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IB DIPLOMA CHEMISTRY · FIRST ASSESSMENT 2025

Structure 3.2
^{1}H NMR & Combining Techniques

Booklet 8 (HL) · Understandings 3.2.10 – 3.2.12

How proton environments, chemical shifts, integration and spin–spin splitting map the carbon–hydrogen skeleton of a molecule, and how MS, IR and ^{1}H NMR together prove the structure of an unknown

Complete revision notes, practice spectra & memory points · Higher Level

How the level tags work in this booklet

HL **Everything in this booklet is Higher Level only.** Understandings 3.2.10 (^{1}H NMR spectroscopy), 3.2.11 (splitting patterns) and 3.2.12 (combining techniques) are not assessed at Standard Level.

SL + HL Short reminder panels recap what the HL work builds on: radio waves and $E = hf$ (Structure 1.3), empirical formulas (Structure 1.4), electronegativity (Structure 2.2) and MS and IR (Booklet 7).

Inside this booklet

1. What the syllabus actually asks of you
2. 3.2.10 — How ^{1}H NMR works
3. 3.2.10 — Chemical environments
4. 3.2.10 — Chemical shift and integration
5. 3.2.11 — Spin–spin splitting
6. 3.2.12 — Combining MS, IR and ^{1}H NMR
7. Key points to memorise
8. Check yourself
9. Answers

1 What the syllabus actually asks of you

Booklet 7 used mass spectrometry to weigh a molecule and its fragments, and infrared spectroscopy to find its bonds. Those two techniques often still leave isomers unresolved: propan-1-ol and propan-2-ol have almost identical IR spectra, and ethyl ethanoate and methyl propanoate share a formula and an ester group. **Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy** settles such questions, because it reports on every hydrogen atom in the molecule: how many different kinds there are, what each is near, how many of each there are, and how many hydrogens sit on the neighbouring carbon atoms. It is the most powerful single technique an organic chemist has.

Understanding	What it says	What you must be able to do	Level
3.2.10 ^{1}H NMR	^{1}H NMR spectroscopy gives information on the different chemical environments of hydrogen atoms in a molecule.	Interpret ^{1}H NMR spectra to deduce the structures of organic molecules from the **number of signals**, the **chemical shifts** and the **relative areas** under the signals (integration traces). Data are given in the data booklet.	HL
3.2.11 Splitting	Individual signals can be split into clusters of peaks.	Interpret ^{1}H NMR spectra from splitting patterns showing **singlets, doublets, triplets and quartets** to deduce greater structural detail.	HL
3.2.12 Combining techniques	Data from different techniques are often combined in structural analysis.	Interpret a variety of data, including analytical spectra and compositional data, to determine the structure of a molecule.	HL

Linking questions and connections for 3.2.10 – 3.2.12

- **Structure 1.3:** radio waves, $c = f\lambda$ and $E = hf$. → section 2
- **Structure 1.4:** empirical and molecular formulas from percentage composition. → section 6
- **Structure 2.2:** electronegativity explains why nearby O, halogens and C=O move signals to higher shift. → section 4
- **Booklet 5 (3.2.6):** NMR is the best way to tell structural isomers apart. → sections 3 and 5
- **Booklet 7 (3.2.8 – 3.2.9):** MS and IR data are combined with NMR in 3.2.12. → section 6
- **Nature of Science and TOK:** magnet technology and MRI. → section 2.4

What the data booklet gives you — and what it does not

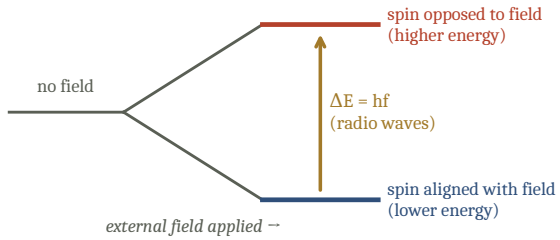
- **Section 21** lists typical chemical shifts (δ / ppm, relative to TMS) for each type of proton. You do not learn these values, but you must match each signal to the right row, and accept that real signals can sit a little outside the printed ranges.
- **Section 20** (IR) and **Section 22** (MS fragments lost) are still needed whenever 3.2.12 combines techniques.
- The data booklet gives nothing on counting environments, the $(n + 1)$ rule or which protons do not couple: those are the skills this booklet practises.
- **Not in the IB course:** ^{13}C NMR spectra, coupling constants and D_2O exchange are not assessed. Splitting is limited to singlets, doublets, triplets and quartets, although you should recognise a larger cluster as a multiplet.

2 Structure 3.2.10 — How ^{1}H NMR works HL

2.1 Nuclear spin in a magnetic field

Nuclei with an **odd number of nucleons** (protons plus neutrons), such as ^{1}H, ^{13}C, ^{19}F and ^{31}P, have a property called **nuclear spin** and behave like tiny bar magnets. Nuclei with an even number of nucleons, such as ^{12}C and ^{16}O, have no spin and give no NMR signal. A ^{1}H nucleus is a single proton, so the words *hydrogen nucleus* and *proton* are used interchangeably in NMR.

Without a magnetic field the two spin states have the same energy. In a strong external magnetic field a proton can line up **with** the field (lower energy) or **against** it (higher energy). The energy gap is tiny, so the radiation that flips a proton from the lower to the higher state is low-energy **radio waves**:



$$\Delta E = hf \quad (f \text{ in the radio-frequency region})$$

The sample sits in the field and is exposed to radio waves. When the frequency exactly matches the energy gap of a set of protons, they absorb energy and flip: they are in **resonance**. A detector records which frequencies are absorbed.

2.2 Shielding: why protons absorb at different frequencies

The electrons around a nucleus circulate in the external field and set up a small opposing field, which **shields** the nucleus. Protons in different electronic environments are shielded by different amounts, so each feels a slightly different effective field, has a slightly different ΔE, and absorbs at a slightly different frequency. That difference is what makes NMR useful: every type of hydrogen in a molecule announces itself at its own position in the spectrum.

The reference: tetramethylsilane (TMS)

Positions are measured relative to **tetramethylsilane**, $Si(CH_3)_4$, whose signal is defined as $\delta = 0$ ppm. TMS is chosen because:

- its **12 protons are all equivalent**, so it gives one strong, sharp signal;
- silicon is **less electronegative** than carbon, so the TMS protons are very strongly shielded and absorb **upfield** of (to the right of) almost every organic signal, with no overlap;
- it is **chemically inert** and non-toxic, and so volatile (b.p. about 27 °C) that it is easily removed from the sample afterwards.

Samples are dissolved in a solvent with no ^{1}H atoms, such as $CDCl_3$ (deuterium, ^{2}H, gives no signal in a ^{1}H spectrum) or CCl_4, so the solvent does not swamp the spectrum.

2.3 The four pieces of information in a spectrum

Feature	What it tells you	Section
number of signals	the number of different **chemical environments** of hydrogen	3
chemical shift, δ	the **type** of proton: which atoms or groups are nearby	4.1
relative area (integration)	the **relative number** of protons in each environment	4.2
splitting pattern	the number of protons on **neighbouring** carbon atoms (high resolution only)	5

2.4 MRI and better magnets

Nature of Science, TOK and global impact

MRI. Magnetic resonance imaging applies the same principle to the hydrogen nuclei in the water and fat of the body (water makes up roughly 60% of body mass). Computers turn the signals into three-dimensional images of soft tissue. Because radio waves are low-energy and **non-ionizing**, MRI avoids the radiation hazard of X-rays and CT scans. The word 'nuclear' was quietly dropped from the medical name: what does that suggest about public perception of science?

Magnets. Resolution improves dramatically with field strength. Iron magnets in the 1950s gave instruments of 30–60 MHz; superconducting magnets, introduced in the 1960s, reached 500 MHz in the 1980s and 1 GHz in 2009. New high-temperature superconductors overcame the limits of earlier materials, and 1.2 GHz spectrometers appeared from 2020. Progress in science is often limited by technology rather than by ideas.

