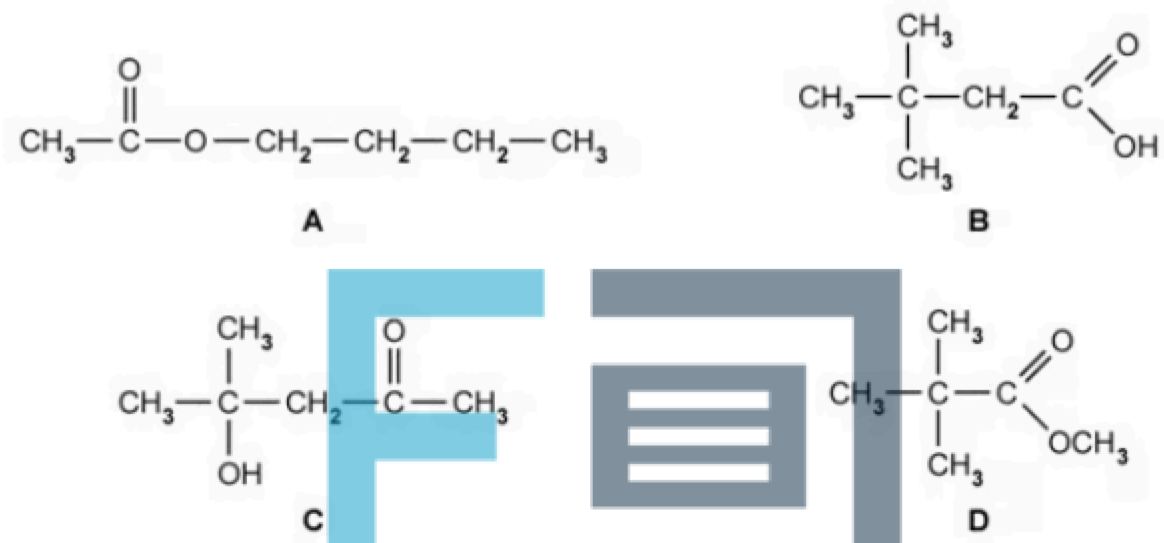

Fig. 1.4

The C-13 NMR spectrum of one of the four isomers of $C_6H_{12}O_2$ is shown in Fig. 1.5.

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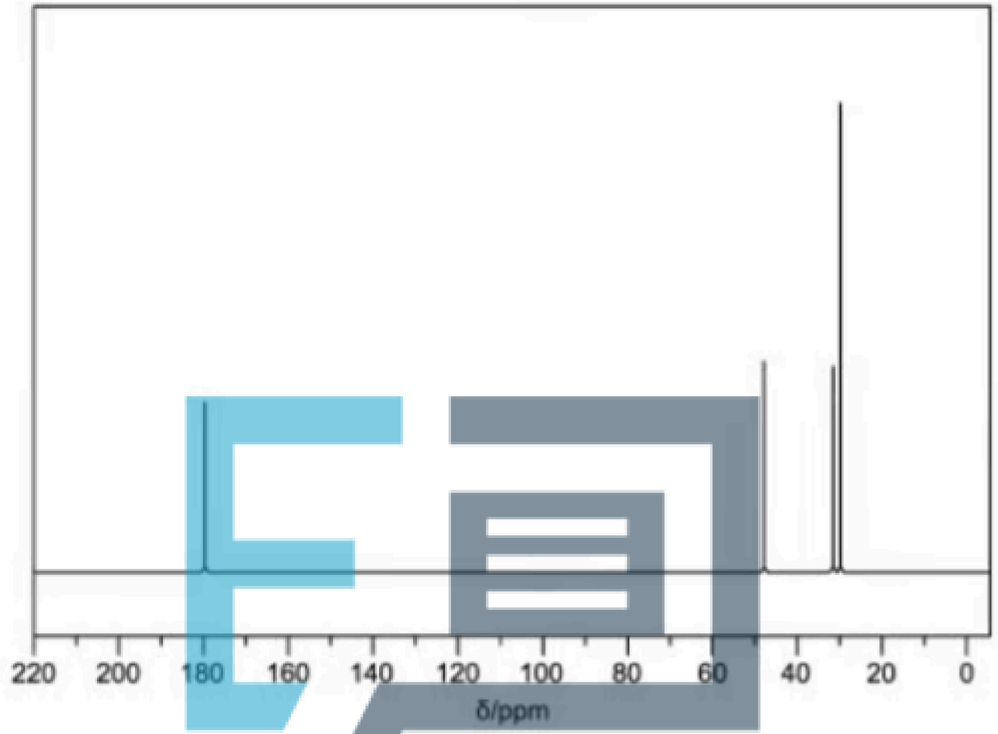

Fig. 1.5

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The data in Table 1.3 should be used in answering this question.

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Identify which of the four isomers, **A, B, C** or **D** of $C_6H_{12}O_2$ produced the C-13 NMR spectrum shown in Fig 1.5.

