

Solving structures with mass, IR and NMR spectra

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Worksheet answers

Each answer links the data to the conclusion, with calculated values in bold. If your structure differs, check each piece of evidence against the data again, because one missed neighbour count often changes the answer.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB S3.2

Problem 1 Molecular ion of ethanol

- M^+ equals the **relative molecular mass** of the compound.
- $2 \times 12 + 6 \times 1 + 16 = 24 + 6 + 16 = \mathbf{46}$.
- CH_2OH^+ : $12 + 2 + 16 + 1 = \mathbf{31}$, so it explains the peak, formed by losing CH_3 from the molecular ion.

Problem 2 Matching IR bands

- $3350\text{ cm}^{-1} = \mathbf{O-H}$ (broad, alcohol); $1715\text{ cm}^{-1} = \mathbf{C=O}$; $2240\text{ cm}^{-1} = \mathbf{C\equiv N}$; $1650\text{ cm}^{-1} = \mathbf{C=C}$.
- None of them: the fingerprint region is below 1500 cm^{-1} .

Problem 3 Counting hydrogen environments

- $\text{CH}_3\text{CH}_2\text{CH}_3$: **2**; CH_3OCH_3 : **1**; $\text{CH}_3\text{CH}_2\text{OH}$: **3**; benzene: **1**.
- The two methyl groups are bonded to the same oxygen, so all six hydrogens are in the same environment.

Problem 4 Predicting the splitting

- CH_3 (3H) has one neighbour, so a **doublet of 3H**; CH (1H) has three neighbours, so a **quartet of 1H**.
- A **singlet of 4H**: all four hydrogens are equivalent, and equivalent hydrogens do not split each other.

Problem 5 Wavelength to wavenumber

- $5.88\text{ }\mu\text{m} = 5.88 \times 10^{-4}\text{ cm}$, so $1 \div 5.88 \times 10^{-4} = \mathbf{1700\text{ cm}^{-1}}$. $3.00\text{ }\mu\text{m} = 3.00 \times 10^{-4}\text{ cm}$, so $1 \div 3.00 \times 10^{-4} = \mathbf{3330\text{ cm}^{-1}}$.
- 1700 cm^{-1} is **C=O**; 3330 cm^{-1} is **O-H**.

Problem 6 Counting carbons from M+1

- Ratio = $2.4 \div 55.0 = 4.36\%$; $4.36 \div 1.1 = 3.97$, so **4 carbon atoms**.
- $88 - 4 \times 12 - 2 \times 16 = 88 - 48 - 32 = 8$, so the formula is **C₄H₈O₂**.

Problem 7 Two ketone isomers

- CH₃CH₂CO⁺: $36 + 5 + 16 = 57$; C₂H₅⁺: $24 + 5 = 29$.
- It is **pentan-3-one**, CH₃CH₂COCH₂CH₃, which breaks on either side of C=O to give C₂H₅CO⁺ and C₂H₅⁺.
- Pentan-2-one would give **43 (CH₃CO⁺) and 71 (loss of CH₃)**.

Problem 8 Alcohol or ketone

- Propanone**: strong C=O at 1715 cm⁻¹ and no O-H.
- Prop-2-en-1-ol would show a **broad O-H absorption at 3230-3550 cm⁻¹** and a **C=C absorption near 1650 cm⁻¹**.

Problem 9 13C environments

- Pentane: CH₃, CH₂ (next to CH₃), middle CH₂: **3**.
- Propanone: CH₃ and C=O: **2**.
- 2-methylpropane: three equivalent CH₃ and one CH: **2**.
- Ethyl ethanoate: CH₃CO, C=O, OCH₂ and CH₃: **4**.
- 1,4-dimethylbenzene: CH₃, ring C-CH₃ and ring CH: **3**.

Problem 10 Propanoic acid data

- A **carboxylic acid**: very broad O-H and C=O at 1710 cm⁻¹.
- δ 11.5 singlet 1H = acid O-H; δ 2.38 quartet 2H = CH₂ next to C=O with 3 neighbouring H from CH₃; δ 1.16 triplet 3H = CH₃ with 2 neighbours.
- CH₃CH₂COOH: $36 + 6 + 32 = 74$ checks. **Propanoic acid**.

Problem 11 Reading integration traces

- $24 : 16 = 3 : 2$.
- Total 10 H over 5 parts = 2 H per part: **6 H and 4 H**.
- The triplet (6H, two equivalent CH₃) next to CH₂ and the quartet (4H, two equivalent CH₂ at δ 3.5 next to oxygen) with no O-H absorption give **ethoxyethane**, CH₃CH₂OCH₂CH₃.

Problem 12 Why TMS is the reference

- TMS is **Si(CH₃)₄**.
- All 12 hydrogens are equivalent, so it gives one sharp signal at δ = 0, away from most signals; it is inert and volatile, so it is easily removed.