3 Structure 3.2.10 — Chemical environments HL

Hydrogen atoms in identical surroundings are **chemically equivalent** and absorb together as one signal. To find the number of signals, count the sets of equivalent hydrogens.

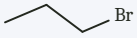
Method — counting environments

1. Draw the full structural or skeletal formula.
2. Look for **symmetry**: hydrogens swapped by a mirror plane through the molecule are equivalent (the two CH_3 groups of propan-2-ol).
3. All H atoms on one CH_3 group are equivalent (free rotation about the C–C bond). Usually the two H atoms of a CH_2 group are too.
4. H atoms on O or N (–OH, –COOH, $–NH_2$) are separate environments of their own.
5. Check: the number of H atoms in all the environments must add up to the molecular formula.

Compound	Formula	Signals	Environments and ratio
ethane	CH_3CH_3	1	6 equivalent H
propane	$CH_3CH_2CH_3$	2	two CH_3 (6H) : CH_2 (2H) = 3 : 1
2-methylpropane	$(CH_3)_3CH$	2	three CH_3 (9H) : CH (1H) = 9 : 1
propan-1-ol	$CH_3CH_2CH_2OH$	4	3 : 2 : 2 : 1
propan-2-ol	$CH_3CH(OH)CH_3$	3	two CH_3 (6H) : CH (1H) : OH (1H) = 6 : 1 : 1
methoxyethane	$CH_3OCH_2CH_3$	3	3 : 2 : 3
propanone	CH_3COCH_3	1	6 equivalent H
1,2-dichloroethane	$ClCH_2CH_2Cl$	1	4 equivalent H
benzene, cyclohexane	C_6H_6, C_6H_{12}	1	all H equivalent by symmetry

Worked example 1 — the two isomers of C_3H_7Br

The ^{1}H NMR spectrum of a compound with formula C_3H_7Br shows two signals with areas in the ratio 6 : 1. Identify the compound.



1-bromopropane: 3 environments, 3 : 2 : 2



2-bromopropane: 2 environments, 6 : 1

1-Bromopropane has no symmetry, so its three carbons carry three different sets of H atoms. 2-Bromopropane has a mirror plane through C2: its two CH_3 groups are equivalent (6H), and the CH carrying the Br is unique (1H). The compound is **2-bromopropane**, $CH_3CHBrCH_3$.

Practice A **Count the environments**

For each compound, state the number of signals in its ^{1}H NMR spectrum and the simplest whole-number ratio of their areas.

	Compound		Compound
(a)	chloroethane, CH_3CH_2Cl	**(g)**	butanone, $CH_3COCH_2CH_3$
(b)	1-chloropropane, $CH_3CH_2CH_2Cl$	**(h)**	pentan-3-one, $CH_3CH_2COCH_2CH_3$
(c)	2-chloropropane, $CH_3CHClCH_3$	**(i)**	2,2-dimethylpropane, $C(CH_3)_4$
(d)	methoxymethane, CH_3OCH_3	**(j)**	2-methylpropan-1-ol, $(CH_3)_2CHCH_2OH$
(e)	ethanoic acid, CH_3COOH	**(k)**	ethyl ethanoate, $CH_3COOCH_2CH_3$
(f)	propanal, CH_3CH_2CHO	**(l)**	1,3-dichloropropane, $ClCH_2CH_2CH_2Cl$

4 Structure 3.2.10 — Chemical shift and integration HL

4.1 Chemical shift

The **chemical shift**, δ, measures how far a signal is from the TMS signal, in parts per million (ppm) of the spectrometer frequency. Expressing it this way makes δ the same on every instrument, whatever its field strength. Note the convention: **0 ppm (TMS) is on the right** and δ increases to the left, up to about 12 ppm.

Why nearby atoms raise the chemical shift

Electronegative atoms (O, N, halogens) and C=O groups pull electron density away from nearby C–H bonds. The protons are less shielded, or **deshielded**: they feel more of the external field and absorb at a **higher chemical shift** (further left). The effect fades quickly with distance. In propan-1-ol, CH_3–CH_2–CH_2–OH, the shifts fall step by step away from the oxygen: –CH_2O at about 3.6, the middle –CH_2– at about 1.6 and –CH_3 at about 0.9 ppm.

Type of proton	Where it is found	δ / ppm	Notes
–CH_3	alkyl methyl	0.9–1.0	most shielded; a little higher if near O or C=O
–CH_2–R	alkyl CH_2	1.3–1.4	
–CHR_2	alkyl CH	1.5	
RO–C(=O)–CH_2–	next to the C=O of an ester or acid	2.0–2.5	CH_3COO– near 2.0
R–C(=O)–CH_2–	next to the C=O of an aldehyde or ketone	2.2–2.7	CH_3CO– singlet near 2.1–2.2
C_6H_5–CH_2–	next to a benzene ring	2.5–3.5	methylbenzene CH_3 about 2.3
–C≡C–H	alkyne	1.8–3.1	
–CH_2–Hal	next to a halogen	3.5–4.4	
R–O–CH_2–	on the C bonded to the O of an alcohol or ether	3.3–3.7	
R–C(=O)–O–CH_2–	on the alkyl (O) side of an ester	3.7–4.8	key ester marker
–CH=CH_2	alkene	4.5–6.0	
C_6H_5–H	benzene ring	6.9–9.0	usually about 7.2
R–CHO	aldehyde	9.4–10.0	methanoate esters, HCOO–, near 8.0
R–O–H	alcohol	1.0–6.0*	* varies with concentration and hydrogen bonding
R–COOH	carboxylic acid	9.0–13.0*	usually about 11–12, broad

Values follow data booklet Section 21 (selected rows). Shifts for groups that combine two effects can fall outside the ranges: a CH_2 between a C=O and an O, as in CH_3COCH_2OH, appears near 4.2 ppm. Always use your own copy of the data booklet in the exam.

4.2 Integration: the area under each signal

The **area** under a signal, not its height, is proportional to the number of protons responsible. Spectra show the areas either as numbers or as an **integration trace**: a line that rises in a step over each signal, the height of each step being proportional to the number of protons.

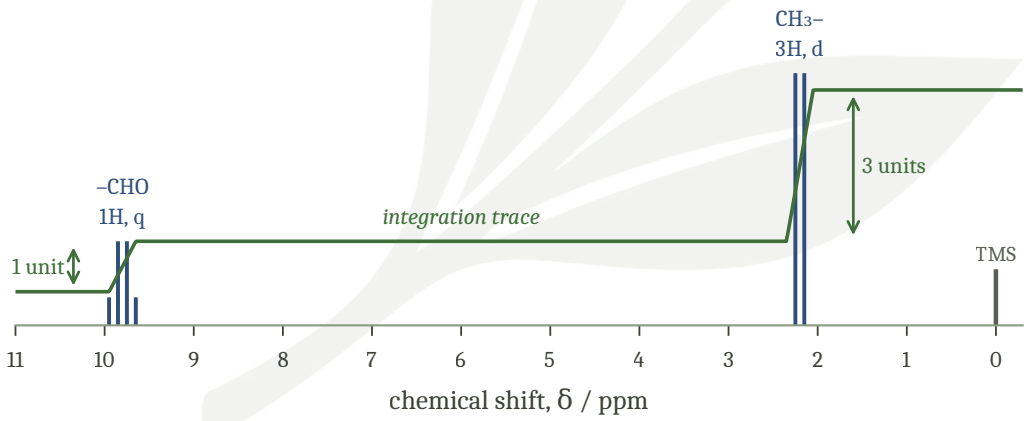


Figure 1 — Simplified ^{1}H NMR spectrum of ethanal, CH_3CHO, with its integration trace (green). The step over the CH_3 signal is three times the step over the CHO signal: a 3 : 1 ratio.