Table 1.3

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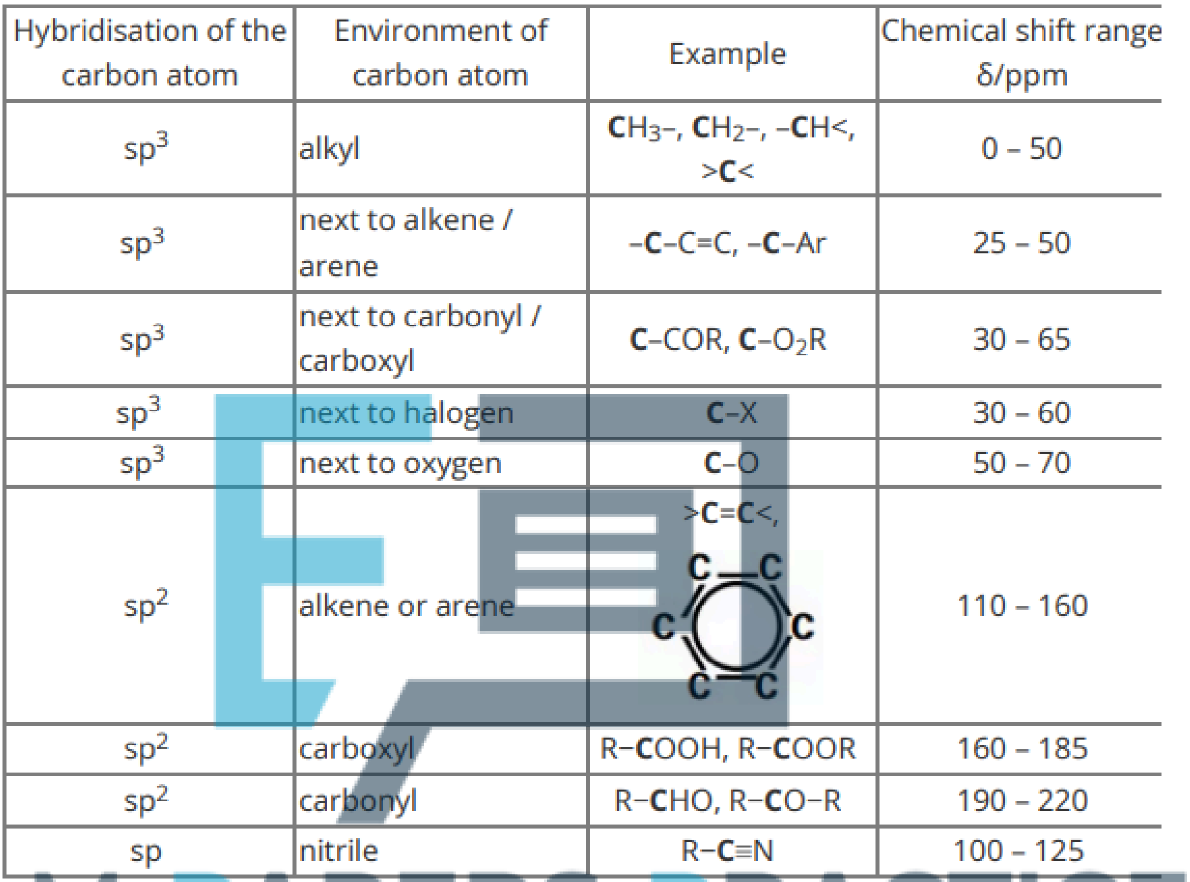

Hybridisation of the carbon atom	Environment of carbon atom	Example	Chemical shift range δ/ppm
sp^3	alkyl	$\mathbf{C}H_3$–, $\mathbf{C}H_2$–, –$\mathbf{C}$H<, >$\mathbf{C}$<	0 – 50
sp^3	next to alkene / arene	–$\mathbf{C}$–C=C, –$\mathbf{C}$–Ar	25 – 50
sp^3	next to carbonyl / carboxyl	$\mathbf{C}$–COR, $\mathbf{C}$–O_2R	30 – 65
sp^3	next to halogen	$\mathbf{C}$–X	30 – 60
sp^3	next to oxygen	$\mathbf{C}$–O	50 – 70
sp^2	alkene or arene	>$\mathbf{C}$=$\mathbf{C}$<,	110 – 160
sp^2	carboxyl	R–$\mathbf{C}$OOH, R–$\mathbf{C}$OOR	160 – 185
sp^2	carbonyl	R–$\mathbf{C}$HO, R–$\mathbf{C}$O–R	190 – 220
sp	nitrile	R–$\mathbf{C}$≡N	100 – 125

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(1 mark)

Question 4.

(a) Ethane-1,2-diol, $C_2H_6O_2$, can be distinguished from ethanedioic acid, $C_2H_2O_4$, by a number of analytic techniques including MS, IR and NMR

Fig. 2.1 (spectrum **A**) and Fig. 2.2 (spectrum **B**) show the mass spectra of ethane-1,2-diol and ethanedioic acid.

