37.4 PROTON ^{1}H NMR SPECTROSCOPY

Learning outcomes

Candidates should be able to:

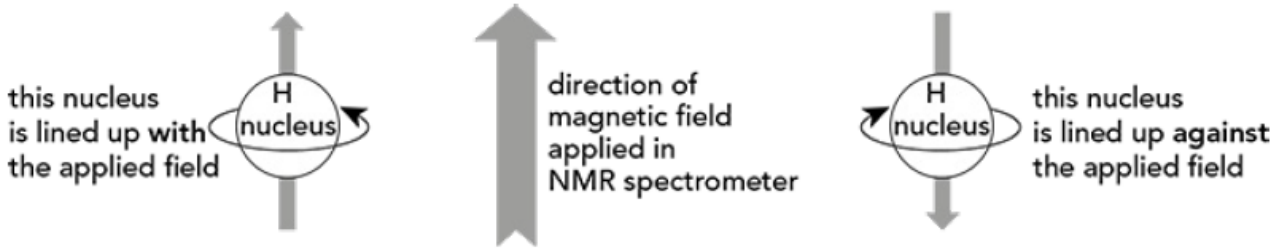
1. analyse and interpret a proton (^{1}H) NMR spectrum of a simple molecule to deduce:
   (a) the different environments of protons present using chemical shift values
   (b) the relative numbers of each type of proton present from the relative peak areas
   (c) the number of equivalent protons on the carbon atom adjacent to the one to which the given proton is attached from the splitting pattern, using the $n + 1$ rule (limited to singlet, doublet, triplet, quartet, and multiplet)
   (d) the possible structures for the molecule
2. predict the chemical shifts and splitting patterns of the protons in a given molecule
3. describe the use of tetramethylsilane, TMS, as the standard for chemical shift measurements
4. state the need for deuterated solvents, e.g., $CDCl_3$, when obtaining a proton NMR spectrum
5. describe the identification of O–H and N–H protons by proton exchange using D_2O

Introduction

NMR Spectroscopy for Visual Learners

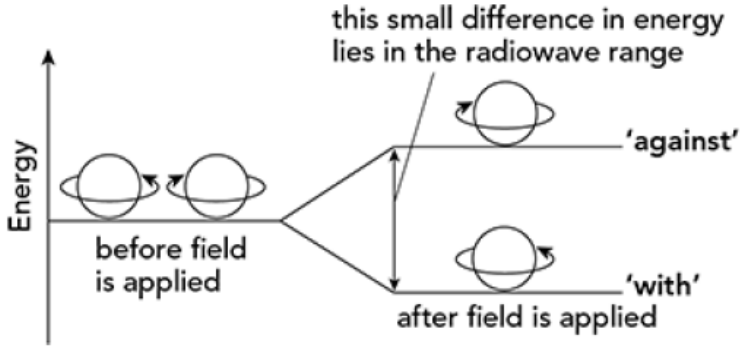
NMR uses the fact that the nucleus of each hydrogen atom in an organic molecule behaves like a tiny magnet. The nucleus of a hydrogen atom consists of a single proton. This proton can spin. The spinning motion of the positively charged proton causes a very small magnetic field to be set up.

In NMR we put the sample to be analysed in a magnetic field. The hydrogen nuclei (protons) either line up with the field or, by spinning in the opposite direction, line up against the magnetic field.



There is a tiny difference in energy between the oppositely spinning 1H nuclei. This difference corresponds to the energy carried by waves in the radiowave range of the electromagnetic radiation spectrum. In NMR spectroscopy, the nuclei 'flip' between the two energy levels

Only atoms whose mass number is an odd number, e.g., ^{1}H or ^{13}C, absorb energy in the range of frequencies that is analysed.



The size of the gap between the nuclear energy levels varies slightly, depending on the location of other atoms in the molecule (the molecular environment). Therefore, NMR can be used to identify 1H atoms in different parts of a molecule.

You will find this easier to understand by looking at an example. If we look at a molecule of methanol, CH_3OH, we can see that there are 1H atoms in two different molecular environments. We have ^{1}H atoms in

both the ─CH_3 group and the ─OH group. The energy absorbed by the ^1H atoms in ─CH_3 is different from the energy absorbed by the 1H atom in ─OH.

In NMR spectroscopy, we vary the magnetic field as that is easier than varying the wavelength of radio waves. As the magnetic field is varied, the ^1H nuclei in different molecular environments flip at different field strengths. The different field strengths are measured relative to a reference compound, which is givenna value of zero. The standard compound chosen is tetramethylsilane (TMS).

TMS is chosen because it is an inert, volatile liquid that mixes well with most organic compounds. Also, its formula is $Si(CH_3)_4$, so all its H atoms are equivalent (i.e., they are all in the same molecular environment).

So, importantly, TMS only gives one sharp absorption, called a peak, and this peak is at a higher frequency than most other protons. All other absorptions are measured by their shift away from the sharp TMS peak on the NMR spectrum. This is called the *chemical shift* (δ), and is measured in units of parts per million (ppm).

ChemDoodle Web Components | Demos > Simulate NMR and MS

1. State the uses of TMS and D_2O in NMR spectroscopy.

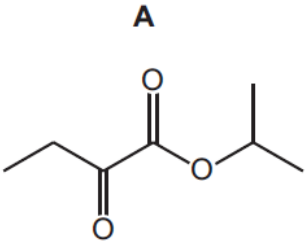
   TMS .....

   D_2O ..... [1]

Predicting the number of peaks in ^{13}C NMR

Carbon-13 NMR produces a spectrum with different chemical shifts for non-equivalent carbon atoms in a molecule.

2. Compound A is analysed by carbon-13 NMR and proton (^1H) NMR spectroscopy.



   (i) State the reference substance and a solvent that can be used in NMR spectroscopy.

   reference .....

   solvent ..... [1]

   (ii) Predict the number of peaks in the carbon-13 NMR spectrum of A.

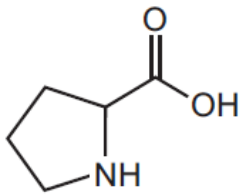
   ..... [1]

3. State the number of different absorptions in the carbon-13 NMR spectrum of diethylamine.

   ..... [1]

4. Proline is a naturally occurring amino acid. The skeletal formula of proline is shown.

proline



State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of proline.

..... [1]

5. The carbon-13 NMR spectra of R, S, T and U are compared.
Complete Table 7.1 to state the number of peaks in the spectrum of each compound. [2]

Table 7.1

compound		number of peaks
R	$(CH_3)_2CHCH_2CHO$	
S	$(CH_3)_3CCHO$	
T	$CH_3CH_2CH_2COCH_3$	
U	$CH_3CH_2COCH_2CH_3$	

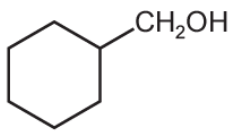
6. Complete Table 9.1 to give the number of peaks in the carbon-13 NMR spectrum of each of the five isomers of $C_5H_{10}O_2$ that has an ester group.

[2]

Table 9.1

structural formula	number of peaks
$CH_3CH_2CH_2CO_2CH_3$	
$CH_3CH_2CO_2CH_2CH_3$	
$CH_3CO_2CH_2CH_2CH_3$	
$(CH_3)_2CHCO_2CH_3$	
$CH_3CO_2CH(CH_3)_2$	

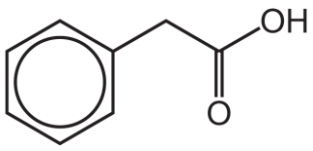
7. Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.



cyclohexylmethanol

..... [1]

8. The structure of phenylethanoic acid is shown.

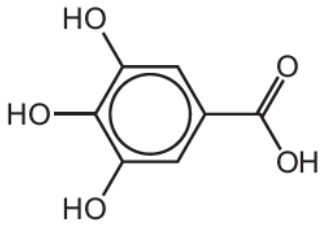


Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

9. State the number of peaks that would be observed in the ^{13}C NMR spectrum of gallic acid.

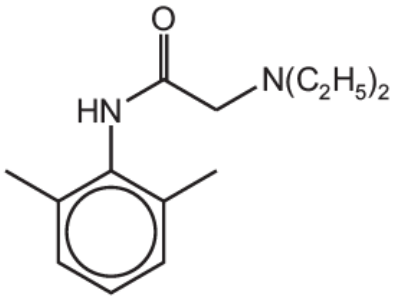
gallic acid



..... [1]

10. Predict the number of peaks in the **carbon-13** (^{13}C) NMR spectrum of lidocaine.

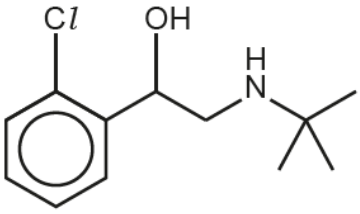
lidocaine



..... [1]

11. Predict the number of peaks that would be seen in the carbon-13 NMR spectrum of tulobuterol.

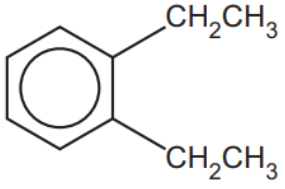
tulobuterol



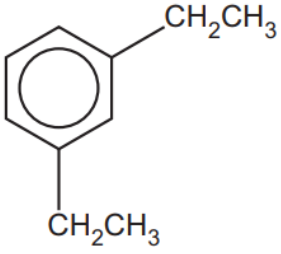
..... [1]

12. Compounds D and E can be distinguished by carbon-13 NMR spectroscopy.
State the number of peaks in each spectrum.

D



E

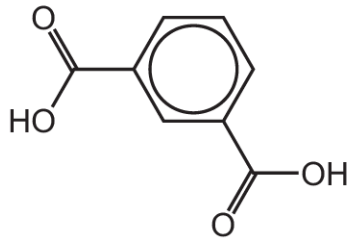


The carbon-13 NMR spectrum of D has ..... peaks.