Method — from integration values to numbers of protons

1. Measure or read the step heights (or the printed areas).
2. Divide every value by the smallest to obtain a ratio; multiply up if necessary to remove fractions (1 : 1.5 → 2 : 3).
3. Compare the total with the number of H atoms in the molecular formula: the ratio 1 : 2 : 3 for $C_3H_6O_2$ gives exactly 1H, 2H and 3H; the ratio 1 : 3 for C_4H_8O (8H) cannot be right, so look again.

Practice B **Integration ratios**

Convert each set of areas into the simplest whole-number ratio. For (e) and (f), also give the number of protons in each environment.

(a) 0.6 : 1.2 : 1.8
(b) 0.8 : 1.2
(c) 0.75 : 0.75 : 0.50
(d) 0.3 : 0.6 : 0.9 : 2.7
(e) 2.4 : 0.8 for $C_4H_8O_2$ (two signals)
(f) 14 mm : 21 mm : 7 mm for $C_6H_{12}O$

5 Structure 3.2.11 — Spin–spin splitting HL

5.1 The (n + 1) rule

In a **high-resolution** spectrum most signals are split into small clusters of lines. The protons on a neighbouring carbon are tiny magnets too; their spins can line up with or against the external field, slightly raising or lowering the field felt by the proton being observed. This is **spin–spin coupling**.

The (n + 1) rule

If a set of equivalent protons has ***n* protons on the adjacent carbon atom(s)** (H–C–C–H, three bonds apart) that are not equivalent to it, its signal is split into ***n* + 1 lines**. The relative intensities of the lines follow **Pascal's triangle**.

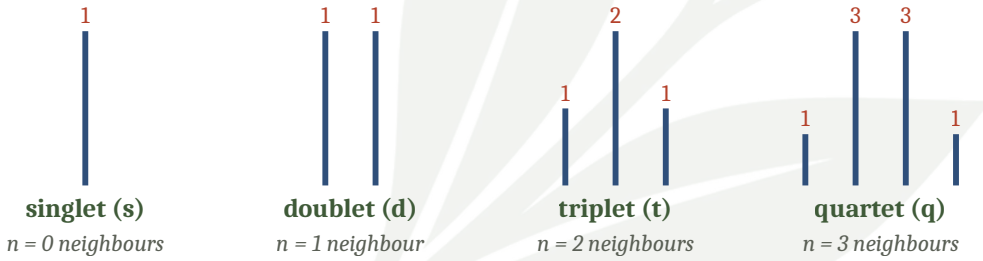


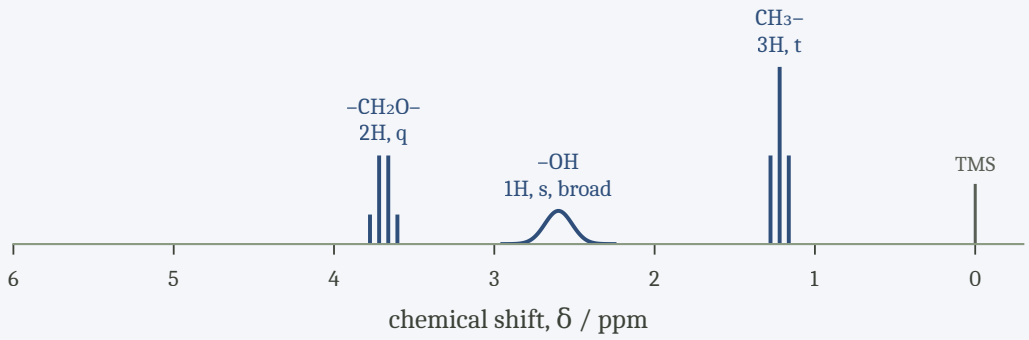
Figure 2 — The four splitting patterns assessed in 3.2.11, with their relative line intensities. Four or more neighbours give a quintet, sextet and so on, often reported simply as a multiplet (m).

Protons on adjacent C (*n*)	Lines (*n* + 1)	Name	Ratio	Typical neighbour
0	1	singlet (s)	1	C with no H, O, C=O
1	2	doublet (d)	1 : 1	–CH– or –CHO
2	3	triplet (t)	1 : 2 : 1	$-CH_2-$
3	4	quartet (q)	1 : 3 : 3 : 1	$-CH_3$

5.2 When signals do not split

- **Equivalent protons do not split each other.** In butane the two middle CH_2 groups are equivalent, so each couples only with its CH_3 neighbour: a quartet, not a sextet. 1,2-Dichloroethane gives a single 4H singlet.
- **Protons further apart** than H–C–C–H are not usually seen to couple at this level. A C=O, an O atom or a carbon with no H 'blocks' coupling: in ethyl ethanoate the CH_3CO– protons are a singlet.
- **–OH (and –NH) protons** normally exchange rapidly between molecules, so they appear as a **singlet** (often broad) and do not split the protons on the neighbouring carbon. Leave them out when you count *n*: in ethanol the CH_2 signal is a quartet, not a quintet.

Worked example 2 — the high-resolution spectrum of ethanol



- δ 3.7 (2H, q): the CH_2 next to O (3.3–3.7 ppm); three neighbouring H on CH_3 → quartet.
- δ 2.6 (1H, s, broad): the O–H (variable shift); no splitting.
- δ 1.2 (3H, t): the CH_3; two neighbouring H on CH_2 → triplet.

Chemists summarise a spectrum like this: δ 3.7 (2H, q), 2.6 (1H, s), 1.2 (3H, t).

5.3 Recognising fragments

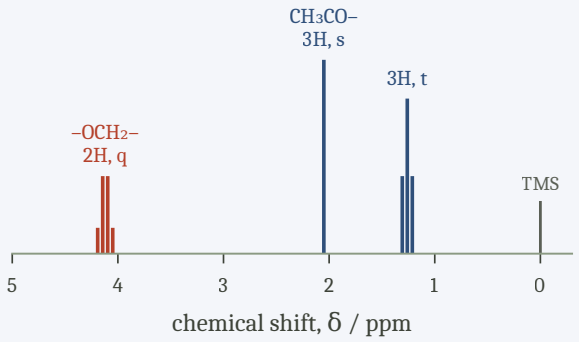
Coupled signals come in pairs: if A splits B, then B also splits A. Matching the pairs gives structural 'jigsaw pieces' that are then joined using the chemical shifts.

Signals seen	Fragment	Notes
2H quartet + 3H triplet	CH_3CH_2–	ethyl group, joined to something with no H (C=O, O, Cl, C)
4H quartet + 6H triplet	two equivalent CH_3CH_2–	e.g. pentan-3-one
2H triplet + 2H triplet	–CH_2CH_2–	the two ends are different (X–CH_2CH_2–Y)
1H quartet + 3H doublet	CH_3CH<	the CH carries no other H neighbours
6H doublet + 1H multiplet	$(CH_3)_2CH$–	the 1H signal is a septet (seven lines)
3H singlet	CH_3–X	X has no H: CH_3CO– (≈ 2.1), CH_3O– (≈ 3.7)
9H singlet	$(CH_3)_3C$–	three equivalent CH_3 on a C with no H
1H singlet, variable or 9–13	–OH or –COOH	never split; does not split neighbours

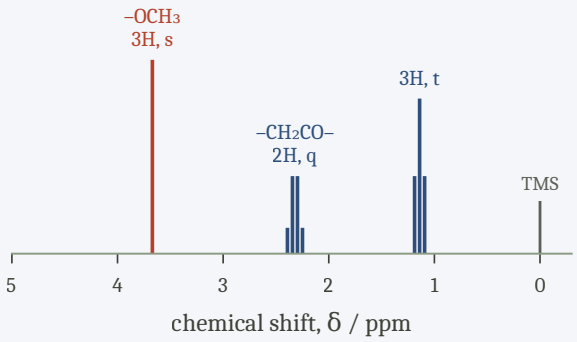
Worked example 3 — two esters with the formula $C_4H_8O_2$