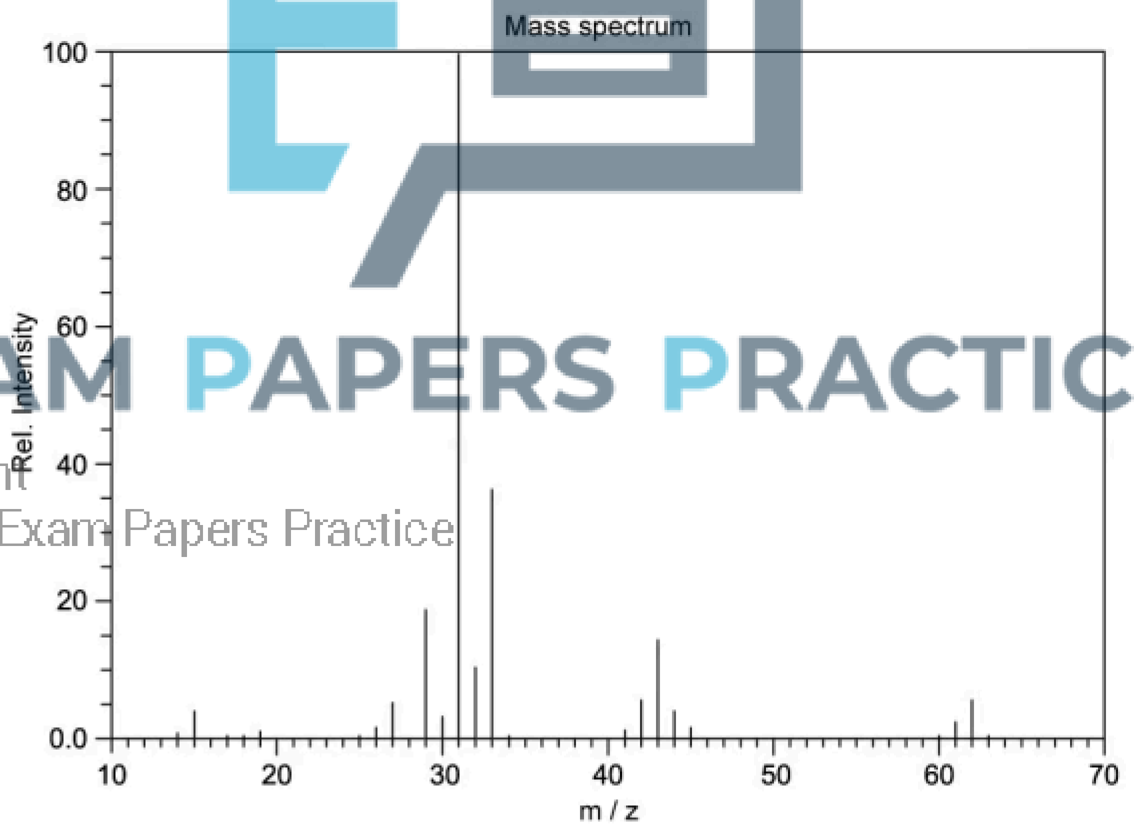

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Fig. 2.1 (spectrum **A**)

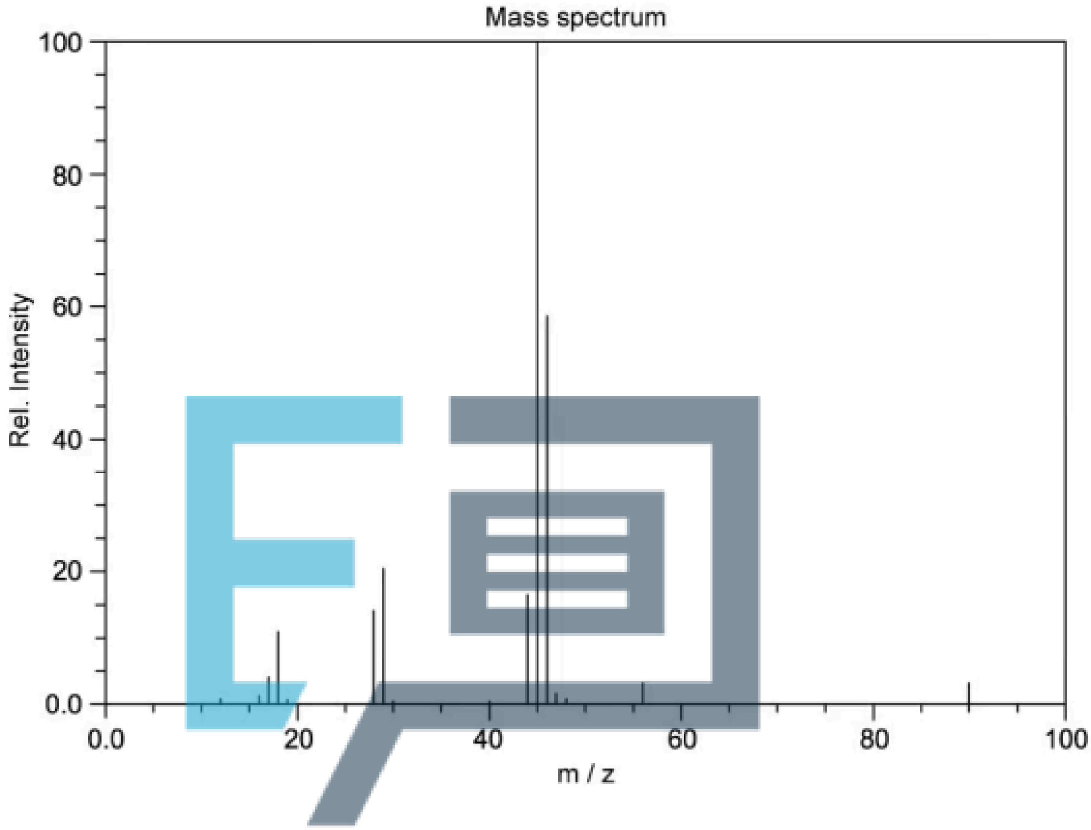

Fig. 2.2 (spectrum B)

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Complete Table 2.1 to suggest which compound is responsible for each spectrum? Explain your answer.

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Table 2.1

Spectrum	Organic compound	Explanation
A		
B		

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(2 marks)

(b) The IR spectra of ethane-1,2-diol, $C_2H_6O_2$, and ethanedioic acid dihydrate, $C_2H_2O_4.2H_2O$, are shown in Fig. 2.3 (Spectrum **C**) and Fig. 2.4 (Spectrum **D**).