The carbon-13 NMR spectrum of E has ..... peaks. [1]

13. The structure of benzene-1,3-dicarboxylic acid is shown.

benzene-1,3-dicarboxylic acid



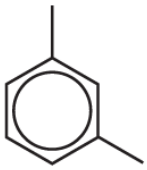
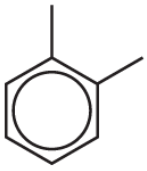
Benzene-1,3-dicarboxylic acid is an isomer of benzene-1,4-dicarboxylic acid. These two isomers can be distinguished by carbon-13 (^{13}C) NMR spectroscopy.

State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of each compound. [2]

benzene-1,3-dicarboxylic acid	
benzene-1,4-dicarboxylic acid	

14. Complete Table 8.1 below to give the number of peaks in the carbon-13 NMR spectrum of each compound. [2]

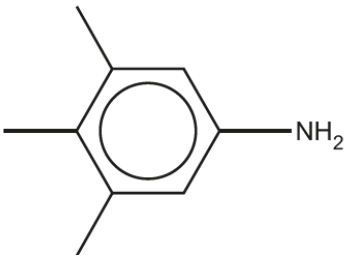
Table 8.1

compound	number of peaks	compound	number of peaks
			
			

15. Compound W is an isomer of Z.

Z

W

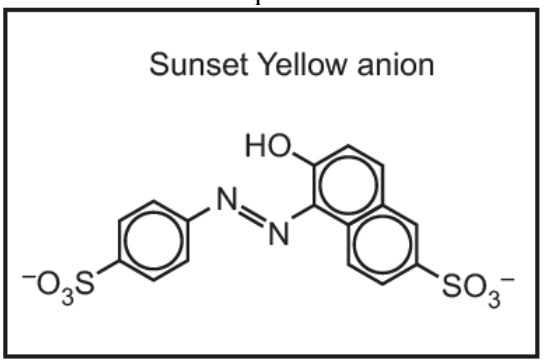


Complete Table 4.1 to show the number of peaks observed in the carbon-13 NMR spectrum for W and Z. [1]

Table 4.1

Compound	number of peaks observed
W	
Z	

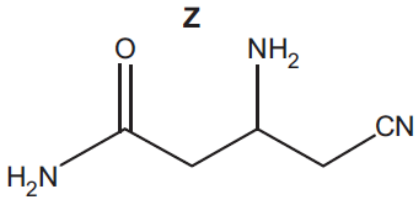
16. Predict the number of peaks in the carbon-13 NMR spectrum of the Sunset Yellow anion. [1]



17. There are four possible structural isomers of C_8H_{10} that contain a benzene ring.
Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given. [4]

isomer 1 three peaks in ^{13}C NMR	isomer 2 four peaks in ^{13}C NMR
isomer 3 five peaks in ^{13}C NMR	isomer 4 six peaks in ^{13}C NMR

18. Compound Z is used in organic synthesis.



Compound Z is dissolved in D_2O and analysed by carbon-13 NMR and proton (^1H) NMR spectroscopy.

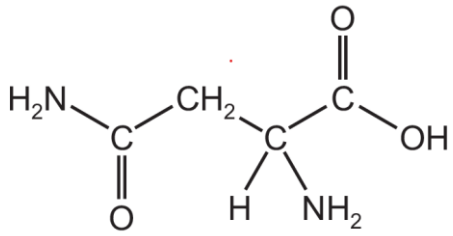
Predict the number of peaks in the carbon-13 NMR spectrum of Z.

..... [1]

Predicting the number of peaks in ^{1}H NMR

19. 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 (^{1}H) NMR spectroscopy.

asparagine



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

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

20. The compound C_6H_6 has many structural isomers. Four suggested structures of C_6H_6 are shown in Fig. 6.1.

Kekulé benzene Dewar benzene Ladenburg benzene delocalised benzene

Fig. 6.1

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

Table 6.2

	number of peaks
Dewar benzene	
Ladenburg benzene	
delocalised benzene	

Predicting the splitting

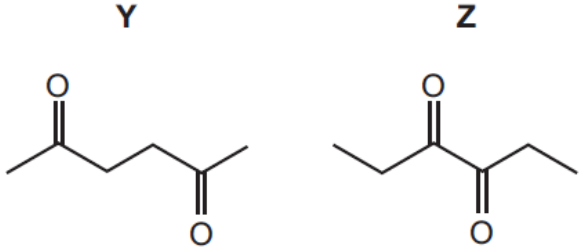
number of signals a peak splits into = *n* + 1 where *n* is the number of 1H atoms on the adjacent carbon atom.

21. State the number of peaks that would be seen in the proton (^{1}H) 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]

22. The two isomeric compounds Y and Z are analysed by proton (^{1}H) NMR spectroscopy.



Complete Table 6.2 to predict the number of peaks observed in the proton (^{1}H) NMR spectra for Y and Z.

Table 6.2

compound	number of peaks observed
Y	
Z	

(ii) Name all the different splitting patterns observed in the proton (^{1}H) NMR spectra for Y and Z.

Y .....

Z ..... [2]

23. 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 (^{1}H) NMR spectrum and in the carbon-13 NMR spectrum for each compound listed. [2]

Table 7.1

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

(ii) State all the ketones with molecular formula $C_5H_{10}O$ that have:
a doublet in their proton (^{1}H) NMR spectrum

.....

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

..... [2]

24. The structures of five isomeric ketones, **P**, **Q**, **R**, **S,** and **T** are given.
P $C_6H_5COCH(CH_3)_2$ **S** $C_6H_5CH_2CH_2COCH_3$ **Q** $C_6H_5COCH_2CH_2CH_3$
T $C_6H_5CH(CH_3)COCH_3$ **R** $C_6H_5CH_2COCH_2CH_3$

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]

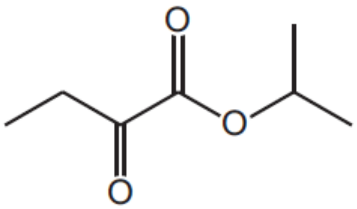
(ii) the compound with only three peaks in its proton (1H) NMR spectrum.

..... [1]

Predicting the chemical shift

25. The proton (^{1}H) NMR spectrum of A shows peaks in four different chemical environments.

A



Complete Table 8.1 for the proton (^{1}H) NMR spectrum of A.

Table 8.1

chemical shift δ/ppm	splitting pattern	number of protons on adjacent carbon atoms	number of ^{1}H atoms responsible for the peak
1.10			
1.50			6
2.85			
3.75			

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

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

27. Methylbenzene and benzoic acid each have five different peaks in the carbon (^{13}C) NMR spectrum.

hybridisation of the carbon atom	environment of carbon atom	example	chemical shift range / ppm
sp^3	alkyl	**C**H_3–, –**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

Use Table 7.1 to complete the two sentences to suggest descriptions of these two spectra.
The carbon (^{13}C) NMR spectrum of methylbenzene:

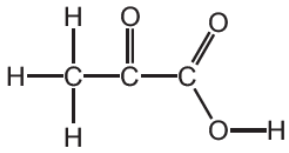
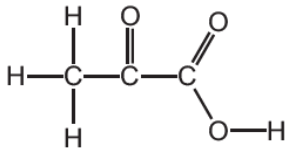
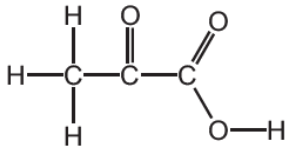
- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of ..... .

The carbon (^{13}C) NMR spectrum of benzoic acid:

- has ..... peak(s) in the chemical shift range of ..... and
- has ..... peak(s) in the chemical shift range of ..... [2]

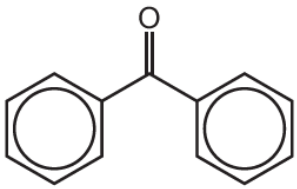
28. A sample of pyruvic acid, CH_3COCO_2H, is analysed by carbon-13 NMR spectroscopy.

Three peaks are observed.
Complete the table by:
●● circling the carbon atom responsible for the chemical shift
●● stating the hybridisation of the circled carbon atom. [2]

chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

29. Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone. [2]

benzophenone



environment of carbon atom	chemical shift range (δ)

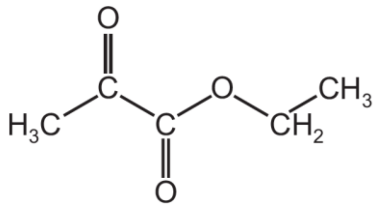
30. The proton (1H) NMR spectra of P, Q, R, S, T, U, and V are compared.
P $CH_3(CH_2)_3CHO$ Q $CH_3CH_2CH(CH_3)CHO$ R $(CH_3)_2CHCH_2CHO$ S $(CH_3)_3CCHO$
T $CH_3CH_2CH_2COCH_3$ U $CH_3CH_2COCH_2CH_3$ V $(CH_3)_2CHCOCH_3$
(i) Identify the only compound that gives a spectrum with two singlets and no other peaks.