Ethyl ethanoate and methyl propanoate both give three signals: a 3H singlet, a 2H quartet and a 3H triplet. Which is which? The chemical shifts decide.

ethyl ethanoate, $CH_3COOCH_2CH_3$

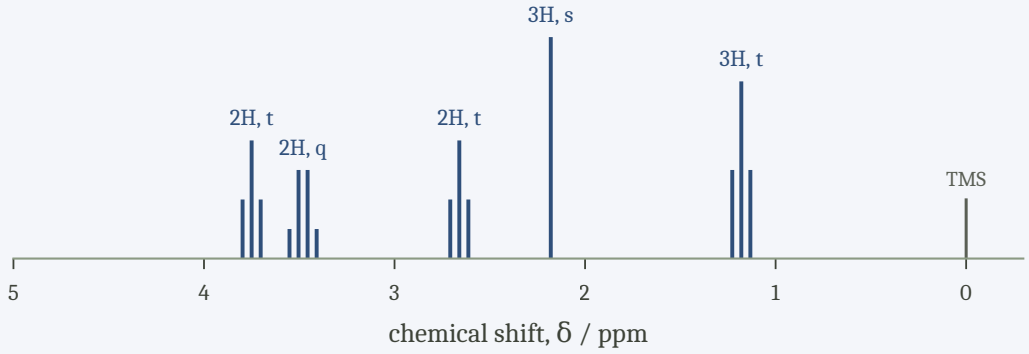


methyl propanoate, $CH_3CH_2COOCH_3$



The group bonded to the single-bonded O of an ester absorbs at 3.7–4.8 ppm (red); the group next to the C=O absorbs at 2.0–2.5 ppm. In ethyl ethanoate it is the **2H quartet** that is near 4 ppm, so the ethyl group is on the oxygen; in methyl propanoate it is the **3H singlet**.

Worked example 4 — assembling the pieces: $C_6H_{12}O_2$



Compound P has the formula $C_6H_{12}O_2$, a strong IR absorption at 1715 cm^{-1} and no O–H absorption. Deduce its structure from the spectrum.

1. δ 2.2 (3H, s): an isolated CH_3 next to C=O (2.2–2.7): **CH_3CO–**.
2. δ 3.5 (2H, q) and δ 1.2 (3H, t): an ethyl group; its CH_2 is on an O (3.3–3.7): **CH_3CH_2O–**, an ether oxygen.
3. δ 3.75 (2H, t) and δ 2.7 (2H, t): two different CH_2 groups next to each other, one on O and one next to C=O: **–OCH_2CH_2CO–**.
4. Join the pieces: CH_3CH_2–O–CH_2CH_2–CO–CH_3, **4-ethoxybutan-2-one**. Check: $C_6H_{12}O_2$, 12 H accounted for.

Worked example 5 — position isomers told apart by splitting

2-Chloropropanoic acid and 3-chloropropanoic acid both give three signals, including the –COOH singlet.

Isomer	Signals (δ / ppm, area, splitting)
2-chloropropanoic acid, $CH_3CHClCOOH$	11.2 (1H, s, COOH); 4.4 (1H, q, CHCl); 1.7 (3H, d, CH_3)
3-chloropropanoic acid, $ClCH_2CH_2COOH$	11.5 (1H, s, COOH); 3.8 (2H, t, CH_2Cl); 2.8 (2H, t, CH_2CO)

A doublet + quartet (3 : 1) shows the $CH_3CH(Cl)$– branch; two triplets (2 : 2) show the unbranched –CH_2CH_2– chain.

Model answer: "Explain the splitting of the signal at 4.1 ppm in the spectrum of ethyl ethanoate." (2 marks)

The signal is due to the –OCH_2– protons, which have three protons on the adjacent carbon (the CH_3 group) **[1]**. By the (n + 1) rule the signal is split into 3 + 1 = 4 lines, a quartet (intensities 1 : 3 : 3 : 1) **[1]**.

Examiner traps in ^{1}H NMR

- The **area** counts the protons giving the signal; the **splitting** counts the protons on the neighbouring carbon. A CH_3 next to a CH_2 is a 3H triplet, not a 2H quartet.
- Do not count –OH protons in n, and do not split the –OH signal.
- Equivalent protons do not split each other (butane, 1,2-dichloroethane).
- Use areas, never peak heights: a quartet's lines are shorter than a singlet of the same area.
- Esters: –O–CH_2– or –O–CH_3 at 3.7–4.8 ppm, –CO–CH_2– or CH_3CO– at 2.0–2.5 ppm.
- 'Number of signals' means the number of environments, not the number of lines in a high-resolution spectrum.

Practice C — Predict the high-resolution spectrum

For each compound give (i) the number of signals, (ii) the ratio of areas and (iii) the splitting of each signal, in the same order. Add a likely chemical shift for each signal from Section 21.

	Compound		Compound
(a)	1,1-dichloroethane, CH_3CHCl_2	**(f)**	2-bromo-2-methylbutane, $CH_3CH_2C(Br)(CH_3)_2$
(b)	1,2-dichloroethane, $ClCH_2CH_2Cl$	**(g)**	methyl ethanoate, CH_3COOCH_3
(c)	propanone, CH_3COCH_3	**(h)**	propanoic acid, CH_3CH_2COOH
(d)	butanone, $CH_3COCH_2CH_3$	**(i)**	2-methylpropan-2-ol, $(CH_3)_3COH$
(e)	pentan-3-one, $CH_3CH_2COCH_2CH_3$	**(j)**	chloroethane, CH_3CH_2Cl

Practice D **Deduce the structure from the ^{1}H NMR data**

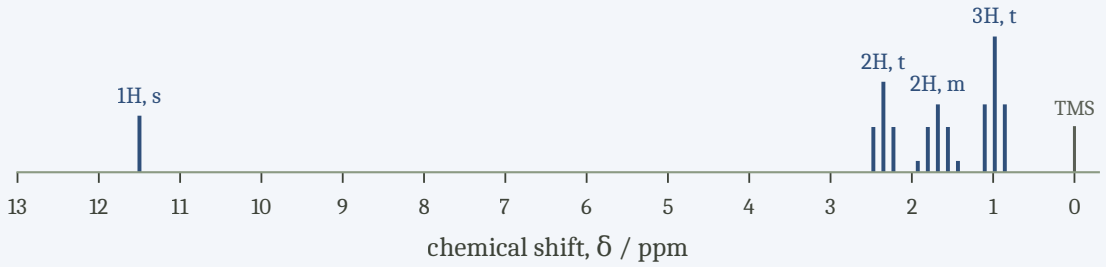
Deduce a structural formula and the name of each compound.

