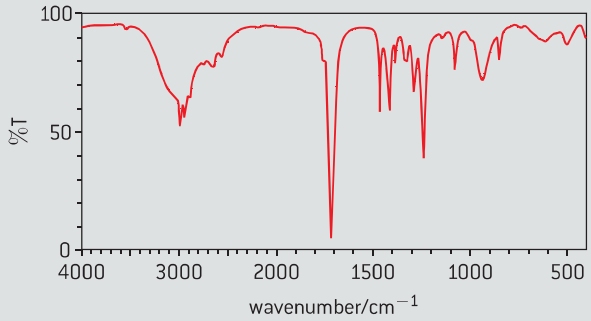
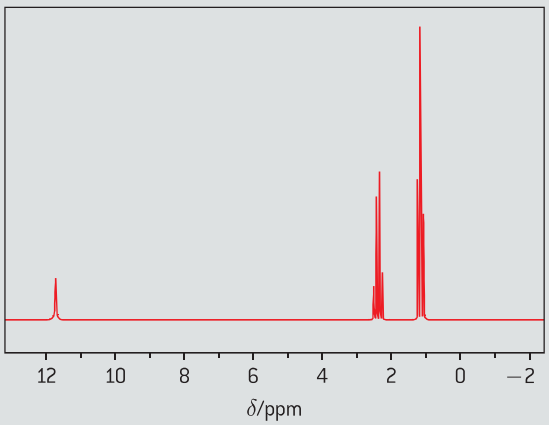
Questions

1 An unknown compound, X, of molecular formula, $C_3H_6O_2$, has the following IR and ^1H NMR spectra.



▲ Figure 12 IR spectrum of X (in CCl_4) solution

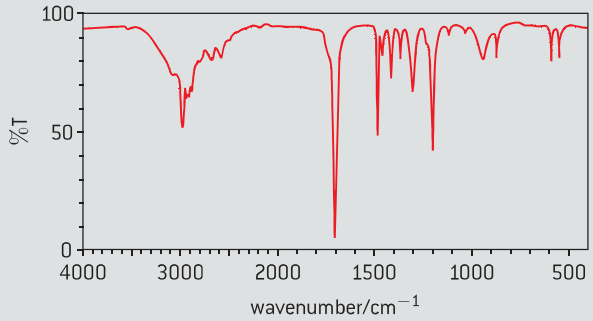


▲ Figure 13 ^1H NMR spectrum (90 MHz in $CDCl_3$) of X

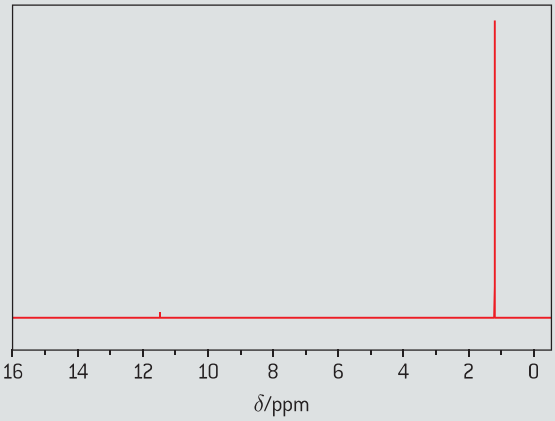
The MS of X showed peaks at *m/z* values = 74, 45, and 29 (other peaks were also found).

Deduce the structure of X using the information given and any other additional information from the *Data booklet*. For each spectrum assign as much spectroscopic information as possible, based on the structure of X.

2 An unknown compound, Y, of molecular formula, $C_5H_{10}O_2$, has the following IR and ^1H NMR spectra.



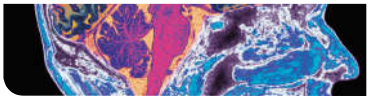
▲ Figure 14 IR spectrum of Y (in CCl_4) solution



▲ Figure 15 ^1H NMR spectrum (300 MHz in $CDCl_3$) of Y

The MS of, Y, showed peaks at *m/z* values = 102 and 57 (other peaks were also found).

Deduce the structure of Y using the information given and any other additional information from the *Data booklet*. For each spectrum assign as much spectroscopic information as possible, based on the structure of Y.