..... [1]

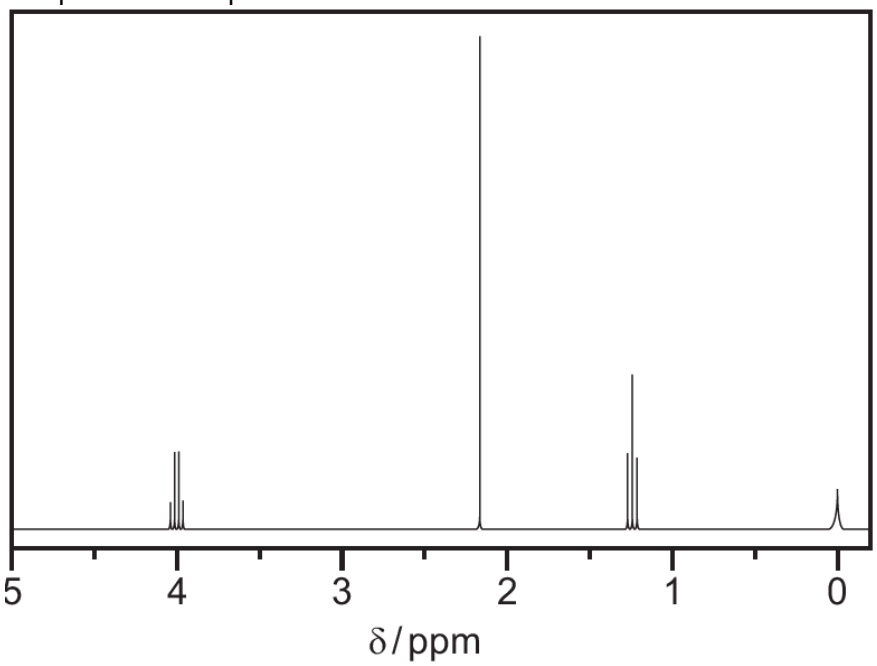
Analyzing the spectrum

31. 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.

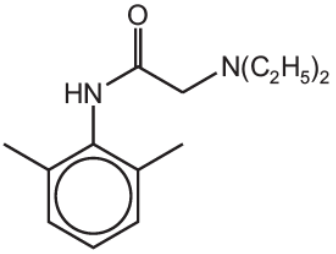


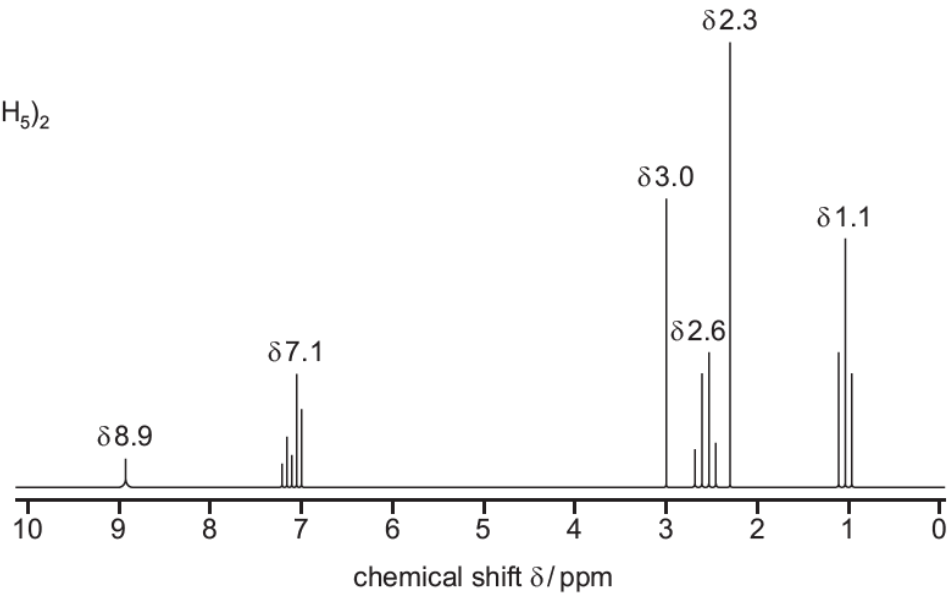
Use the proton NMR spectrum of **F** to complete the table. [3]

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

32. The proton (^1H) NMR spectrum of lidocaine is shown in Fig. 6.2.

lidocaine





(i) Name the splitting patterns at δ 2.6 and δ 1.1.

δ 2.6 ..... δ 1.1 ..... [1]

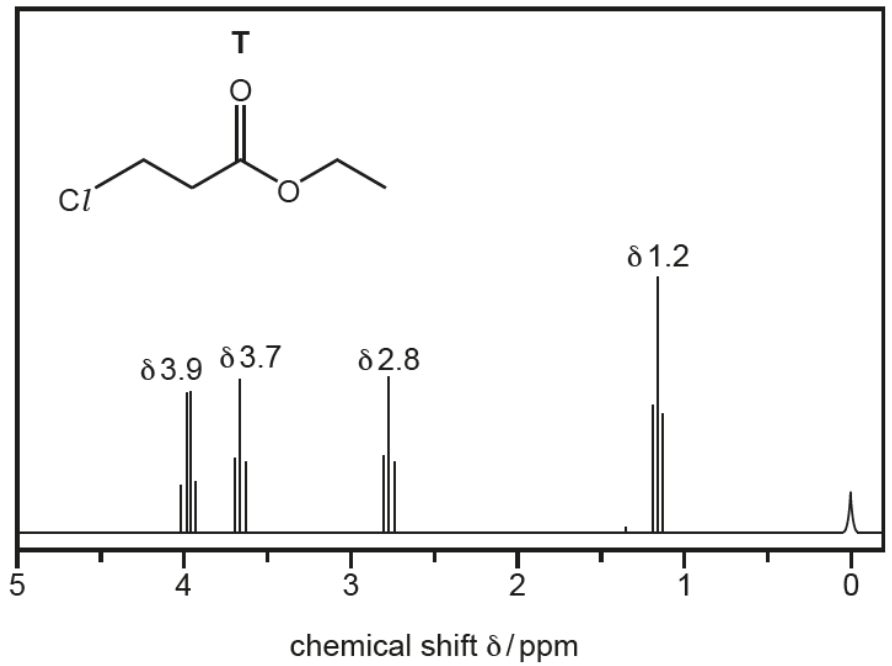
(ii) The relative peak area of the peaks at δ 3.0 and δ 2.3 is 1 : 3 respectively.
Identify the protons in the ^{1}H NMR spectrum of lidocaine that are responsible for the peaks at the following chemical shift values.

δ 7.1 .....

δ 3.0 .....

δ 2.3 ..... [2]

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



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

.....

..... [1]

(ii) Complete Table 8.2 for the proton (^{1}H) NMR spectrum of T. [4]

Table 8.2

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

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

.....

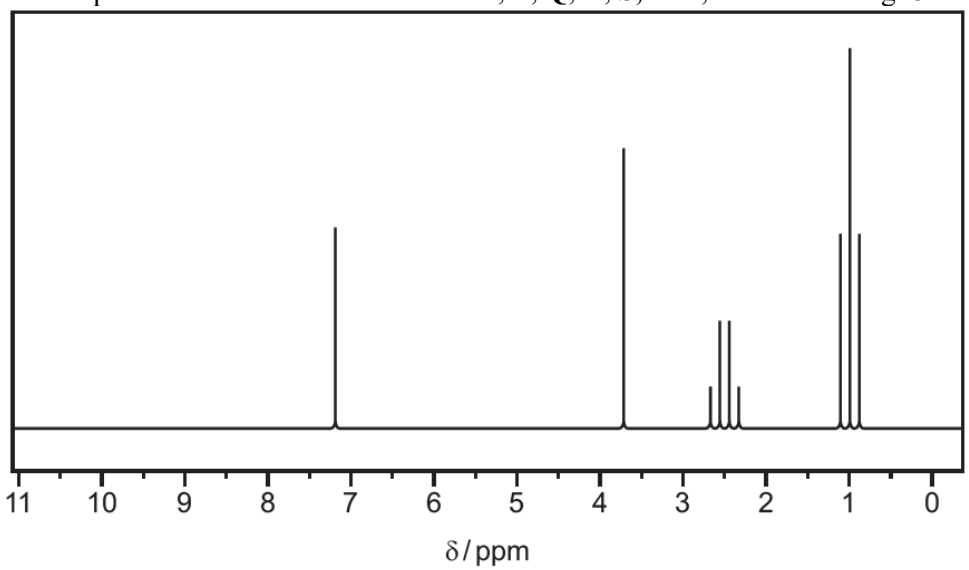
..... [1]

34. 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 $\delta = 7.2$ in a proton (^{1}H) NMR spectrum.
The structures of five isomeric ketones, **P**, **Q**, **R**, **S,** and **T** are given.

P $C_6H_5COCH(CH_3)_2$ **S** $C_6H_5CH_2CH_2COCH_3$ **Q** $C_6H_5COCH_2CH_2CH_3$

T $C_6H_5CH(CH_3)COCH_3$ **R** $C_6H_5CH_2COCH_2CH_3$

The proton ($_1$H) NMR spectrum of one of the five isomers, **P**, **Q**, **R**, **S,** or **T**, is shown in 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 $\delta = 3.7$, $\delta = 2.5$, and $\delta = 1.0$ on the structure you have drawn. [2]

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

.....