1. $C_2H_3Cl_3$: δ 5.8 (1H, t), 3.9 (2H, d)
2. $C_4H_{10}O$: δ 2.0 (1H, s), 1.25 (9H, s)
3. $C_3H_6O_2$: δ 4.2 (2H, s), 3.1 (1H, s, broad), 2.15 (3H, s)
4. $C_5H_{10}O_2$, an ester: δ 4.05 (2H, t), 2.05 (3H, s), 1.65 (2H, m), 0.95 (3H, t)
5. $C_5H_{10}O$: δ 2.6 (1H, m), 2.15 (3H, s), 1.1 (6H, d)
6. C_3H_5ClO: δ 4.1 (2H, s), 2.3 (3H, s)
7. C_4H_9Br: δ 4.1 (1H, m), 1.85 (2H, m), 1.7 (3H, d), 1.05 (3H, t)
8. **Challenge** — $C_7H_{12}O_3$, containing one ketone and one ester group: δ 4.14 (2H, q), 2.75 (2H, t), 2.58 (2H, t), 2.20 (3H, s), 1.26 (3H, t)

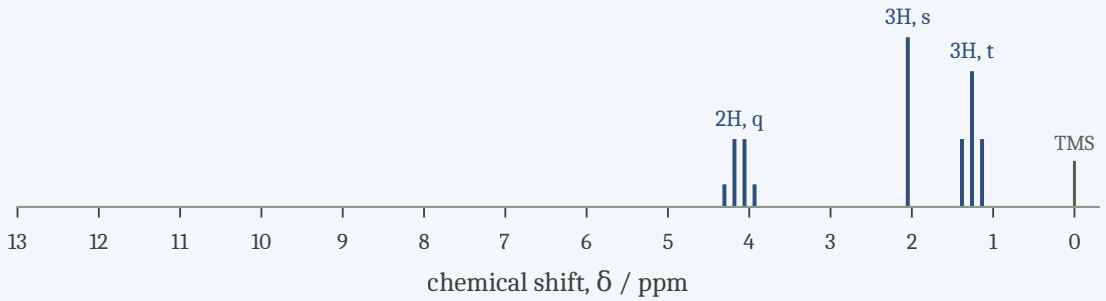
Practice E **Match the spectra: four isomers of $C_4H_8O_2$**

The spectra belong to butanoic acid, ethyl ethanoate, methyl propanoate and propyl methanoate, $HCOOCH_2CH_2CH_3$. Match them, and assign every signal.

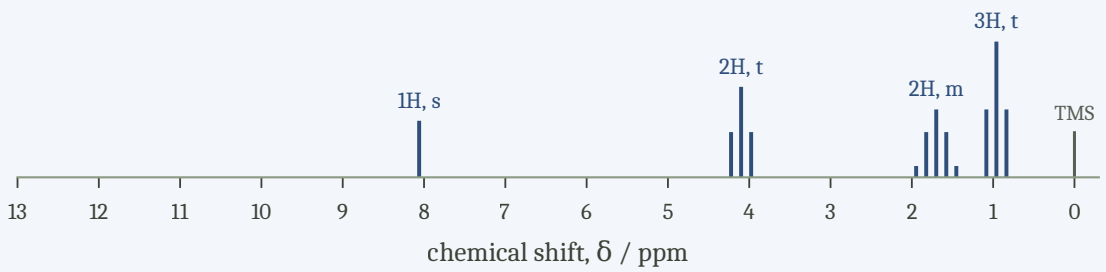
Spectrum 1



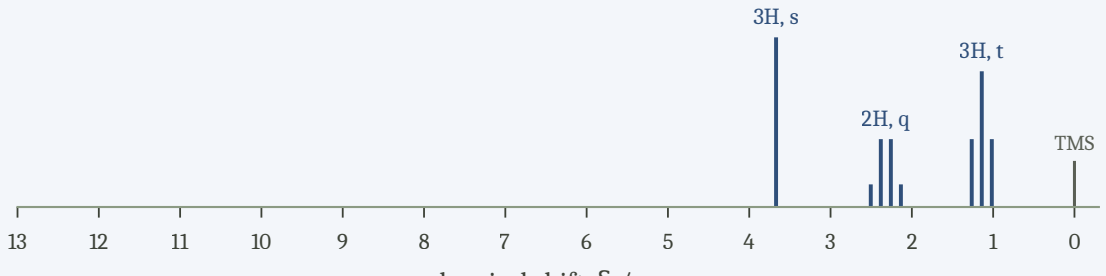
Spectrum 2



Spectrum 3



Spectrum 4



6 Structure 3.2.12 — Combining MS, IR and ^{1}H NMR HL

6.1 What each technique contributes

Technique	What it gives	Why you still need the others
composition analysis	% by mass → empirical formula	says nothing about molecular size or structure
mass spectrometry	M^+ → M_r and molecular formula; fragments (Section 22); Cl and Br isotope patterns	different isomers can give the same fragments (43 = $C_3H_7^+$ or CH_3CO^+)
infrared	bonds and functional groups (Section 20), including what is **absent**	rarely distinguishes isomers within one class
^{1}H NMR	number and type of H environments, their ratio, and their neighbours (Section 21)	no direct molecular mass; C=O and other H-free groups seen only through their effect on neighbours

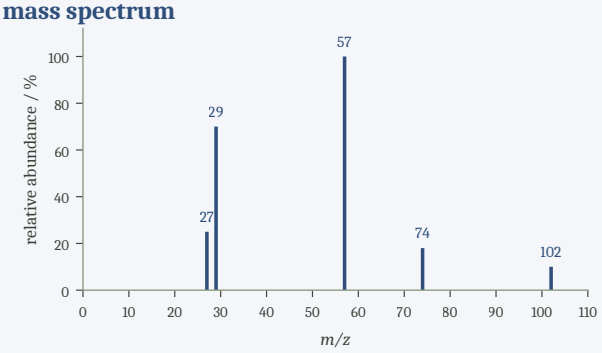
Method — deducing a structure from combined data

1. **Molecular formula:** empirical formula from % composition; divide M_r (from M^+) by the empirical formula mass.
2. **Fewer H than an alkane?** Compare with C_nH_{2n+2} (ignore O; count halogens as H): every 2 H missing means one C=C, one C=O or one ring.
3. **IR:** identify the bonds, quoting bond and range, and use absences ('no broad O–H at 2500–3000, so not an acid').
4. **^{1}H NMR:** list each signal (δ, area, splitting), build the fragments and join them; check all the H atoms are used.
5. **MS fragments:** check that the main peaks (written as ions, with + charges) fit your structure and that it predicts no large peaks that are missing.

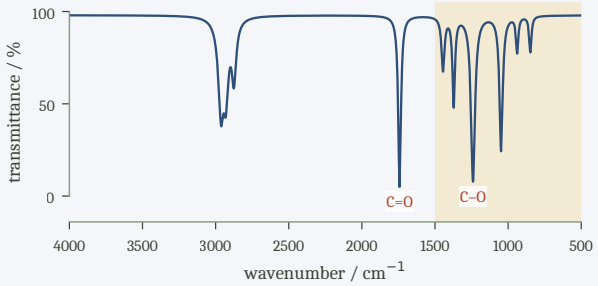
Worked example 6 — a full deduction

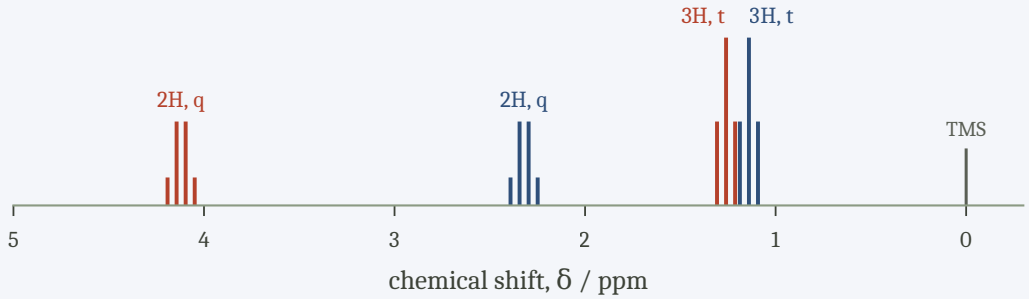
Compound X contains 58.8% C, 9.8% H and 31.4% O by mass. Its spectra are summarised below. Deduce its structure.

mass spectrum



IR spectrum





1. C 58.8/12.01 = 4.90; H 9.8/1.01 = 9.7; O 31.4/16.00 = 1.96; ratio 2.5 : 5 : 1 = 5 : 10 : 2. Empirical formula $C_5H_{10}O_2$ (102). M^+ = 102, so the molecular formula is **$C_5H_{10}O_2$**, two H fewer than an alkane: one C=O (or C=C, or ring).
2. IR: strong C=O at 1740 (1700–1750) and C–O at 1240 (1050–1410), no O–H: an **ester**.
3. ^{1}H NMR: two ethyl groups (each a 2H quartet + 3H triplet). One CH_2 is at 4.1 ppm (on the ester O, 3.7–4.8); the other at 2.3 ppm (next to C=O, 2.0–2.5). So CH_3CH_2–C(=O)–O–CH_2CH_3.
4. MS: 57 = $C_2H_5CO^+$ (base peak), 29 = $C_2H_5^+$, 74 = M − 28 (loss of C_2H_4). X is **ethyl propanoate**, $CH_3CH_2COOCH_2CH_3$.

