Chemistry Units 3 & 4

Chapter 8 — Structure and properties of organic compounds

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Chapter 8 Structure and properties of organic compounds — 8A Structural diversity in organic compounds

Theory

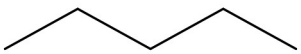
Organic chemistry is the chemistry of the compounds of carbon. A single element, carbon, is the basis of many millions of different compounds — more than all of the compounds of the other elements combined. This extraordinary diversity springs from a few properties of the carbon atom itself, and understanding it is the starting point for the whole of organic chemistry.

The carbon atom and the diversity of organic compounds. Carbon lies in Group 14 and has **four valence electrons**, so each carbon atom forms **four covalent bonds**. These four bonds point towards the corners of a tetrahedron and may be made to hydrogen, to other carbon atoms, or to atoms such as oxygen, nitrogen and the halogens. The carbon–carbon bond is **relatively strong**, and the bonds that carbon forms with these other elements are **relatively stable**, so a carbon framework survives intact through many reactions rather than falling apart.

The most important consequence of tetravalency is **catenation** — the ability of carbon atoms to bond to one another over and over, building **chains** (straight or branched) and **rings** of almost unlimited length. Because every carbon still forms four bonds, a chain can carry hydrogen atoms along its length and can branch wherever a carbon is bonded to three or more other carbons. Two further features multiply the possibilities again: carbon atoms can share more than one pair of electrons, forming **double and triple bonds** (a *degree of unsaturation*), and the atoms of one molecular formula can often be connected in more than one way, giving **structural isomers**. Together, tetravalency, catenation, unsaturation and isomerism account for the sheer number of organic compounds.

Representing organic molecules. Because a structure carries so much information, chemists use several kinds of formula, each showing a different amount of detail. The *same* molecule can be written in any of them, and converting between them is a core skill.

- The **molecular formula** gives the actual number of atoms of each element in one molecule, for example C_4H_{10} for butane.
- The **structural formula** (fully displayed formula) shows **every atom and every bond**, so the way the atoms are joined together is completely specified.
- The **semi-structural (condensed) formula** collapses the structure onto a single line by grouping the atoms attached to each carbon and leaving the C–H and C–C bonds implied, for example $CH_3CH_2CH_2CH_3$; a repeated group may be bracketed, as in $CH_3(CH_2)_2CH_3$, and a branch is written in brackets immediately after the carbon that carries it: $CH_3CH(CH_3)CH_2CH_3$.
- The **skeletal formula** (line-angle formula) is the most economical of all. Each line represents a carbon–carbon bond; **every vertex and every free line end is a carbon atom**; the carbon atoms and the hydrogen atoms bonded to them are not drawn. Only atoms *other* than carbon and hydrogen — and the hydrogens attached to those atoms — are shown.



The skeleton drawn above — four lines meeting at five vertices, with no other atoms shown — is pentane, $CH_3CH_2CH_2CH_2CH_3$. Moving between the representations (counting the implied hydrogens on a skeletal or semi-structural formula to reach the molecular formula, or expanding a molecular formula into a valid structure) is practised throughout this chapter.

Saturated and unsaturated compounds. A compound whose carbon atoms are joined only by C–C **single** bonds carries the maximum possible number of hydrogen atoms and is described as **saturated**. A compound that contains one or more carbon–carbon **double** ($C=C$) or **triple** ($C\equiv C$) bonds holds fewer hydrogen atoms and is **unsaturated**. Relative to the saturated chain, each carbon–carbon double bond (or each ring) lowers the hydrogen count by two, and

each triple bond lowers it by four; benzene, C_6H_6, is a ring that is highly unsaturated. In this course the term *unsaturated* refers specifically to carbon–carbon multiple bonds — the double bond in a functional group such as $C=O$ is described by naming that group, not by calling the molecule unsaturated.