..... [1]

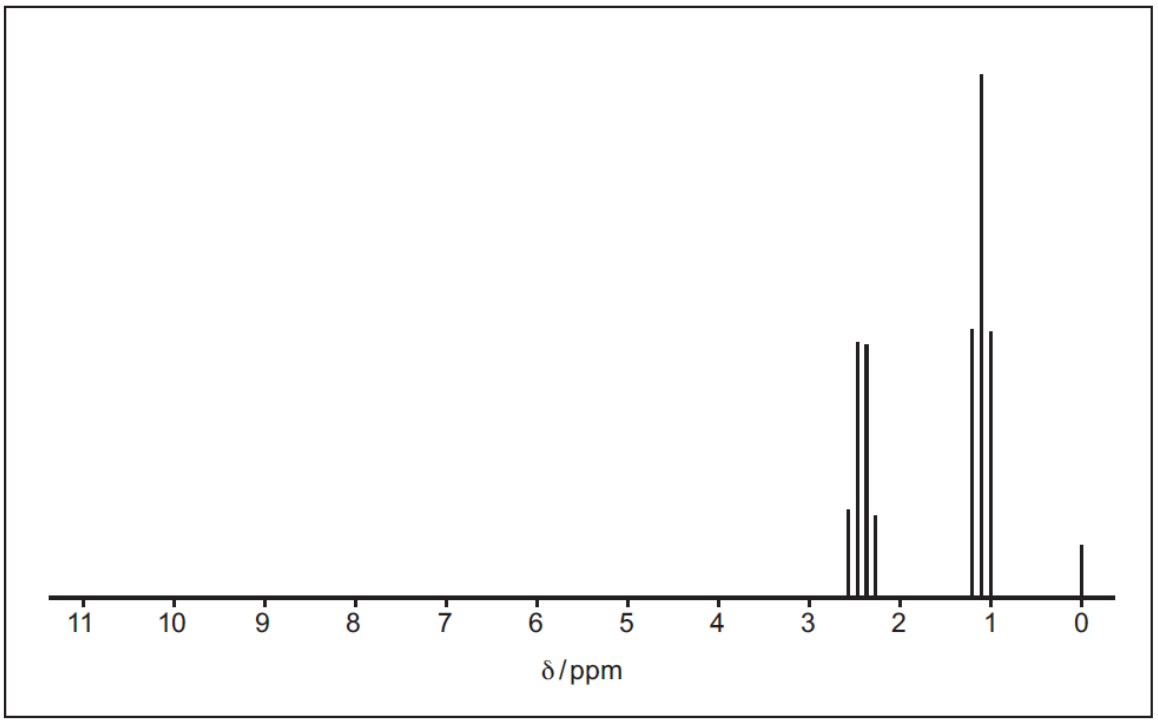
(iii) Suggest a suitable solvent that should be used for obtaining the spectrum shown in Fig. 8.1.

..... [1]

35. The proton (1H) NMR spectra of P, Q, R, S, T, U, and V are compared.

P $CH_3(CH_2)_3CHO$ Q $CH_3CH_2CH(CH_3)CHO$ R $(CH_3)_2CHCH_2CHO$ S $(CH_3)_3CCHO$
T $CH_3CH_2CH_2COCH_3$ U $CH_3CH_2COCH_2CH_3$ V $(CH_3)_2CHCOCH_3$

Fig. 7.1 shows the spectrum obtained from one of the compounds.



(ii) Identify the compound that gives this spectrum.

..... [1]

(iii) Name the splitting pattern of the peak at δ = 1.1 in Fig. 7.1.
Give the reason for this splitting.

name .....

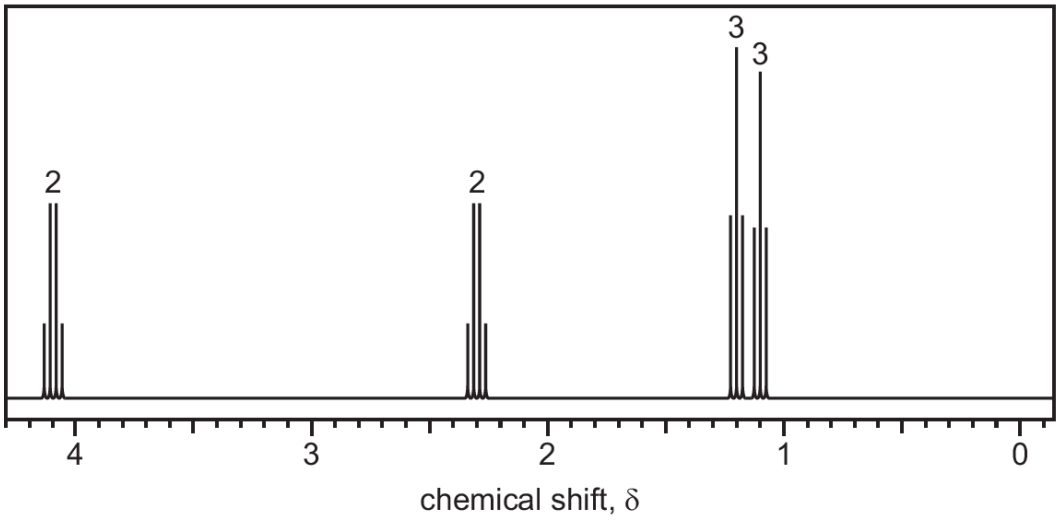
reason ..... [1]

(iv) Identify the substance that gives the small peak at δ = 0 in Fig. 7.1.

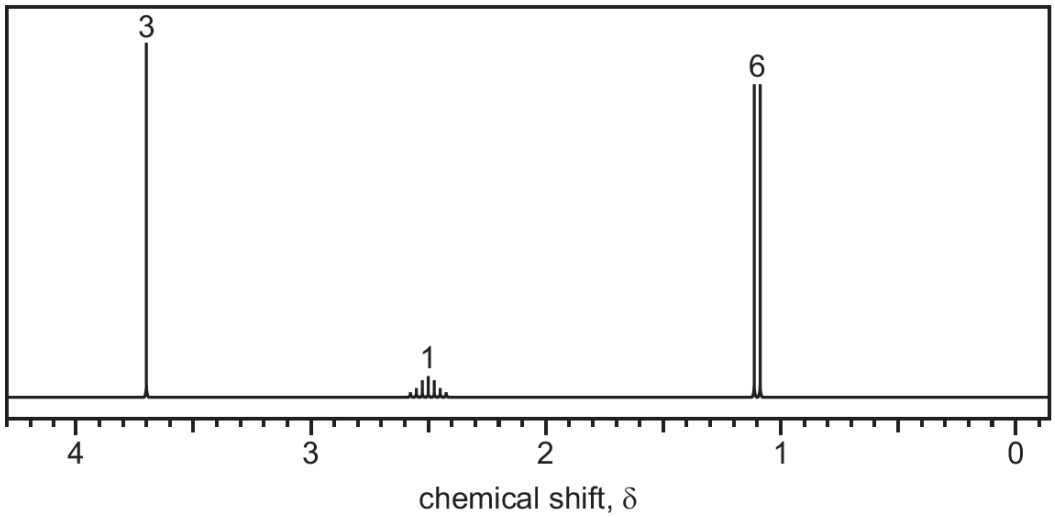
..... [1]

36. **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



E



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

(i) Deduce the structures of the two esters **D** and **E** and draw their displayed formulae in the boxes below. [2]

D
$C_5H_{10}O_2$

E
$C_5H_{10}O_2$

(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]

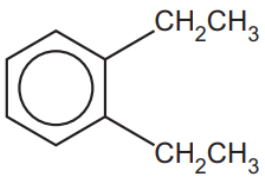
(iii) The spectrum of **E** has a doublet at δ 1.1.
Identify the protons responsible for this doublet on your structure in **(i)** by labelling these protons with the letter **G**.
Explain why this peak has a chemical shift of 1.1.

.....

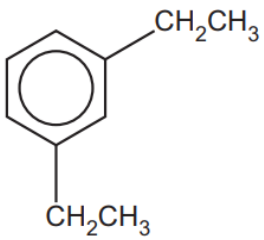
..... [1]

37. A hydrocarbon is known to be either compound D or compound E.

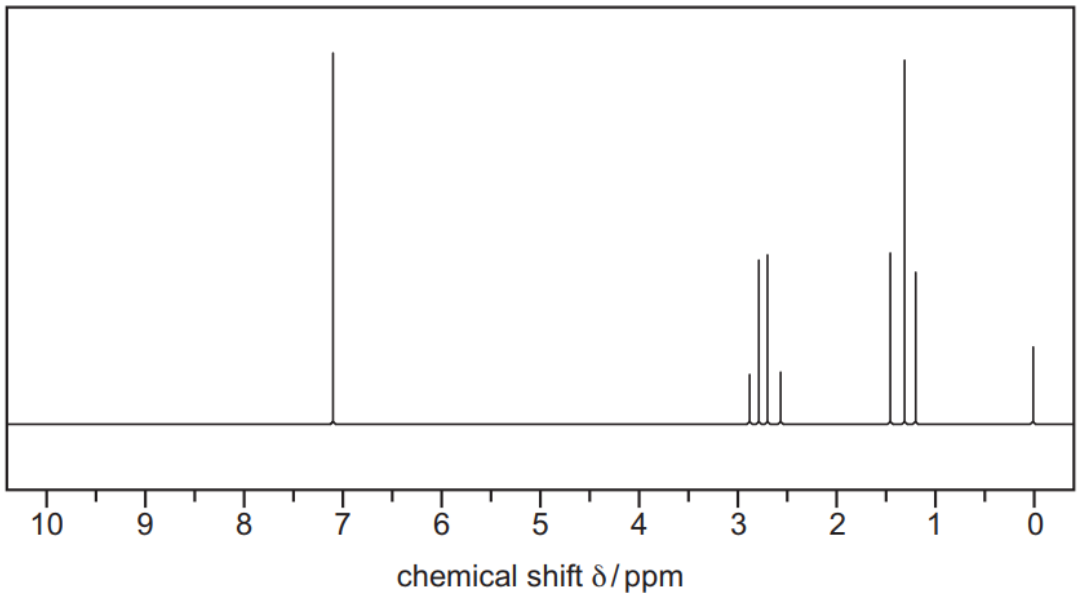
D



E



The proton (^{1}H) NMR spectra of D and E are compared. They are very similar.
The proton (^{1}H) NMR spectrum of D is shown in Fig. 7.2



(i) Suggest a suitable solvent for obtaining the spectrum in Fig. 7.2.