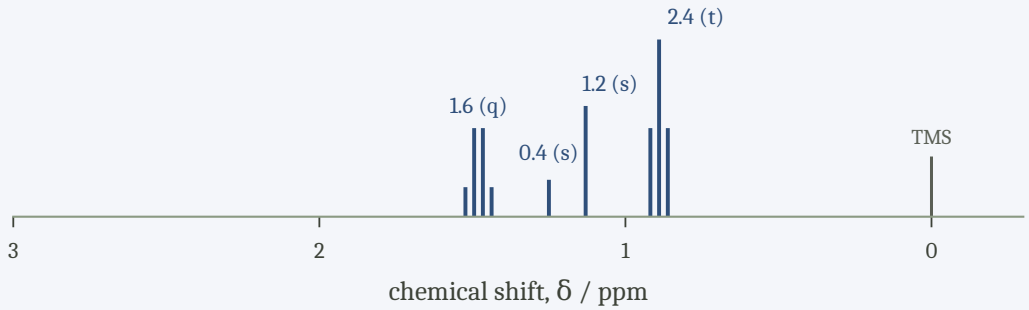
Worked example 7 — a ring or a C=C? Using absences

A hydrocarbon contains 85.6% C and 14.4% H. Its molecular ion is at m/z = 70. Its IR spectrum shows C–H absorption near 2950 cm^{-1} but nothing at 1620–1680 cm^{-1}, and its ^{1}H NMR spectrum is a single signal at 1.5 ppm. Identify it.

- C 85.6/12.01 = 7.13; H 14.4/1.01 = 14.3; ratio 1 : 2, so CH_2 (14). 70 ÷ 14 = 5: C_5H_{10}.
- Pentane is C_5H_{12}, so C_5H_{10} has one C=C or one ring. No C=C absorption at 1620–1680, and no alkene signal at 4.5–6.0 ppm: it must be a **ring**.
- One NMR signal means all 10 H atoms are equivalent, which is only possible for **cyclopentane**. (Methylcyclobutane, for instance, would give several signals.)

Worked example 8 — a tertiary alcohol

Compound R, $C_6H_{14}O$, has a strong, broad IR absorption at 3360 cm^{-1} and none at 1700–1750 cm^{-1}. Its ^{1}H NMR spectrum shows four signals with relative areas 1.6 : 0.4 : 1.2 : 2.4, from left to right.



1. IR: broad O–H at 3200–3600: an **alcohol**; no C=O.
2. Areas ÷ 0.4 = 4 : 1 : 3 : 6, total 14 = all the H in $C_6H_{14}O$.
3. 4H quartet + 6H triplet: **two equivalent ethyl groups**. 3H singlet: a CH_3 on a carbon with no H. 1H singlet: the O–H. No signal at 3.3–3.7, so there is **no H on the C–OH carbon**: a tertiary alcohol.
4. Joining OH, CH_3 and two C_2H_5 to one carbon: **3-methylpentan-3-ol**, $CH_3C(OH)(CH_2CH_3)_2$.

Worked example 9 — all singlets: a hydroxyketone

Compound S, $C_6H_{12}O_2$, shows a broad IR absorption at 3450 cm^{-1} and a sharp one at 1710 cm^{-1}. Its ^{1}H NMR spectrum has four singlets: δ 3.8 (1H), 2.6 (2H), 2.2 (3H) and 1.2 (6H).

- IR: alcohol O–H (3200–3600) and C=O (1700–1750).
- All singlets: no C–H group has an H-bearing neighbour.
- δ 2.2 (3H): CH_3CO–. δ 2.6 (2H): –$COCH_2$–, bonded on its other side to a carbon with no H. δ 1.2 (6H): two equivalent CH_3 on that carbon. δ 3.8 (1H): the O–H, also on that carbon.
- S is **4-hydroxy-4-methylpentan-2-one**, $(CH_3)_2C(OH)CH_2COCH_3$.

Worked example 10 — chlorine isotopes, IR and NMR together

Compound Q, C_4H_7ClO, has molecular ion peaks at m/z = 106 and 108 (ratio 3 : 1) and a large peak at 43; a strong IR absorption at 1724 cm^{-1}; and ^{1}H NMR signals at δ 4.4 (1H, q), 2.3 (3H, s) and 1.6 (3H, d).

- 106 and 108 in a 3 : 1 ratio: one Cl atom (^{35}Cl and ^{37}Cl). 43 is CH_3CO^+.
- IR: C=O at 1724.
- δ 2.3 (3H, s): CH_3CO–. δ 4.4 (1H, q) + δ 1.6 (3H, d): a $CH_3CH<$ group, the CH deshielded by both Cl and C=O.
- Q is **3-chlorobutan-2-one**, $CH_3COCHClCH_3$.

Practice F **Combined analysis cases**

Each case is in the style of a Paper 2 data question.

Case 1. Compound W contains 54.5% C, 9.1% H and 36.4% O. M^+ = 88; other MS peaks at 71, 45 and 43. IR: very broad 2500–3300 and sharp 1710 cm^{-1}. ^{1}H NMR: δ 11.8 (1H, s), 2.35 (2H, t), 1.68 (2H, m), 0.98 (3H, t). (a) Deduce the molecular formula. (b) Identify the bonds responsible for the IR absorptions and the ions at 71 and 45. (c) Deduce the structure of W.

Case 2. An isomer of W, compound V, gives the same IR absorptions and MS peaks at 88, 73, 45 and 43, but its ^{1}H NMR spectrum shows δ 11.6 (1H, s), 2.58 (1H, m) and 1.19 (6H, d). Deduce its structure and explain the splitting of the signal at 1.19 ppm.

Case 3. Compound U, $C_5H_{10}O$, absorbs strongly at 1715 cm^{-1} and not above 3100 cm^{-1}. Its mass spectrum shows M^+ = 86 and a base peak at 57; its ^{1}H NMR spectrum has just two signals, δ 2.44 (4H, q) and 1.06 (6H, t). Identify U, and give two pieces of evidence that rule out its isomer pentan-2-one.

Case 4. Compound T has molecular ion peaks at 92 and 94 in the ratio 3 : 1. Its IR spectrum shows only C–H absorptions above 1500 cm^{-1}. Its ^{1}H NMR spectrum: δ 3.35 (2H, d), 1.95 (1H, m), 1.02 (6H, d). Deduce its structure, and state the number of signals its isomer 2-chloro-2-methylpropane would give.

7 Key points to memorise

Everything below is either wording that examiners look for, or knowledge you must carry into the exam yourself.

A Principles, chemical shift and integration (3.2.10)

- Nuclei with an odd number of nucleons (^{1}H, ^{13}C) have spin; in a magnetic field radio waves flip the spin ($\Delta E = hf$).
- Electrons shield the nucleus; different environments absorb at different chemical shifts, δ / ppm.
- TMS, $Si(CH_3)_4$, $\delta = 0$: 12 equivalent H (one signal), absorbs upfield of other signals, inert, volatile. Solvents without ^{1}H, e.g. $CDCl_3$.
- Number of signals = number of H environments (use symmetry). Area (integration) $\propto$ number of H.
- Electronegative atoms and C=O deshield nearby protons → higher δ. Use data booklet Section 21.