Topic 21 – Measurement and analysis (AHL)

Quick question (page 469)

The peaks with $\frac{m}{z} = 59$ and 60 are probably produced by the molecules of propanal that contain heavier isotopes of carbon (^{13}C instead of ^{12}C) and/or hydrogen (^{2}H instead of ^{1}H); other peaks (with $\frac{m}{z} = 69–75$) probably belong to some impurities in the analysed sample of propanal;

End of topic questions (page 470)

1. The *IHD* (see Chapter 11) for $C_3H_6O_2$ is $3 - 0.5 \times 6 + 1 = 1$, so compound **X** contains either one double bond or one ring; the strong absorption at 1710 cm^{-1} in the IR spectrum suggests the presence of a carbonyl group, so the compound is probably acyclic; the signal at 11.7 ppm in the ^{1}H NMR spectrum and the peak with $\frac{m}{z} = 45$ in the mass spectrum suggest the presence of a COOH group, so compound **X** is a carboxylic acid; this is consistent with the IR spectrum, which shows a very broad absorption of the O–H bond in the 3000 cm^{-1} region.

Therefore, the formula of **X** is $CH_3–CH_2–COOH$ (propanoic acid).

Note: another possible structure, $CH_3–CH_2–O–CHO$ (ethyl formate), is inconsistent with the ^{1}H NMR spectrum (as the signal of the CHO group would appear at 9.4–10 ppm) and the IR spectrum (there would be no broad O–H absorption in the 3000 cm^{-1} region).

The spectroscopic information for compound **X** is summarized below:

IR spectrum

Absorption / cm^{-1}	Bond(s) involved
2800–3300 (strong, very broad)	O–H (in the hydrogen-bonded COOH group)
2900–3000 (several medium peaks)	C–H (in CH_2 and CH_3 groups)
1710 (strong)	C=O (in the COOH group)
1250 (strong)	probably C–O (in the COOH group)

^{1}H NMR spectrum

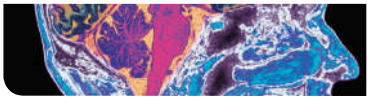
Chemical shift / ppm	Splitting pattern	Number of protons at adjacent atoms	Hydrogen environment
11.7	singlet	0	COOH
2.4	quartet	3	CH_2
1.1	triplet	2	CH_3

Mass spectrum

Peak with *m/z* of	Produced by	Due to the loss of
74	$C_3H_6O_2^{+\bullet}$ (molecular ion)	—
45	$COOH^+$	$C_2H_5^\bullet$
29	$C_2H_5^+$	$COOH^\bullet$

2. The solutions for this and previous questions are similar: the *IHD* for $C_5H_{10}O_2$ ($5 - 0.5 \times 10 + 1 = 1$) and the strong absorption at 1700 cm^{-1} in the IR spectrum of **Y** suggest the presence of a carbonyl group; the signal at 11.4 ppm in the ^{1}H NMR spectrum and the broad absorption in the 3000 cm^{-1} region of the IR spectrum belong to a COOH group, so compound **Y** is also a carboxylic acid.

There are only two signals in the ^{1}H NMR spectrum of **Y**: if the H atom of the COOH group in $C_5H_{10}O_2$ produces the signal at 11.4 ppm, then the other nine H atoms must be in the same chemical environment (as they produce only one sharp signal at 1.2 ppm); in addition, the signal at 1.2 ppm is a singlet, so the molecule of **Y** must not contain any adjacent CH_x groups; such



an arrangement of atoms takes place in a *tert*-butyl group, $(CH_3)_3C-$; the presence of this group is consistent with the mass spectrum of **Y**, where the peak with $\frac{m}{z} = 57$ can be produced by a $C_4H_9^+$ ion.

Therefore, the formula of **Y** is $(CH_3)_3C-COOH$ (2,2-dimethylpropanoic acid).

The spectroscopic information for compound **Y** is summarized below:

IR spectrum

Absorption / cm^{-1}	Bond(s) involved
2800–3300 (strong, very broad)	O—H (in the hydrogen-bonded COOH group)
2900–3000 (several medium peaks)	C—H (in CH_3 groups)
1700 (strong)	C=O (in the COOH group)
1200 (strong)	probably C—O (in the COOH group)

^{1}H NMR spectrum

Chemical shift / ppm	Splitting pattern	Number of protons at adjacent atoms	Hydrogen environment
11.4	singlet	0	COOH
1.2	singlet	0	$(CH_3)_3C$

Mass spectrum

Peak with *m/z* of	Produced by	Due to the loss of
102	$C_5H_{10}O_2^{+\bullet}$ (molecular ion)	—
57	$C_4H_9^+$	$COOH^\bullet$