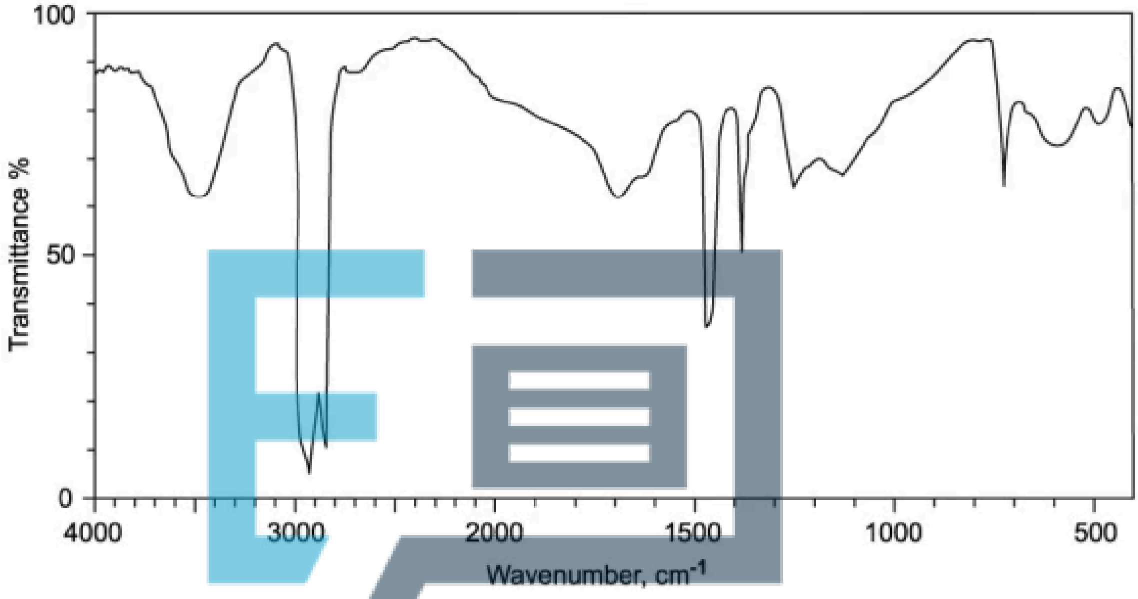

Fig. 2.3 (spectrum **C**)

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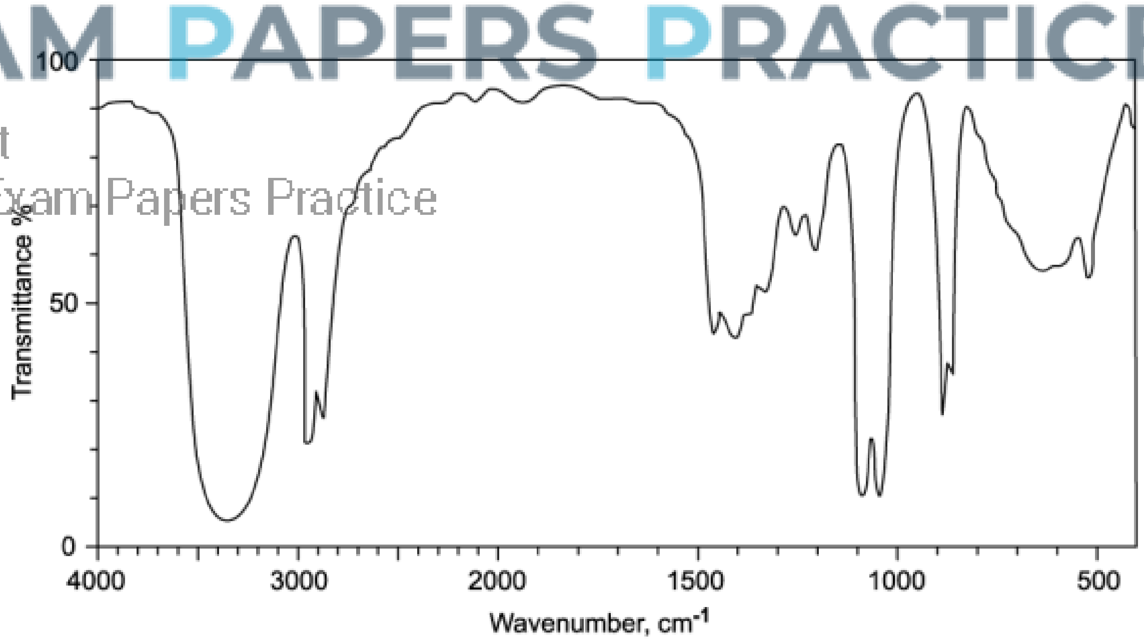

Fig. 2.4 (spectrum **D**)

The data in Table 2.3 should be used in answering this question.

Complete Table 2.2 to suggest which compound is responsible for each spectrum? Explain your answer.

Table 2.2

Spectrum	Organic compound	Explanation
C		
D		

Table 2.2

Bond	Functional groups containing the bond	Characteristic infrared absorption range (in wavenumber) / cm^{-1}
C−O	hydroxy, ester	1040 – 1300
C=C	aromatic compound, alkene	1500 – 1680
C=O	amide	1640 – 1690
	carbonyl, carboxyl	1670 – 1740
	ester	1710 – 1750
C≡N	nitrile	2200 – 2250
C−H	alkane	2850 – 2950
N−H	amine, amide	3300 – 3500
O−H	carboxyl	2500 – 3000
	hydroxy	3200 – 3600

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(2 marks)

(c) The proton NMR spectrum of ethane-1,2-diol is shown in Fig. 2.5.

Describe and explain the splitting patterns of the spectrum.