..... [1]

(ii) Complete Table 7.1 for the proton (^{1}H) NMR spectrum of D. [3]

Table 7.1

chemical shift δ/ppm	number of ^{1}H atoms responsible for the peak	group responsible for the peak	splitting pattern
1.3			
2.7			
7.1			

38. The proton (^{1}H) NMR spectra of ethylbenzene, $C_6H_5C_2H_5$, in $CDCl_3$ and of benzene-1,2-dioic acid, $C_6H_4(COOH)_2$, in $CDCl_3$ are shown. They have not been identified

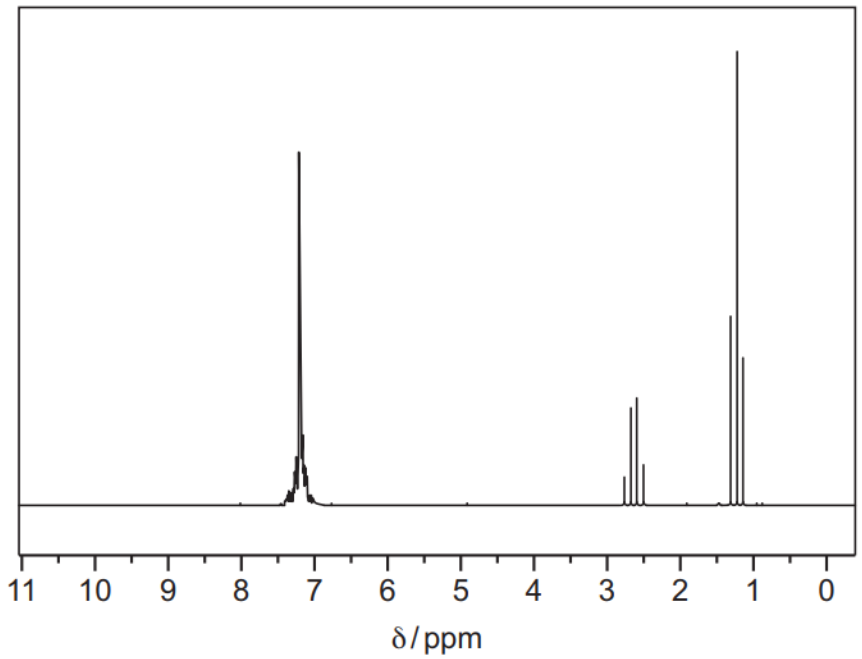
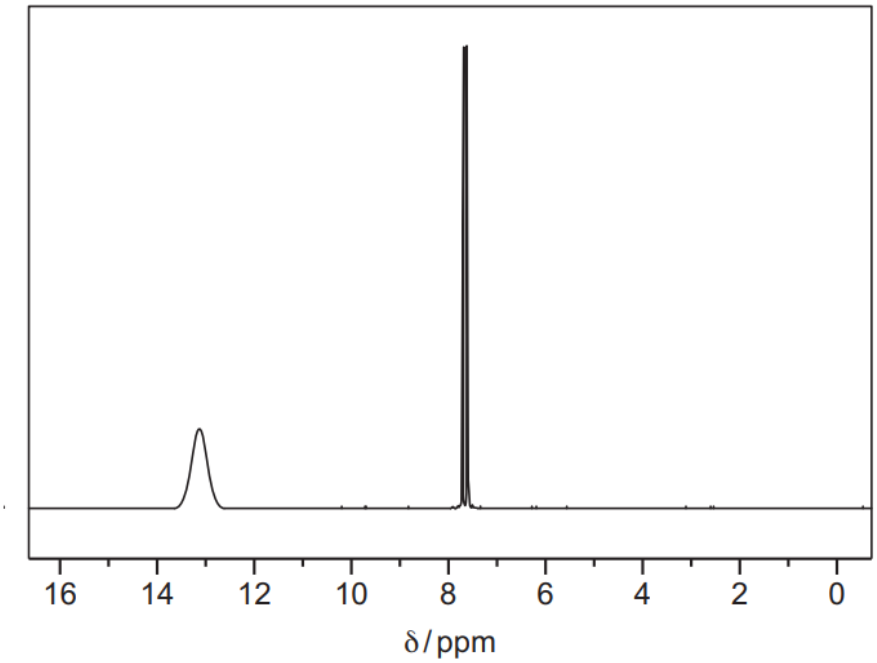


Fig. 6.1



(i) Explain the use of $CDCl_3$, instead of $CHCl_3$, as the solvent when obtaining these spectra.

..... [1]

(ii) Identify the substance shown by the spectrum in Fig. 6.1, and complete Table 6.1. [3]

substance .....

Table 6.1

	peak at δ = 1.2	peak at δ = 2.6
name of splitting pattern		
group responsible for peak		
explanation of splitting pattern		

(iii) Identify the substance shown by the spectrum in Fig. 6.2, and complete Table 6.2. [1]

substance .....

Table 6.2

	peak at δ = 7.8	peak at δ = 13.1
group responsible for peak		

(iv) When D_2O is used as a solvent, the spectrum obtained is different from the spectrum in Fig. 6.2. Describe this difference and explain your answer.

.....

.....

..... [1]

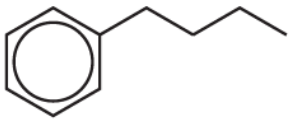
Questions involving reactions

39. There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table. Suggest the structural formulae of the three other carbocations. [3]

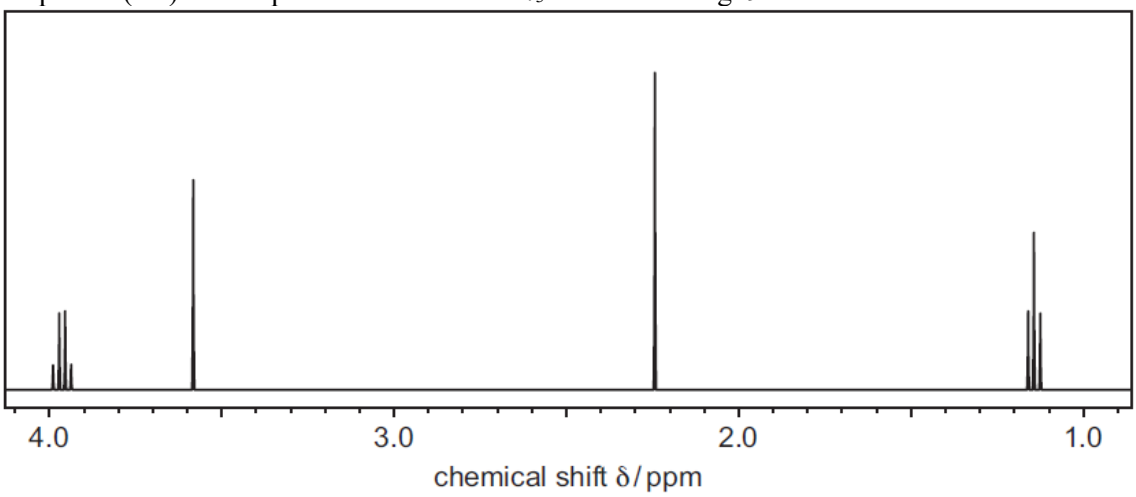
structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.

In each reaction an organic compound with formula C10H14 is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.
Suggest the structures for the three other compounds. [4]

 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

40. 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 (1H) NMR spectrum of **H** in $CDCl_3$ is shown in Fig. 9.2.



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

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

..... [1]

(ii) Complete Table 9.2 for the proton (1H) NMR spectrum of **H**, $C_6H_{10}O_3$. [4]

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			

(iii) Suggest a structure for **H**, $C_6H_{10}O_3$. [1]

41. Compound **V** is an amino acid.
The proton (^{1}H) NMR spectrum of **V** shows hydrogen atoms in five different environments, **a**, **b**, **c**, **d,** and **e**, as shown in Fig. 6.2.

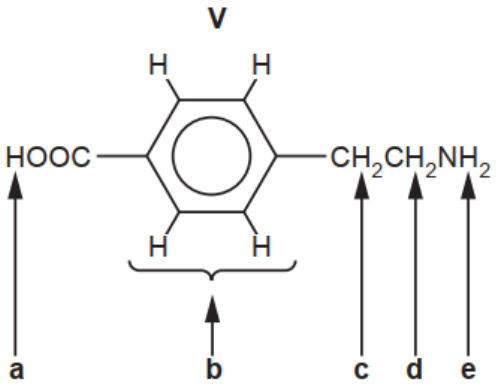


Fig. 6.2

(i) Complete Table 6.2 for the proton (^{1}H) NMR spectrum of **V** taken in $CDCl_3$.
Table 6.1 gives some relevant data. [4]

Table 6.2

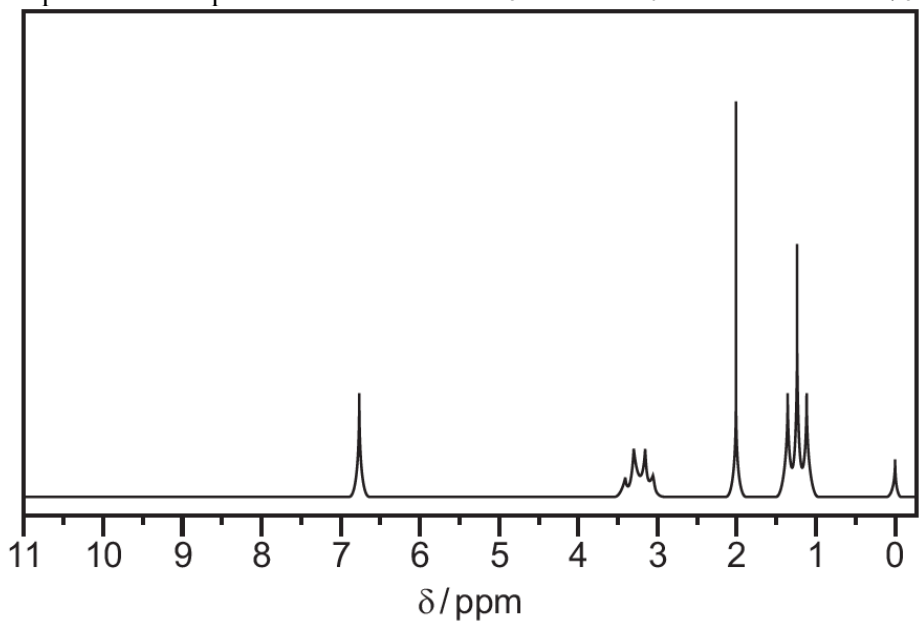
proton	a	b	c	d	e
chemical shift range, δ/ppm					
name of splitting pattern		multiplet			