3. CDCl_3 has deuterium instead of hydrogen, so the solvent gives **no proton signal** that would hide the sample's signals.

Problem 13 Halogen isotope patterns

- ^{35}Cl compound: $\text{C}_3\text{H}_7^{35}\text{Cl} = 36 + 7 + 35 = \mathbf{78}$; ^{37}Cl compound: **80**. Heights $78 : 80 = \mathbf{3 : 1}$.
- $\text{C}_4\text{H}_9^{79}\text{Br} = 48 + 9 + 79 = \mathbf{136}$; $\text{C}_4\text{H}_9^{81}\text{Br} = \mathbf{138}$. Heights **1 : 1**.

Problem 14 An alcohol from its IR

- The broad absorption is the **O-H** bond of an alcohol, broadened by hydrogen bonding.
- Ethoxyethane has no O-H, so it could not give an absorption near 3340 cm^{-1} .
- The 1060 cm^{-1} band lies in the fingerprint region, where many C-O and C-C absorptions overlap; it matches a compound only against a reference spectrum, and cannot name the bond.

Problem 15 Fragments of a small aldehyde

- The molecular ion is at m/z **44** ($24 + 4 + 16 = 44$).
- $15 = \text{CH}_3^+$; $29 = \text{CHO}^+$ ($12 + 1 + 16$); $43 = [\text{M} - \text{H}]^+$, that is CH_3CO^+ ($24 + 3 + 16 = 43$).
- IR at 1730 cm^{-1} shows $\text{C}=\text{O}$, so the compound is **ethanal**, CH_3CHO .

Problem 16 A full ester analysis

- IR 1738 cm^{-1} and no O-H: an **ester** ($\text{C}=\text{O}$ at 174 ppm supports this).
- δ 4.12 quartet 2H = O- CH_2 next to a CH_3 ; δ 1.25 triplet 3H = the CH_3 of that ethyl group; δ 2.31 quartet 2H = CH_2 next to $\text{C}=\text{O}$ and CH_3 ; δ 1.12 triplet 3H = the CH_3 of the propanoyl group.
- Ethyl propanoate**, $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ ($60 + 10 + 32 = 102$). Five different carbons (two CH_3 , two CH_2 , one $\text{C}=\text{O}$) give **5 signals**, as observed; fragments 57 ($\text{C}_2\text{H}_5\text{CO}^+$) and 29 (C_2H_5^+) agree.

Problem 17 A nitrogen compound

- $M = 55$ with C, H, N: $\text{C}_3\text{H}_5\text{N} = 36 + 5 + 14 = 55$, so **$\text{C}_3\text{H}_5\text{N}$** .
- A sharp absorption at 2250 cm^{-1} is the **$\text{C}\equiv\text{N}$** bond.
- Triplet 3H + quartet 2H means an ethyl group, so the structure is $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$, **propanenitrile**; the ^{13}C signal near 120 ppm is the nitrile carbon, and 3 carbons give 3 signals.

Problem 18 A bromoalkane with a single carbon branch

- $5.5 \div 1.1 = \mathbf{5}$ **carbon atoms**.
- Equal M and M+2 (150 and 152) show one bromine. $150 - 79 = 71$; $71 - 60 = 11$, so the formula is **$\text{C}_5\text{H}_{11}\text{Br}$** .

3. **1-bromo-2,2-dimethylpropane**, $(\text{CH}_3)_3\text{CCH}_2\text{Br}$. Nine equivalent H (δ 1.05) sit on three CH_3 groups attached to a quaternary carbon, and the two H of CH_2Br (δ 3.3) have no hydrogens on the adjacent carbons, so **both signals are singlets**. Three ^{13}C signals: CH_3 , central C and CH_2Br .

Problem 19 Telling aldehyde isomers apart

1. Butanal: **4** (CHO , CH_2 , CH_2 , CH_3); butanone: **4** (CH_3CO , $\text{C}=\text{O}$, CH_2 , CH_3); 2-methylpropanal: **3** (two equivalent CH_3 , CH , CHO).
2. **2-methylpropanal**, $(\text{CH}_3)_2\text{CHCHO}$: 6H doublet ($2 \times \text{CH}_3$, one neighbour), 1H multiplet (CH), 1H doublet (CHO).
3. The CHO hydrogen has **one** neighbouring hydrogen (on the CH carbon), so the $n + 1$ rule gives a doublet.

Problem 20 Propanol isomers in forensics

1. CH_2OH^+ : $12 + 2 + 16 + 1 = \mathbf{31}$; CH_3CHOH^+ : $\text{C}_2\text{H}_5\text{O}^+ = 24 + 5 + 16 = \mathbf{45}$.
2. P (base peak 31) is **propan-1-ol**; Q (base peak 45) is **propan-2-ol**.
3. Both contain O-H, C-H and C-O, so absorptions above 1500 cm^{-1} are almost the same. ^{13}C NMR gives **3 signals for propan-1-ol** and **2 signals for propan-2-ol**.