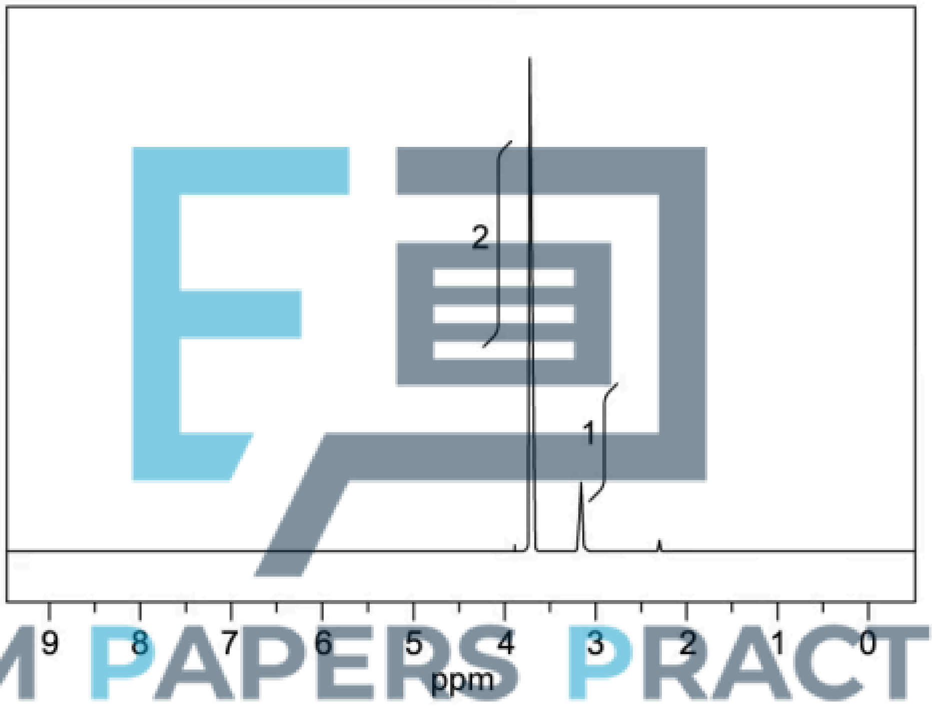

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Fig. 2.5

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(3 marks)

(d) Suggest the number of proton NMR peaks and splitting pattern for ethanedioic acid.

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(2 marks)

Question 5.

(a) Lidocaine is used as a local anaesthetic. The structure of lidocaine is shown in Fig. 3.1.

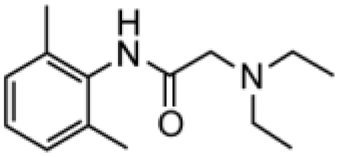

Fig. 3.1

A sample of lidocaine was analysed by carbon-13 NMR spectroscopy.

Predict the number of peaks in the carbon-13 NMR spectrum of lidocaine.

____

(1 mark)

(b) Lidocaine was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded as shown in Fig. 3.2.

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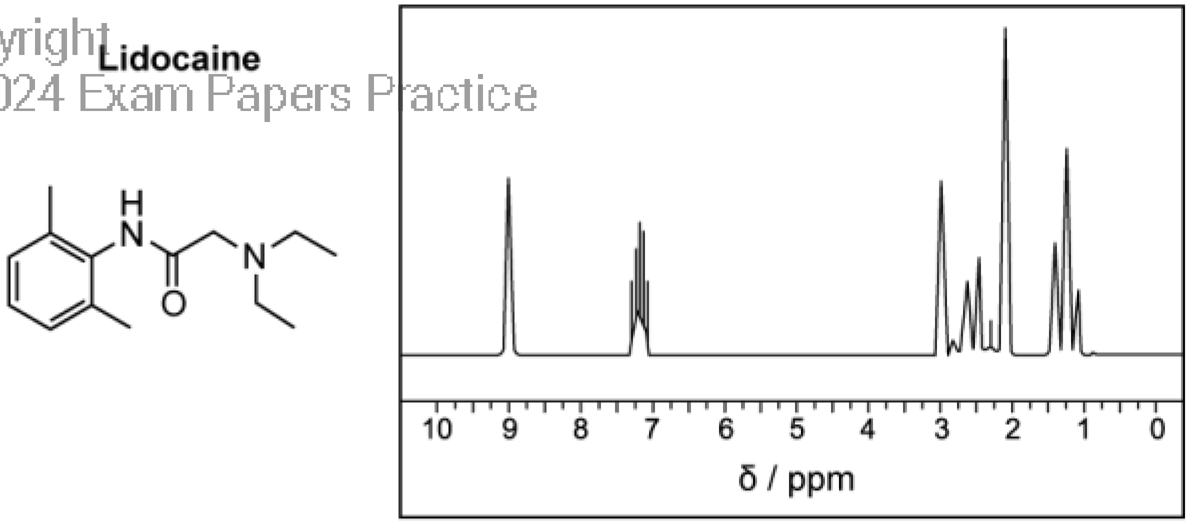

Fig. 3.2

Using Table 3.2 to complete Table 3.1 for the chemical shifts δ 1.2 ppm, 3.5 ppm and 5.5 ppm.

Table 3.1

δ / ppm	environment of proton	number of ^1H atoms responsible for the peak	splitting pattern
1.2	terminal methyl groups next to CH_2	6	triplet
2.3			
3.0			
7.1 - 7.4	attached to the aromatic ring	3	overlapping peaks
9.0			

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Table 3.2

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

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(3 marks)

(c) Explain the splitting pattern for the absorption at δ 1.2 ppm.

(1 mark)

Question 6.

(a) Compound **P** is a naturally occurring chemical found in strawberries, apples and Parmesan cheese.

The percentage by mass is carbon 58.82%, hydrogen 9.80% and oxygen 31.38%.

The mass spectrum of compound **P** is recorded in Fig. 1.1.