(ii) Complete Table 6.3 by placing a tick (✓) to indicate any protons whose peaks are still present in the proton (^{1}H) NMR spectrum of **V** taken in D_2O. [1]

Table 6.3

proton	a	b	c	d	e
present in D_2O					

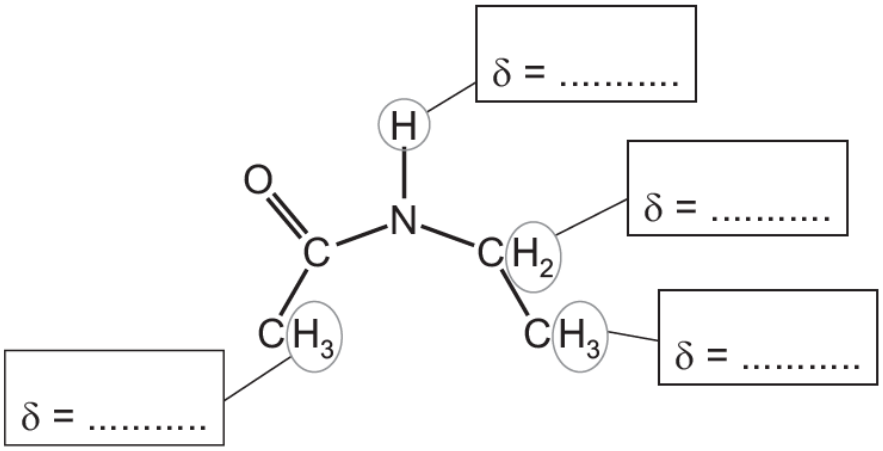
42. Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.
The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(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.



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

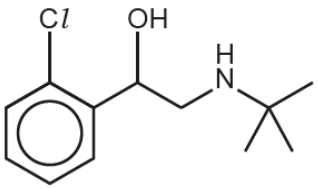
.....

.....

..... [2]

43. The proton (^{1}H) NMR spectrum of tulobuterol dissolved in D_2O shows peaks in four different types of proton environment.

tulobuterol



The peak for the —CH_2N— environment is a doublet in the chemical shift range d = 2.0–3.0 ppm.
Give details for each of the other three peaks in the proton NMR spectrum of tulobuterol, to include:
• chemical shift
• environment of the proton
• splitting pattern
• number of 1H atoms responsible.
Table 5.1 gives information about typical chemical shift values.

.....

.....

.....

.....

.....

.....

..... [3]

44. 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

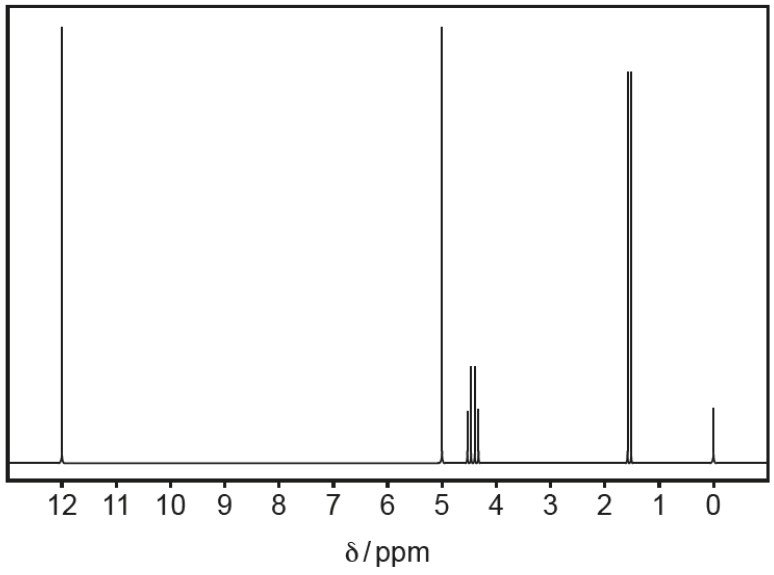


Fig. 8.1

Use Fig. 8.1 and Table 8.1 to complete Table 8.2. [3]

Table 8.2

proton environment	chemical shift (δ)	name of splitting pattern
–COOH		
CH		
–OH		
$–CH_3$		

(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]

45. 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.

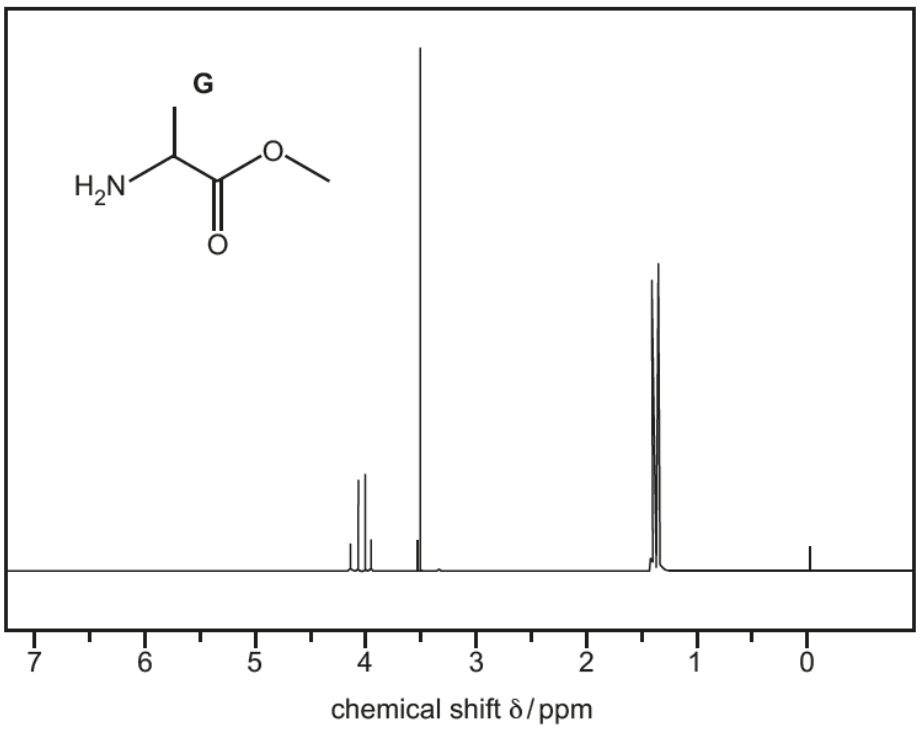


Fig. 7.3

(i) Complete Table 7.2 for the proton (^1H) NMR spectrum of G. [3]

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			

(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.

.....

.....

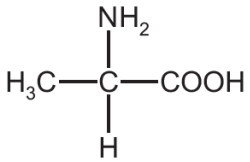
..... [1]

46. 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. [3]
Table 8.1

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

47. 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.

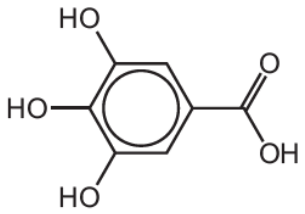
.....

.....

..... [2]

48. The proton NMR spectrum of gallic acid dissolved in D_2O is recorded.

gallic acid



●● Predict the number of peaks observed and any expected splitting pattern.
●● State the expected chemical shift range (δ) of each peak predicted.

.....

.....

..... [2]

49. Each compound, HCO_2H, HO_2CCO_2H and $HO_2CCH_2CH_2CO_2H$, is dissolved seperately in $CDCl_3$. Proton (^1H) NMR and carbon-13 (^{13}C) NMR spectra are then obtained.
Complete the table. [2]

Compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR
HCO_2H		
HO_2CCO_2H		
$HO_2CCH_2CH_2CO_2H$		

(i) The proton NMR spectrum of HCO_2H in D_2O is obtained.
Describe and explain the difference observed between this spectrum and the proton NMR spectrum of HCO_2H in **(i)**.

.....

.....

..... [1]

50. A group of drugs known as statins are used to lower cholesterol in the blood. A commonly used statin is atorvastatin.

atorvastatin

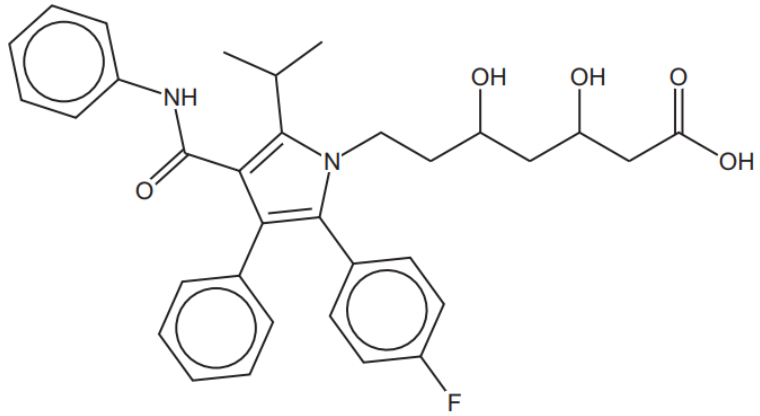


Fig. 5.1

The proton (^{1}H) NMR spectrum of atorvastatin dissolved in $CDCl_3$ is recorded.
(i) Use Table 5.1 to deduce the number of hydrogen atoms that could produce peaks in the region δ = 6.5–13.0ppm.