B Splitting (3.2.11) and combining (3.2.12)

- (n + 1) rule: n H on adjacent C → n + 1 lines. Singlet 1; doublet 1 : 1; triplet 1 : 2 : 1; quartet 1 : 3 : 3 : 1.
- No splitting between equivalent H; –OH appears as a singlet and is not counted in n.
- Ethyl = 2H q + 3H t; isopropyl = 6H d + 1H m; tert-butyl = 9H s; $CH_3CO–$ = 3H s near 2.1.
- Esters: $–O–CH_2–$ at 3.7–4.8 ppm, $–CO–CH_2–$ at 2.0–2.5 ppm. Aldehyde 9.4–10.0; acid 9.0–13.0.
- Combined: % composition + M^+ → molecular formula → H deficiency → IR bonds and absences → NMR fragments → check MS fragments.

C Command terms — what each one is actually asking for

- **State / Identify** — the bond and range (IR), the ion with its + charge (MS), or the group of protons (NMR).
- **Predict** (a spectrum) — number of signals, likely shifts from Section 21, areas and splitting for each.
- **Deduce** (a structure) — show the chain of reasoning from each piece of data to the structure.
- **Explain** (a shift or a splitting) — give the cause: deshielding by an electronegative atom, or n neighbouring protons giving n + 1 lines.
- **Distinguish** (two compounds) — name a feature present in one and absent or different in the other.

8 Check yourself

Exam-style questions on the whole booklet. Use a copy of the data booklet (Sections 20–22). All questions are Higher Level.

1. Which region of the electromagnetic spectrum is absorbed in ^{1}H NMR spectroscopy?

   A ultraviolet B infrared C microwaves D radio waves

2. Which nucleus cannot be detected by NMR spectroscopy?

   A ^{1}H B ^{12}C C ^{13}C D ^{19}F

3. Which compound gives only one signal in its ^{1}H NMR spectrum?

   A CH_3OCH_3 B CH_3CH_2OH
   C CH_3COOCH_3 D CH_3CH_2Cl

4. What is the ratio of the areas of the signals in the spectrum of 3,3-dimethylbutan-2-one, $CH_3COC(CH_3)_3$?

   A 1 : 3 B 3 : 3 : 3 : 3 C 1 : 1 D 3 : 1 : 9

5. Which compound gives a 3H singlet and two 2H triplets?

   A $CH_3COCH_2CH_2Cl$ B $CH_3CH_2COCH_2Cl$
   C $CH_3CHClCOCH_3$ D $ClCH_2COCH_2CH_3$

6. In the high-resolution spectrum of 1-chloropropane, what is the splitting of the signal from the $-CH_2Cl$ protons?

   A singlet B doublet C triplet D quartet

7. Which isomer of C_4H_9Br gives only one signal?

   A 1-bromobutane B 2-bromobutane
   C 1-bromo-2-methylpropane D 2-bromo-2-methylpropane

8. Which statement about TMS is **not** correct?

   A Its protons are all equivalent.
   B It is inert and volatile.
   C Its protons are deshielded because Si is more electronegative than C.
   D Its signal is set at $\delta = 0$ ppm.

9. Give **three** reasons why tetramethylsilane is used as the reference in ^{1}H NMR. **[3]**

10. Predict the ^{1}H NMR spectrum of methyl butanoate, $CH_3CH_2CH_2COOCH_3$: number of signals, approximate shifts, areas and splitting. **[4]**

11. Describe **two** ways in which the ^{1}H NMR spectra of propan-1-ol and propan-2-ol differ. **[3]**

12. Explain why the CH_2 signal in the spectrum of ethanol is a quartet, and why the O–H signal is a singlet. **[2]**

13. Explain why the protons on C1 of 1-chlorobutane absorb at a higher chemical shift than those on C4. **[2]**

14. A compound C_4H_8O shows a strong IR absorption at 1730 cm^{-1}. Its ^{1}H NMR spectrum: δ 9.6 (1H, d), 2.45 (1H, m), 1.1 (6H, d). Deduce its structure and explain each signal. **[4]**

15. Explain how ^{1}H NMR spectroscopy could distinguish 1,1-dichloroethane from 1,2-dichloroethane. **[3]**

16. Propan-1-ol is oxidized to a product that could be propanal or propanoic acid. State **two** differences you would expect between the ^{1}H NMR spectra of these two products. **[2]**

17. Compound X contains 64.8% C, 13.6% H and 21.6% O. Its mass spectrum shows $M^+ = 74$ and peaks at 59 and 45 (base peak). Its IR spectrum shows a broad absorption at 3350 cm^{-1} and none at 1700–1750 cm^{-1}. Its ^{1}H NMR spectrum: δ 3.7 (1H, m), 2.0 (1H, s), 1.5 (2H, m), 1.2 (3H, d), 0.9 (3H, t). (a) Deduce the molecular formula. (b) Deduce the structure of X, using all the data. (c) Identify the ion responsible for the base peak. **[7]**

18. Compound Z contains 58.8% C, 9.8% H and 31.4% O and has $M^+ = 102$. Its IR spectrum shows strong absorptions at 1740 and 1240 cm^{-1} and none above 3100 cm^{-1}. Its mass spectrum has a base peak at 43, and its ^{1}H NMR spectrum shows δ 5.0 (1H, m, seven lines), 2.0 (3H, s) and 1.2 (6H, d). Deduce the structure of Z, explaining each piece of evidence. **[6]**

19. Explain why the ethanal CH_3 signal is a doublet and the CHO signal a quartet. **[2]**

9 Answers

Practice A — environments

(a) 2; 3 : 2
(b) 3; 3 : 2 : 2
(c) 2; 6 : 1
(d) 1
(e) 2; 3 : 1
(f) 3; 3 : 2 : 1
(g) 3; 3 : 3 : 2 (CH_3CO, CH_3, CH_2)
(h) 2; 3 : 2 (6H : 4H)
(i) 1 (12 equivalent H)
(j) 4; 6 : 1 : 2 : 1
(k) 3; 3 : 2 : 3
(l) 2; 2 : 1 (4H : 2H)

Practice B — integration

(a) 1 : 2 : 3
(b) 2 : 3
(c) 3 : 3 : 2
(d) 1 : 2 : 3 : 9
(e) 3 : 1 → 6H and 2H
(f) 2 : 3 : 1 → 4H, 6H, 2H

Practice C — predicted spectra

(a) 2; 3 : 1; CH_3 d (≈ 2.1), $CHCl_2$ q (≈ 5.9)
(b) 1; s (≈ 3.7)
(c) 1; s (≈ 2.2)
(d) 3; 3 : 3 : 2; CH_3CO s (2.1), CH_3 t (1.0), CH_2 q (2.4)
(e) 2; 3 : 2 (6H : 4H); t (1.1), q (2.4)
(f) 3; 3 : 2 : 6; t (1.0), q (1.8), s (1.7)
(g) 2; 1 : 1; s (2.0, CH_3CO), s (3.7, OCH_3)
(h) 3; 3 : 2 : 1; t (1.1), q (2.4), s (11–12)
(i) 2; 9 : 1; s (1.3), s (OH, variable)
(j) 2; 3 : 2; t (1.5), q (3.6)

Practice D — structures from NMR data

1. 1,1,2-trichloroethane, $CHCl_2CH_2Cl$: $CHCl_2$ (two Cl, high δ) split by 2H → t; CH_2Cl split by 1H → d.
2. 2-methylpropan-2-ol, $(CH_3)_3COH$: 9H s = tert-butyl; 1H s = OH.
3. 1-hydroxypropanone, CH_3COCH_2OH: CH_3CO s; CH_2 between C=O and O (≈ 4.2, s); OH broad s.
4. propyl ethanoate, $CH_3COOCH_2CH_2CH_3$: OCH_2 t (4.05); CH_3CO s; middle CH_2 m; CH_3 t.
5. 3-methylbutan-2-one, $CH_3COCH(CH_3)_2$: CH next to C=O, m; CH_3CO s; two CH_3 split by the CH → 6H d.
6. 1-chloropropanone, CH_3COCH_2Cl: CH_2 between Cl and C=O (s, 4.1); CH_3CO s.
7. 2-bromobutane, $CH_3CHBrCH_2CH_3$: CHBr m (4.1, next to Br); CH_2 m; CH_3 on C1 d (next to CH); CH_3 on C4 t.
8. ethyl 4-oxopentanoate, $CH_3COCH_2CH_2COOCH_2CH_3$: ethyl on the ester O (q 4.14 + t 1.26); CH_3CO s; two triplets for the $-CH_2CH_2-$ bridge between the two C=O groups.