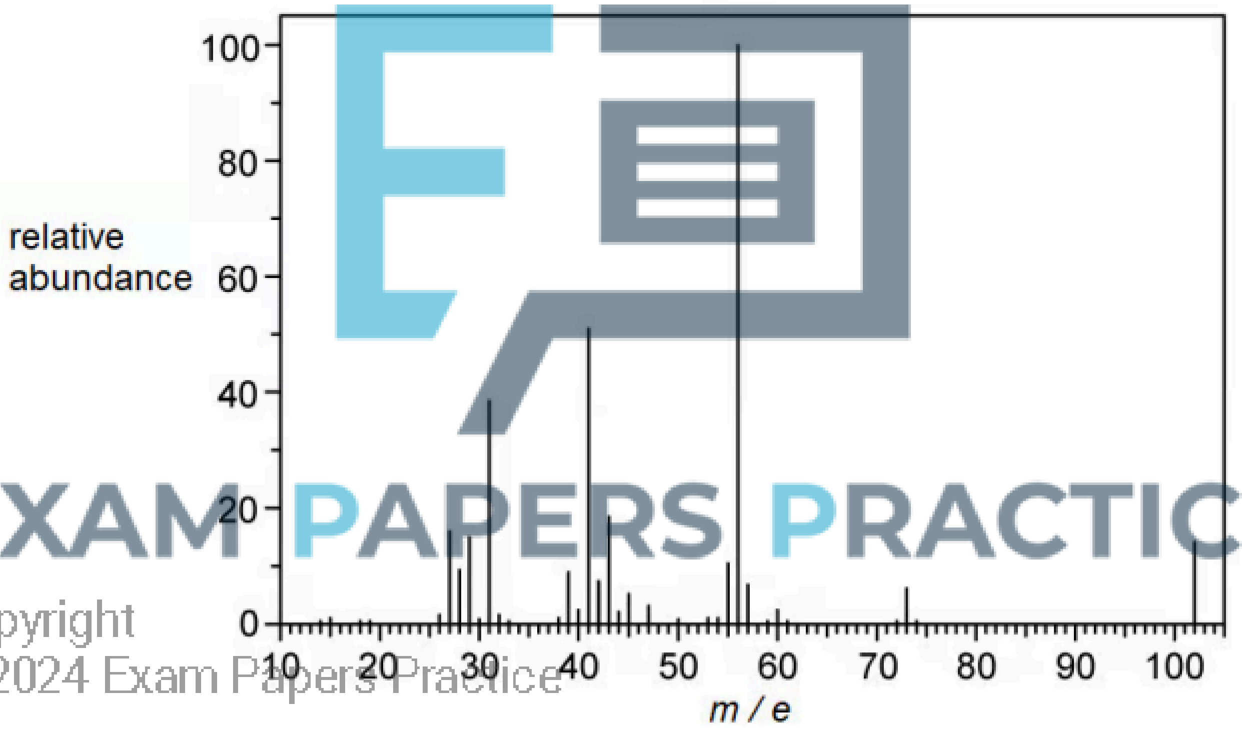

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Fig. 1.1

Determine the molecular formula of compound **P**. Show your working.

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(3 marks)

(b) Table 1.1 shows the results of qualitative tests performed on compound **P**.

Table 1.1

Test	**Observation**
Addition of H_2O	Forms separate layers
Na_2CO_3 (aq)	No visible change
2,4-DNPH	No visible change
Tollens' reagent	No visible change

Analyse the potential functional groups in compound **P**. Explain your answers.

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(4 marks)

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(c) The carbon-13 (^{13}C) NMR spectrum of compound **P** is shown in Fig. 1.2.

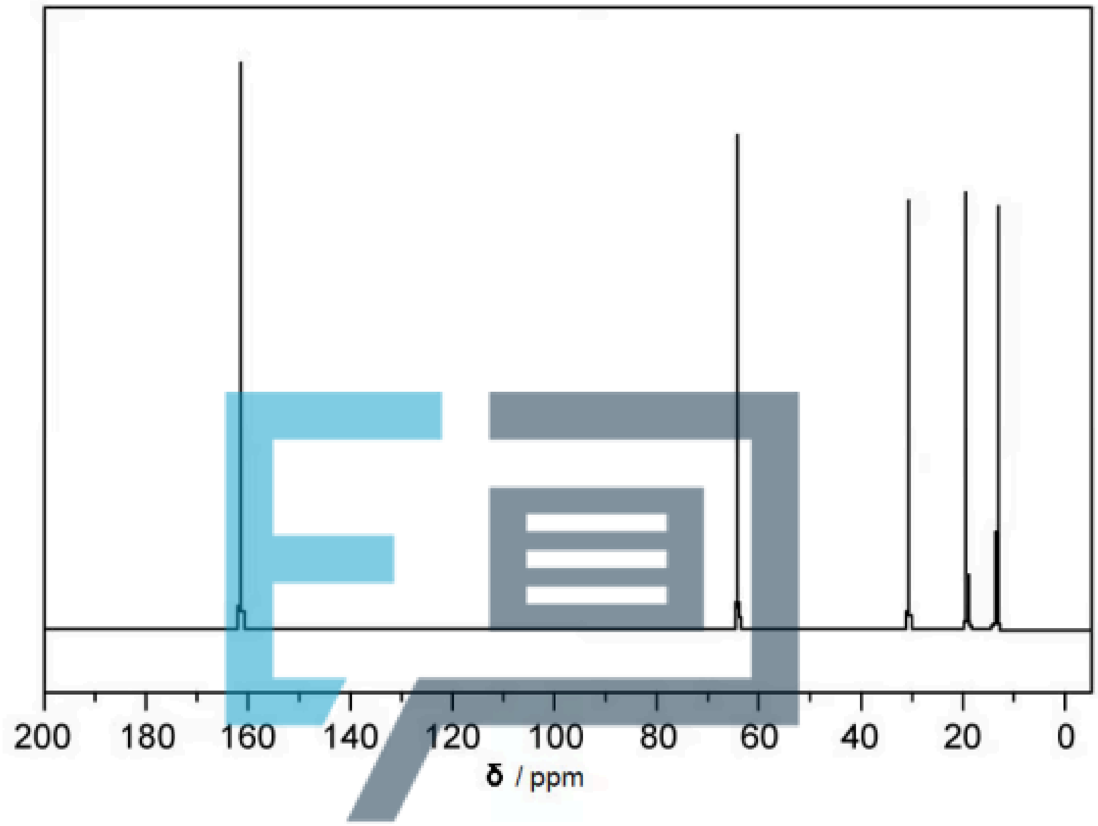

Fig. 1.2

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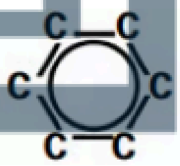
Table 1.2