Homologous series. The families of organic compounds are organised into **homologous series**. The members of a homologous series:

1. contain the **same functional group**, and so undergo similar chemical reactions;
2. can be described by a single **general formula**;
3. differ from one member to the next by a CH_2 unit; and
4. show a steady **gradation in physical properties** (such as boiling and melting point) as the carbon chain lengthens.

The simplest series is the **alkanes**, saturated hydrocarbons of general formula C_nH_{2n+2}: methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10}, and so on, each differing from the previous member by CH_2. The **alkenes** (one $C=C$) have the general formula C_nH_{2n} and the **alkynes** (one $C\equiv C$) the general formula C_nH_{2n-2}. Series built around a functional group follow the same pattern: the **alcohols** have the general formula $C_nH_{2n+2}O$ (equivalently $C_nH_{2n+1}OH$). Given the general formula, the molecular formula of any member follows by substituting its value of n; conversely, the number of carbon atoms can be deduced from the number of hydrogen atoms. The detailed *reasons* for the property trends, in terms of intermolecular forces, are developed in subtopic 8E.

Structural isomers. Because the atoms of a molecule can often be connected in more than one way, two or more different compounds can share the **same molecular formula**. Such compounds are **structural isomers**: they have the same molecular formula but a different arrangement of atoms, and are therefore genuinely different substances, each with its own name and its own physical and chemical properties. The molecular formula C_4H_{10}, for example, describes two compounds — the straight chain butane and the branched 2-methylpropane — while C_3H_8O describes both propan-1-ol, $CH_3CH_2CH_2OH$, whose hydroxyl group sits on an end carbon, and propan-2-ol, $CH_3CH(OH)CH_3$, whose hydroxyl group sits on the middle carbon. As the number of carbon atoms grows, the number of possible isomers rises steeply, which is one more reason for the diversity of organic compounds. The isomers of a given molecular formula are found systematically: draw the longest carbon chain first, then progressively shorten it and move the removed carbons (or the functional group) to new positions, checking each time that no two structures are in fact the same compound.

Worked examples

Worked Example 1 — The semi-structural formula of pentane is $CH_3CH_2CH_2CH_2CH_3$. Write its molecular formula, state whether it is saturated or unsaturated, and describe its skeletal formula (drawn in the Theory above).

Working	Comment
Count the atoms in $CH_3CH_2CH_2CH_2CH_3$: 5 carbon, and $3+2+2+2+3=12$ hydrogen	Add the atoms group by group along the chain.
Molecular formula $=C_5H_{12}$	The actual number of each atom in one molecule.
Only C–C single bonds are present → **saturated**	No $C=C$ or $C\equiv C$; the chain holds the maximum number of hydrogens.
Skeletal: four lines meeting at five vertices, with no other atoms shown	Each vertex and free line end is a carbon; every C–H is implied.

Worked Example 2 — Ethanol (CH_3CH_2OH), propan-1-ol ($CH_3CH_2CH_2OH$) and butan-1-ol ($CH_3CH_2CH_2CH_2OH$) are successive members of the alcohol homologous series. Write the molecular formula of each, deduce the general formula of the series, and state what the members share and how one member differs from the next.

Working	Comment
Ethanol: 2 C, 6 H, 1 O $\rightarrow \mathrm{C_2H_6O}$	Count the atoms in the semi-structural formula.
Propan-1-ol: 3 C, 8 H, 1 O $\rightarrow \mathrm{C_3H_8O}$	One $\mathrm{CH_2}$ unit larger than ethanol.
Butan-1-ol: 4 C, 10 H, 1 O $\rightarrow \mathrm{C_4H_{10}O}$	One $\mathrm{CH_2}$ unit larger again.
For n carbons: $\mathrm{H} = 2n + 2$ and $\mathrm{O} = 1$, so the general formula is $\mathrm{C_nH_{2n+2}O}$	Check: $n = 2$ gives $\mathrm{C_2H_6O}$, which is ethanol.
Shared feature: the hydroxyl ($-\mathrm{OH}$) functional group	The same functional group gives similar chemical properties.
Consecutive members differ by $\mathrm{CH_2}$	The defining step of any homologous series.