Practice E — matching

- Spectrum 1: **butanoic acid** (COOH at 11.5; CH_2CO t 2.35; CH_2 m; CH_3 t).
- Spectrum 2: **ethyl ethanoate** (OCH_2 q at 4.1; CH_3CO s 2.05; CH_3 t).
- Spectrum 3: **propyl methanoate** (HCOO s at 8.1; OCH_2 t 4.1; CH_2 m; CH_3 t).
- Spectrum 4: **methyl propanoate** (OCH_3 s 3.7; CH_2CO q 2.3; CH_3 t).

Practice F — combined cases

- **Case 1.** (a) C 4.54, H 9.0, O 2.28 → C_2H_4O (44); 88 ÷ 44 = 2 → $C_4H_8O_2$. (b) O–H (acid) 2500–3000; C=O 1700–1750; 71 = $C_3H_7CO^+$ (M − 17, OH lost); 45 = $COOH^+$. (c) NMR: COOH s; $-CH_2CO-$ t; middle CH_2 m; CH_3 t: **butanoic acid**, $CH_3CH_2CH_2COOH$.
- **Case 2.** 6H d + 1H m: an isopropyl group: **2-methylpropanoic acid**, $(CH_3)_2CHCOOH$. The 1.19 ppm signal is the two equivalent CH_3 groups, split by the single H on the adjacent carbon → doublet.
- **Case 3. Pentan-3-one**, $CH_3CH_2COCH_2CH_3$ (two equivalent ethyl groups: 4H q + 6H t). Not pentan-2-one: that would give four signals including a 3H singlet near 2.1 ppm; and its base peak would be 43 (CH_3CO^+), not 57 ($C_2H_5CO^+$).

- **Case 4.** 92/94 (3 : 1): one Cl; 92 − 35 = 57 = C_4H_9: C_4H_9Cl. CH_2Cl d (next to CH), CH m, 6H d: **1-chloro-2-methylpropane**, $(CH_3)_2CHCH_2Cl$. 2-Chloro-2-methylpropane would give one signal.

Check yourself

1. **D.**
2. **B.** ^{12}C has an even number of nucleons and no nuclear spin.
3. **A.** Both CH_3 groups are equivalent.
4. **A.** CH_3CO (3H) : $(CH_3)_3C$ (9H) = 1 : 3.
5. **A.** CH_3CO singlet; $–COCH_2–$ and $–CH_2Cl$ are each split by the other CH_2 → triplets.
6. **C.** Two H on the adjacent CH_2.
7. **D.** Nine equivalent H.
8. **C.** Si is **less** electronegative than C, so the TMS protons are strongly shielded.
9. Any three: 12 equivalent H give one strong signal **[1]**; absorbs upfield of (away from) almost all other signals **[1]**; inert / non-toxic **[1]**; volatile, so easily removed **[1]**.
10. Four signals **[1]**; OCH_3 s, 3H, ≈ 3.7 **[1]**; $–CH_2CO–$ t, 2H, ≈ 2.3 **[1]**; CH_2 m (sextet), 2H, ≈ 1.65, and CH_3 t, 3H, ≈ 0.95 **[1]**.
11. Propan-1-ol has four signals, propan-2-ol three **[1]**; propan-2-ol has a 6H signal (doublet) from two equivalent CH_3 groups **[1]**; propan-1-ol has a 2H triplet at 3.3–3.7 (CH_2O) where propan-2-ol has a 1H multiplet **[1]**.
12. The CH_2 has three H on the adjacent CH_3 → 3 + 1 = 4 lines **[1]**; the O–H proton exchanges rapidly, so it neither splits nor is split **[1]**.
13. Cl is electronegative and withdraws electron density from nearby C–H bonds **[1]**; the C1 protons are less shielded (deshielded), so they absorb at higher δ; the effect is negligible at C4 **[1]**.
14. **2-Methylpropanal**, $(CH_3)_2CHCHO$ **[1]**; 9.6: CHO (9.4–10.0), doublet because of the one adjacent H **[1]**; 2.45: CH next to C=O, split by 7 H → multiplet **[1]**; 1.1: two equivalent CH_3, doublet (one adjacent H) **[1]**.
15. 1,1-Dichloroethane: two signals, 3 : 1 **[1]**; a doublet (CH_3) and a quartet ($CHCl_2$) **[1]**; 1,2-dichloroethane: one signal (all 4H equivalent), a singlet **[1]**.
16. Propanal shows a 1H signal at 9.4–10.0 (CHO); propanoic acid at 9.0–13.0 (COOH, typically 11–12) **[1]**; the propanal CHO signal is a triplet, the acid COOH signal a singlet **[1]**.
17. (a) C 5.40, H 13.5, O 1.35 → 4 : 10 : 1, $C_4H_{10}O$ (74) = M^+ **[1]**. (b) IR: alcohol O–H, no C=O **[1]**; NMR: CH–O at 3.7 (1H), OH (1H, s), CH_2 (2H, m), CH_3 doublet next to CH, CH_3 triplet next to CH_2 **[1]**; so $CH_3CH(OH)CH_2CH_3$, **butan-2-ol** **[1]**; 59 = M − 15 (CH_3 lost) **[1]**. (c) 45 = CH_3CHOH^+ (M − 29, loss of C_2H_5) **[2]**.
18. $C_5H_{10}O_2$ (from 58.8 / 9.8 / 31.4 and M^+ = 102) **[1]**; IR: C=O and C–O, no O–H → ester **[1]**; $CH_3CO–$ singlet at 2.0 and base peak 43 = CH_3CO^+ **[1]**; 6H d + 1H septet → isopropyl group **[1]**; the CH at 5.0 is on the ester O (3.7–4.8 or slightly above) **[1]**; Z is **propan-2-yl ethanoate** (isopropyl ethanoate), $CH_3COOCH(CH_3)_2$ **[1]**.
19. The CH_3 protons have one H on the adjacent carbon → 1 + 1 = 2 lines **[1]**; the CHO proton has three H on the adjacent carbon → 3 + 1 = 4 lines **[1]**.

Where this fits in Structure 3.2

- **Booklet 4** — 3.2.1 to 3.2.4: formulas, functional groups, homologous series and physical trends.
- **Booklet 5** — 3.2.5 and 3.2.6: IUPAC nomenclature and structural isomers.
- **Booklet 6** (HL) — 3.2.7: stereoisomers.
- **Booklet 7** (HL) — 3.2.8 and 3.2.9: mass spectrometry and infrared spectroscopy.
- **Booklet 8** (this booklet, HL) — 3.2.10 to 3.2.12: ^{1}H NMR and combining techniques. This completes Structure 3.2.

These notes are a free resource, shared for any IB student who finds them useful.

If a particular idea here still isn't clicking, specialist one-to-one support in Physics, Chemistry and Maths from a past A Level examiner is available at iBLaurel — call or message **+44 7404 710097**, or use the contact form at **www.iB-Laurel.com**.

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