Hybridisation of the carbon atom	**Environment of carbon atom**	**Example**	**Chemical shift range δ / ppm**
sp^3	alkyl	$\mathbf{C}H_3$–, $\mathbf{C}H_2$–, –**C**H<, >**C**<	0 – 50
sp^3	next to alkene / arene	–**C**–C=C, –**C**–Ar	25 – 50
sp^3	next to carbonyl / carboxyl	**C**–COR, **C**–O_2R	30 – 65
sp^3	next to halogen	**C**–X	30 – 60
sp^3	next to oxygen	**C**–O	50 – 70
sp^2	alkene or arene	>**C**=**C**<, 	110 – 160
sp^2	carboxyl	R–**C**OOH, R–**C**OOR	160 – 185
sp^2	carbonyl	R–**C**HO, R–**C**O–R	190 – 220
sp	nitrile	R–**C**≡N	100 – 125

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Identify the functional group(s) present in compound **P** using your answer in **(b)** and information from Fig. 1.2 and Table 1.2. Explain your answer.

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(3 marks)

(d) The high-resolution **proton** NMR spectrum of compound **P** was recorded as shown in Fig. 1.3.

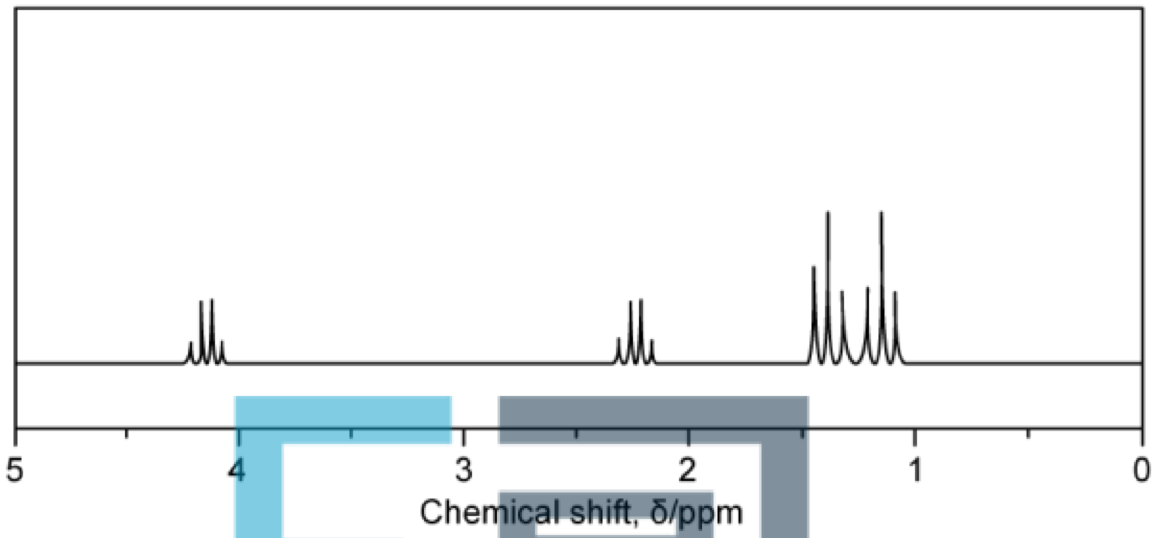

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Fig. 1.3

Table 1.3

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

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Suggest the structure of compound **P** using your answers to **(a)**, **(b)** and **(c)** and information from Fig. 1.3 and Table 1.3**.** Explain your answer.

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(3 marks)

Question 7.

(a) A chemist prepares and analyses some esters.

The chemist prepares an ester by reacting propan-2-ol with ethanoic anhydride.

Using structural formulae, write an equation for the reaction of propan-2-ol and ethanoic anhydride.

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(1 mark)

(b) A sample contains a mixture of two esters contaminated with an alkane and an alcohol.

The chemist attempts to separate the four organic compounds in the mixture using gas chromatography. The stationary phase in the gas chromatograph column is a liquid alkane.

i) How does a liquid stationary phase separate the organic compounds in a mixture?

[1]

ii) Predict the separation of these four compounds using the alkane stationary phase, including relative retention times. Explain your answer.

[2]

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(3 marks)

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(c) Gas chromatography is often used in conjunction with other techniques such as mass spectrometry and NMR spectroscopy.

An ester is isolated from a perfume by gas chromatography and then analysed.

The percentage by mass is carbon 66.63%, hydrogen 11.18% and oxygen 22.19%.

The mass spectrum and high-resolution proton NMR spectrum of the ester are recorded in Fig. 2.1 and Fig. 2.2 respectively.