Worked Example 3 — Draw and name all of the structural isomers of molecular formula $\mathrm{C_5H_{12}}$, and confirm that each one has this molecular formula.

Work outward from the longest possible carbon chain, then shorten it step by step, moving each removed carbon to a branch.

A five-carbon straight chain gives **pentane**, $\mathrm{CH_3CH_2CH_2CH_2CH_3}$.

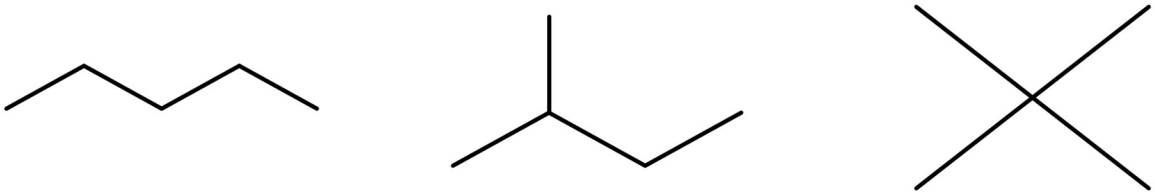
A four-carbon chain leaves one carbon for a branch. Placing a $\mathrm{CH_3}$ branch on the second carbon gives **2-methylbutane**, $\mathrm{CH_3CH(CH_3)CH_2CH_3}$. (A branch on an end carbon would simply lengthen the chain back to pentane, and a branch on the third carbon is the same molecule counted from the other end.)

A three-carbon chain leaves two carbons for branches, and both must go on the central carbon, giving **2,2-dimethylpropane**, $\mathrm{C(CH_3)_4}$.

2,2-dimethylpropane

2-methylbutane

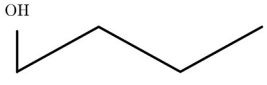
pentane



Each structure contains 5 carbon atoms and 12 hydrogen atoms — for 2,2-dimethylpropane the central carbon carries no hydrogen and each of the four $\mathrm{CH_3}$ groups carries three, giving $4 \times 3 = 12$ — so all three share the molecular formula $\mathrm{C_5H_{12}}$ while differing in the way their atoms are connected.

∴ there are **three** structural isomers of $\mathrm{C_5H_{12}}$: pentane, 2-methylbutane and 2,2-dimethylpropane.

Worked Example 4 — The skeletal formula of a compound is shown below. Deduce its semi-structural and molecular formulae, and state whether the molecule is saturated or unsaturated.



Every vertex and free line end is a carbon atom, so the chain has four carbons; the $-\mathrm{OH}$ drawn at the left-hand end is a hydroxyl group bonded to the first carbon. Add hydrogen atoms until each carbon has four bonds in total:

- C1 is bonded to OH and to C2 (two bonds), so it carries two hydrogens: $\mathrm{CH_2OH}$.
- C2 and C3 are each bonded to two carbons, so each carries two hydrogens: $\mathrm{CH_2}$.
- C4 is an end carbon bonded to one carbon, so it carries three hydrogens: $\mathrm{CH_3}$.

Reading along the chain gives the semi-structural formula $\mathrm{CH_3CH_2CH_2CH_2OH}$ (butan-1-ol). Counting the atoms: 4 C, $3+2+2+2+1=10$ H and 1 O. All of the carbon–carbon bonds are single bonds.

$\therefore$ the compound is $\mathrm{CH_3CH_2CH_2CH_2OH}$, molecular formula $\mathrm{C_4H_{10}O}$, and it is **saturated**.

Practice questions

Question 1 — Propane has the semi-structural formula $\mathrm{CH_3CH_2CH_3}$.

a. Write its molecular formula.
b. Draw its skeletal formula, and state what each line and each vertex or free line end in your drawing represents.
c. State whether propane is saturated or unsaturated, and give a reason.