..... [1]

(ii) The proton (^{1}H) NMR spectrum of atorvastatin dissolved in D_2O is recorded.
Predict the number of hydrogen atoms that would not show a peak in this spectrum.
Explain your answer.

.....

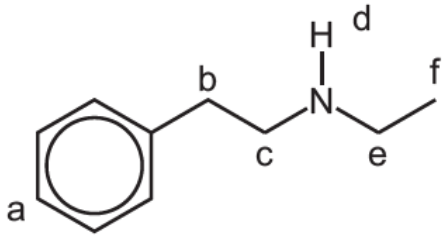
.....

..... [2]

Table 5.1

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	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

51. 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]

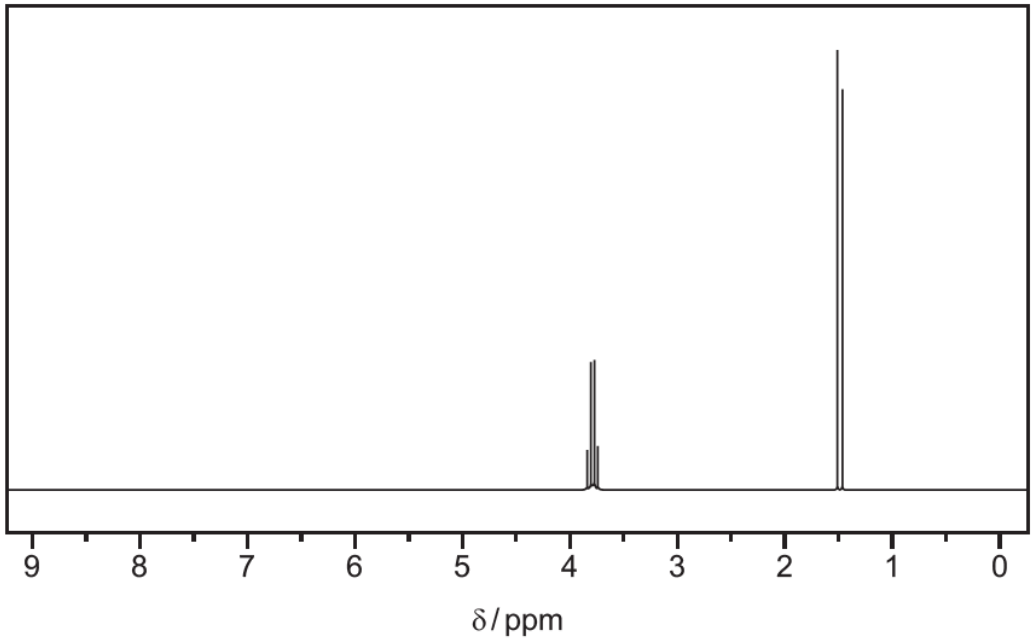
(iii) Identify the proton or protons whose peak is a triplet.

..... [1]

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

..... [1]

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

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

T $C_6H_5CH(CH_3)COCH_3$

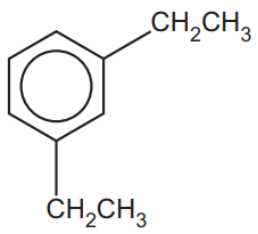
Describe any difference between the two spectra. Explain your answer.

.....

..... [1]

54. The proton (^1H) NMR spectrum of E is obtained twice, once before and once after shaking with D_2O. Describe any differences between these two spectra. Explain your answer.

E



.....

..... [1]

55. The proton (^{1}H) NMR spectra of ethylbenzene, $C_6H_5C_2H_5$, in $CDCl_3$ and of benzene-1,2-dioic acid, $C_6H_4(COOH)_2$, in $CDCl_3$ are shown. They have not been identified

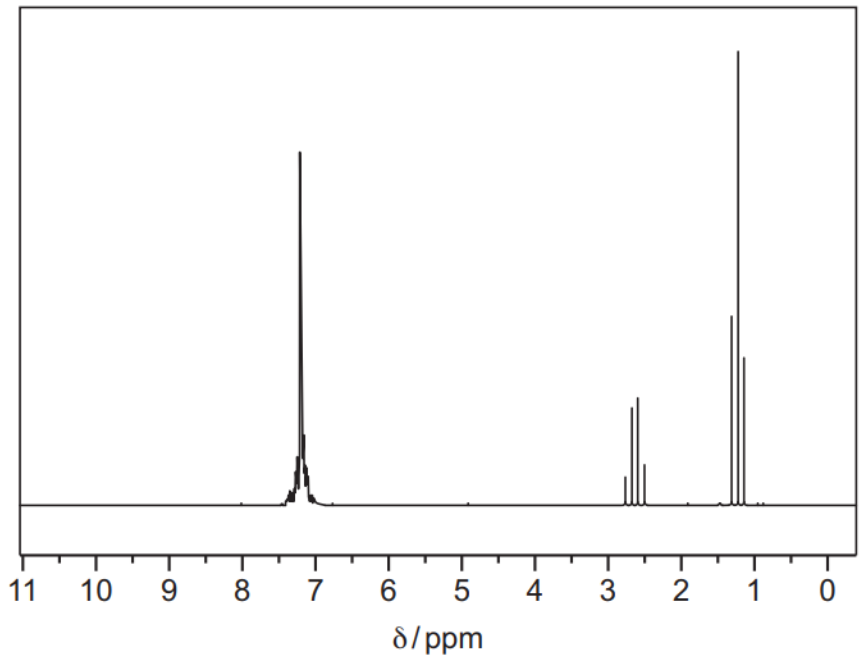
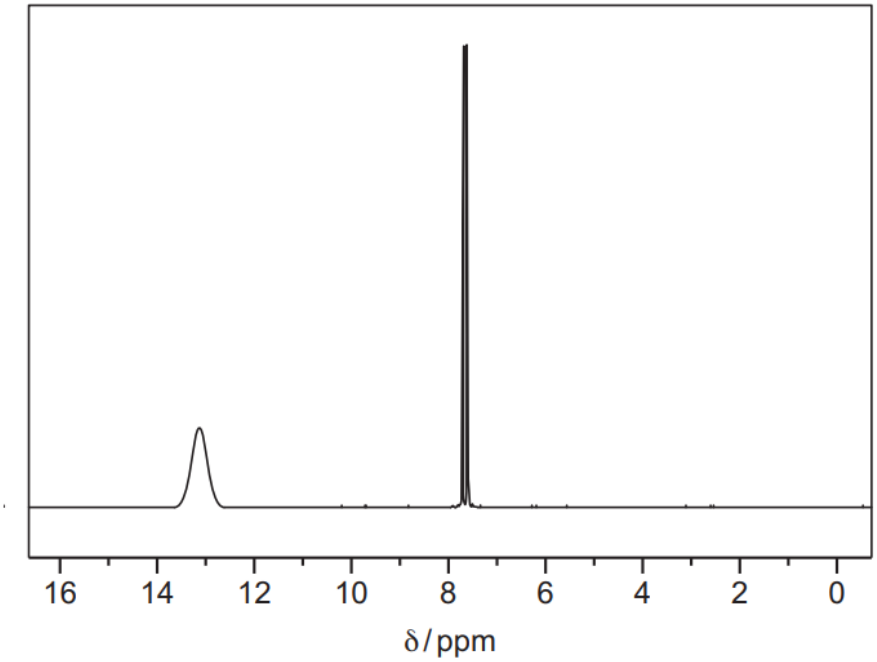


Fig. 6.1



(iii) Explain the use of $CDCl_3$, instead of $CHCl_3$, as the solvent when obtaining these spectra.

..... [1]

(iv) Identify the substance shown by the spectrum in Fig. 6.1, and complete Table 6.1. [3]

substance .....

Table 6.1

	peak at δ = 1.2	peak at δ = 2.6
name of splitting pattern		

group responsible for peak		
explanation of splitting pattern		

(iii) Identify the substance shown by the spectrum in Fig. 6.2, and complete Table 6.2. [1]

substance .....

Table 6.2

	peak at δ = 7.8	peak at δ = 13.1
group responsible for peak		

(iv) When D_2O is used as a solvent, the spectrum obtained is different from the spectrum in Fig. 6.2. Describe this difference and explain your answer.

.....

.....

..... [1]

Question involving mass spectrum

56. The relative abundance of the molecular ion peak in the mass spectrum of ethylamine is 62.
(i) Calculate the relative abundance of the M+1 peak in the mass spectrum of ethylamine.

relative abundance = ... [1]

(ii) The mass spectrum of compound **T** contains several fragments. The *m*/*e* values of two of these fragments are 29 and 91.
Draw the structures of the ions responsible for these peaks. [2]

m/*e*	structure of ion
29	
91	

57. The mass spectrum of glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, is obtained.
(i) State the *m*/*e* value of the molecular ion peak in this spectrum.