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Fig. 2.1

Fig. 2.1

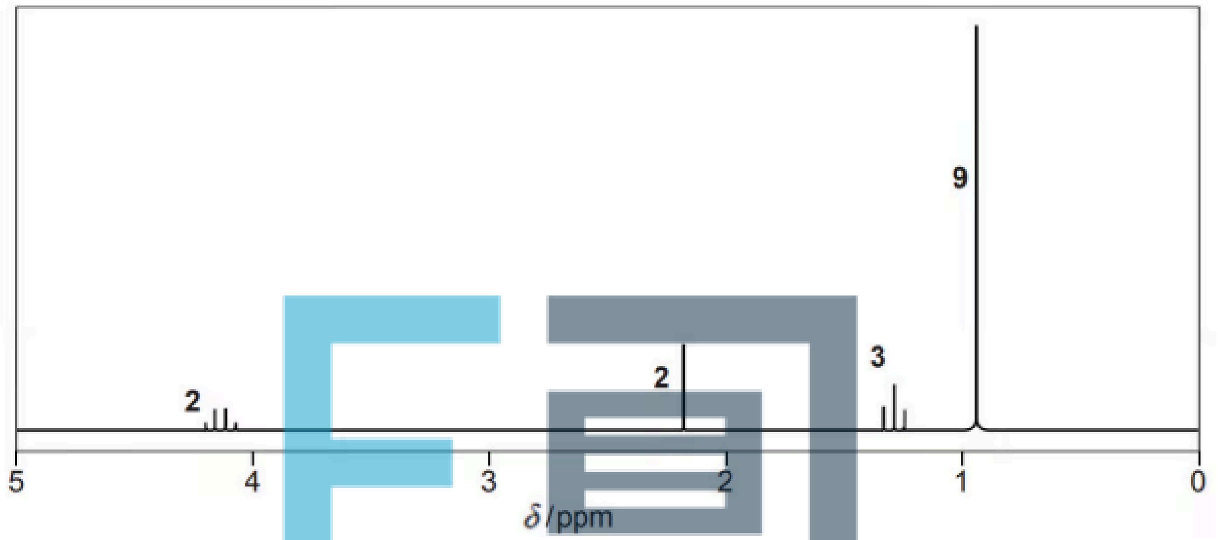

Fig. 2.2

Table 2.1

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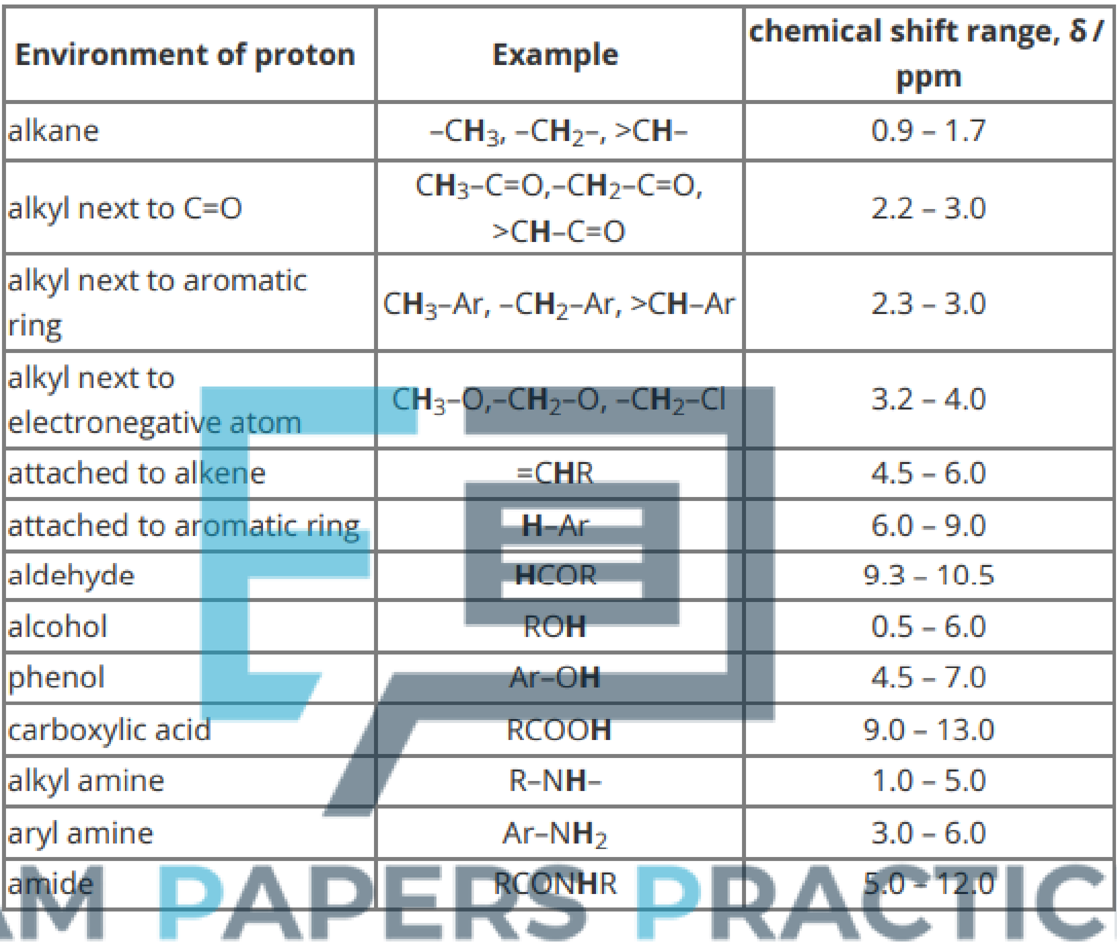

Environment of proton	Example	chemical shift range, δ / ppm
alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9 – 1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2 – 3.0
alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3 – 3.0
alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$	3.2 – 4.0
attached to alkene	=CHR	4.5 – 6.0
attached to aromatic ring	H–Ar	6.0 – 9.0
aldehyde	HCOR	9.3 – 10.5
alcohol	ROH	0.5 – 6.0
phenol	Ar–OH	4.5 – 7.0
carboxylic acid	RCOOH	9.0 – 13.0
alkyl amine	R–NH–	1.0 – 5.0
aryl amine	$Ar-NH_2$	3.0 – 6.0
amide	RCONHR	5.0 – 12.0

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Use all of the information to draw the structure of the ester. Explain your answer.

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(8 marks)

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