Question 2 — Ethene ($\mathrm{CH_2=CH_2}$), propene ($\mathrm{CH_3CH=CH_2}$) and but-1-ene ($\mathrm{CH_3CH_2CH=CH_2}$) are the first three members of the alkene homologous series.

a. Write the molecular formula of each compound.
b. Deduce the general formula of the alkenes.
c. State the structural feature that the members share, and how each member differs from the next.

Question 3 — Two compounds share the molecular formula $\mathrm{C_4H_{10}}$.

a. Write the semi-structural formula of each of the two structural isomers.
b. Confirm that both isomers have the molecular formula $\mathrm{C_4H_{10}}$.
c. Explain why the two isomers are classified as different compounds.

Question 4 — Propan-1-ol has the semi-structural formula $\mathrm{CH_3CH_2CH_2OH}$.

a. Write its molecular formula.
b. State the general formula of the alcohol homologous series, to which propan-1-ol belongs.
c. Name the functional group present, and state whether the molecule is saturated.

Question 5 — The alkanes form a homologous series with the general formula $\mathrm{C_nH_{2n+2}}$.

a. Write the molecular formula of the alkane that contains six carbon atoms.
b. An alkane molecule contains 20 hydrogen atoms. Determine its number of carbon atoms and write its molecular formula.
c. Explain what is meant by the term *homologous series*.

Question 6 — Consider ethane ($\mathrm{C_2H_6}$), ethene ($\mathrm{C_2H_4}$) and ethyne ($\mathrm{C_2H_2}$).

a. Classify each compound as saturated or unsaturated.
b. State the type of carbon–carbon bond present in each compound.
c. Explain how the three molecular formulae show an increasing degree of unsaturation from ethane to ethyne.

Question 7 — Write the molecular formula of butane, $\mathrm{CH_3CH_2CH_2CH_3}$, and state how many carbon–carbon bonds and how many carbon–hydrogen bonds appear in its structural (fully displayed) formula.

Question 8 — Write the molecular formula of the straight-chain alkene that contains five carbon atoms, and state whether it is saturated or unsaturated.

Question 9 — Deduce the molecular formula of the compound with the semi-structural formula $\mathrm{CH_3CH_2CH(CH_3)CH_2CH_3}$.

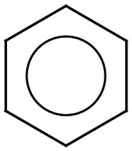
Question 10 — An alkane (general formula $\mathrm{C_nH_{2n+2}}$) contains 12 hydrogen atoms. Determine the number of carbon atoms in the molecule and write its molecular formula.

Question 11 — Four alcohols share the molecular formula $\mathrm{C_4H_{10}O}$. Write the semi-structural formula of each of these four structural isomers.

Question 12 — The skeletal formula of a hydrocarbon is shown below.

a. Deduce its molecular formula.
b. State whether it is saturated or unsaturated, and justify your answer.

Question 13 — Benzene has the molecular formula $\mathrm{C_6H_6}$ and the ring structure shown below. Explain whether benzene is saturated or unsaturated, referring to its hydrogen content.



Question 14 — Explain, with reference to the properties of the carbon atom, why there are far more organic compounds than compounds of any other element.

Question 15 — Heptane is the straight-chain alkane whose molecules contain seven carbon atoms. Deduce its molecular formula, calculate its molar mass, and hence calculate the mass of $0.150\,\mathrm{mol}$ of heptane. (Take $M(\mathrm{C}) = 12.0$ and $M(\mathrm{H}) = 1.0\,\mathrm{g\ mol^{-1}}$.)

Question 16 — Explain the difference between a structural (fully displayed) formula and a semi-structural (condensed) formula. Illustrate your answer using propane.

Question 17 — But-1-ene and but-2-ene both have the molecular formula $\mathrm{C_4H_8}$. Explain how the two molecules differ from each other, and identify one further compound that is a structural isomer of the same molecular formula.

Question 18 — The aldehydes form a homologous series with the general formula $\mathrm{C_nH_{2n}O}$.

a. Write the molecular formulae of the first three members.
b. State and briefly explain how the boiling points of the members change as the series is ascended.