..... [1]

(ii) The spectrum has peaks with *m*/*e* values of 88 and 131.
Draw the structures of the ions responsible for these peaks. [2]

m/e	structure of ion
88	
131	

58. The mass spectrum of the amide $CH_3CONHC_2H_5$ includes a fragment ion with *m*/*e* value of 58.
Give the molecular formula of this fragment ion.

fragment ion with *m*/*e* value of 58 is ..... [1]

59. 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**. [2]

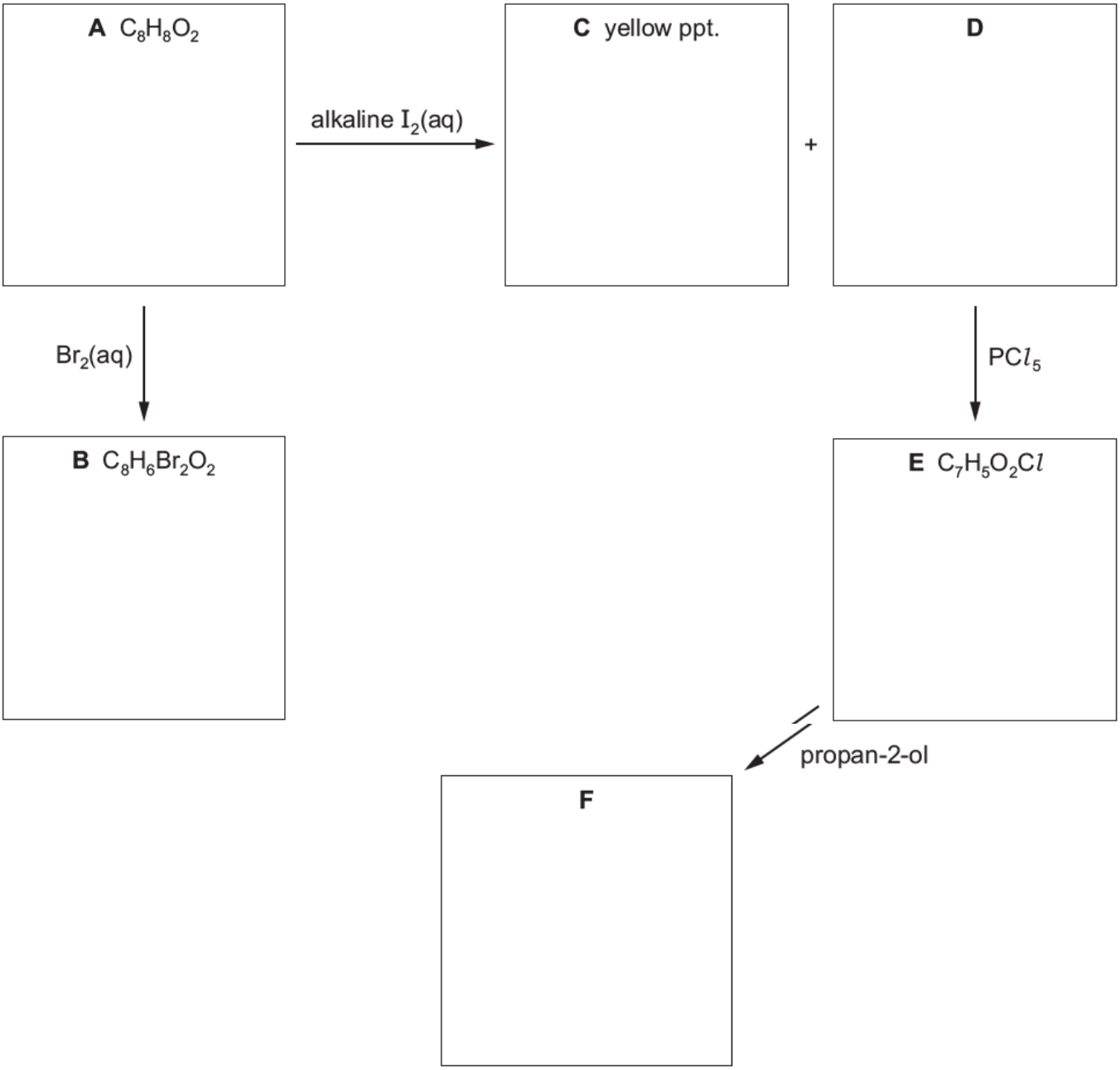
Table 7.1

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

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

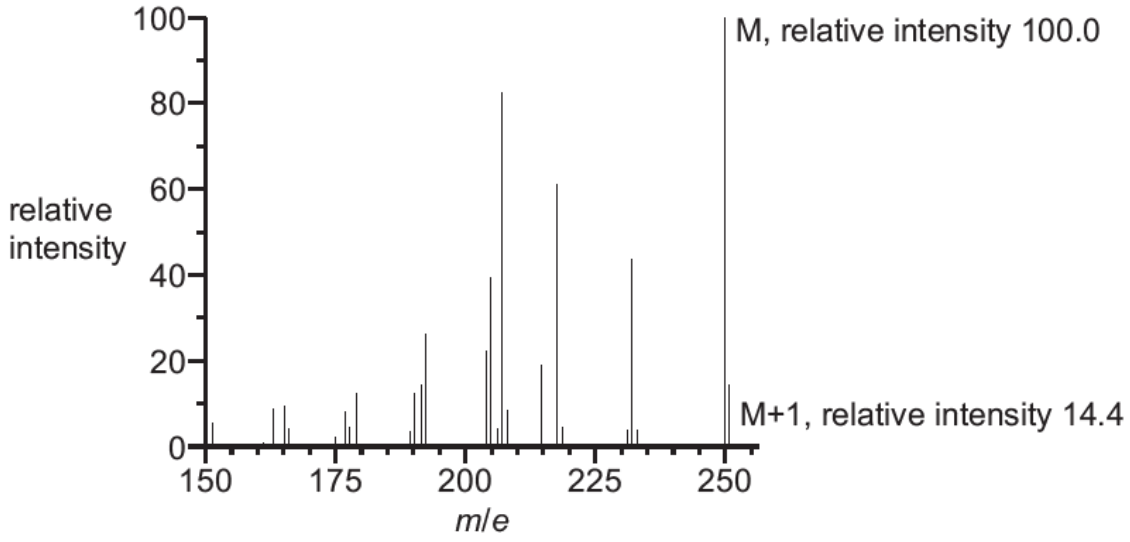
..... [1]

60. The carbon-13 (^{13}C) NMR spectrum of compound **A**, $C_8H_8O_2$, contains six peaks.
Compound **A** reacts with an excess of bromine water to give compound **B**, $C_8H_6Br_2O_2$.
Compound **A** reacts with alkaline aqueous iodine to form a yellow precipitate **C** and compound **D**.
Compound **D** reacts with PCl_5 to form compound **E**, $C_7H_5O_2Cl$.
Compound **E** reacts with propan-2-ol to form compound **F**.
Draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F** in the boxes.



[6]

Compound **J**, C*x*H*y*O*z*, is also found in some cereals.
Part of the mass spectrum of **J** is shown. The M and M+1 peaks are labelled, along with their relative intensities.



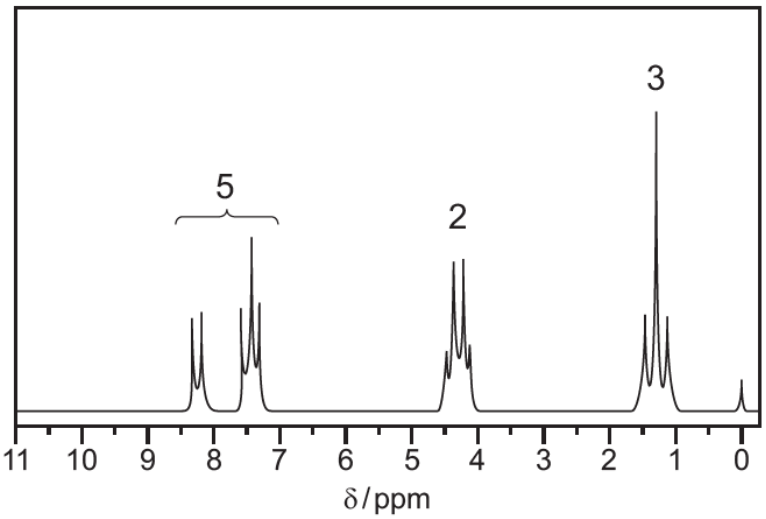
(i) Calculate the number of carbon atoms, x, present in **J**.

x = ... [2]

(ii) The mass spectrum has a peak at m/e = 205.
Suggest the identity of the fragment lost from **J** to form this peak.

..... [1]

61. 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 $\delta = 0$.

..... [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 $\delta = 1.4$ and $\delta = 4.3$.

splitting pattern at $\delta = 1.4$ .....

reason for splitting pattern at $\delta = 1.4$ .....

splitting pattern at $\delta = 4.3$ .....

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]

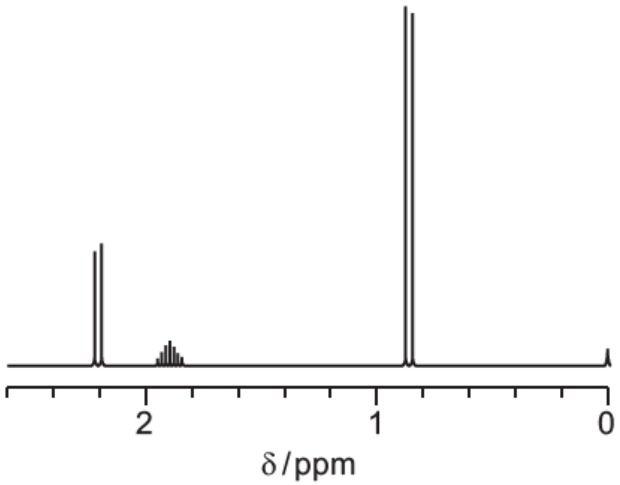
(e) The mass spectrum of compound **E** includes fragment ions with *m*/*e* values of 29 and 77.
Give the formulae of these fragment ions.

fragment ion with *m*/*e* = 29 .....

fragment ion with *m*/*e* = 77 ..... [2]

Question requiring data booklet

62. 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. [3]

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

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****