Question 19 — Ethanol, $\mathrm{CH_3CH_2OH}$, is a liquid at 25 °C and is used as a renewable fuel. Write its molecular formula, and write a balanced equation, including states, for its complete combustion in oxygen.

Question 20 — Explain why the molecular formula $\mathrm{C_4H_{10}}$ describes two different compounds, whereas $\mathrm{C_3H_8}$ describes only one.

Question 21 — Pentan-1-ol has the semi-structural formula $CH_3CH_2CH_2CH_2CH_2OH$. Draw its skeletal formula, and state how many carbon atoms and how many hydrogen atoms your drawing leaves implied rather than showing explicitly.

Answers

1 a C_3H_8; b a two-line zig-zag with no other atoms shown — each line is a carbon–carbon bond, and each vertex or free line end is a carbon atom (its hydrogens implied); c saturated — only C–C single bonds, so it holds the maximum number of hydrogens. **2** a C_2H_4, C_3H_6, C_4H_8; b C_nH_{2n}; c all contain a carbon–carbon double bond ($C=C$); each member differs from the next by CH_2. **3** a butane $CH_3CH_2CH_2CH_3$ and 2-methylpropane $CH_3CH(CH_3)CH_3$; b both are C_4H_{10}; c same molecular formula but a different arrangement of atoms, so they are different compounds with different properties. **4** a C_3H_8O; b $C_nH_{2n+2}O$; c hydroxyl ($-OH$); saturated. **5** a C_6H_{14}; b 9 carbon atoms, C_9H_{20}; c a family of compounds with the same functional group and general formula, in which successive members differ by CH_2 and the physical properties change gradually. **6** a ethane saturated; ethene and ethyne unsaturated; b single, double and triple carbon–carbon bond respectively; c each loss of two hydrogens ($C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$) corresponds to one more degree of unsaturation. **7** C_4H_{10}; 3 carbon–carbon bonds and 10 carbon–hydrogen bonds. **8** C_5H_{10}; unsaturated. **9** C_6H_{14}. **10** 5 carbon atoms; C_5H_{12}. **11** $CH_3CH_2CH_2CH_2OH$ (butan-1-ol), $CH_3CH_2CH(OH)CH_3$ (butan-2-ol), $CH_3CH(CH_3)CH_2OH$ (2-methylpropan-1-ol) and $(CH_3)_3COH$ (2-methylpropan-2-ol). **12** a C_6H_{12}; b unsaturated — it contains a carbon–carbon double bond. **13** unsaturated — a saturated six-carbon compound would be C_6H_{14}, but benzene has only 6 hydrogens, a deficiency of 8 H (four degrees of unsaturation) consistent with a ring containing carbon–carbon double-bond character. **14** carbon forms four strong covalent bonds and catenates into chains, branches and rings; it also forms multiple (double/triple) bonds and stable bonds to H, O, N and the halogens, and a given molecular formula gives rise to structural isomers — together producing millions of compounds. **15** C_7H_{16}; $M = 100.0\ \text{g mol}^{-1}$; $m = 15.0\ \text{g}$. **16** a structural formula shows every atom and every bond; a semi-structural formula groups the atoms around each carbon and leaves the bonds implied. Propane is $CH_3CH_2CH_3$ (semi-structural). **17** they differ in the position of the $C=C$ double bond (C1–C2 in but-1-ene, C2–C3 in but-2-ene); a further C_4H_8 isomer is 2-methylprop-1-ene (or cyclobutane). **18** a CH_2O, C_2H_4O, C_3H_6O; b the boiling point rises as the series is ascended, because longer molecules have more electrons and stronger dispersion forces (developed in 8E). **19** C_2H_6O; $CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$. **20** four carbon atoms can be joined either as an unbranched chain (butane) or as a three-carbon chain carrying a methyl branch (2-methylpropane); with only three carbon atoms the single possible branch position simply re-creates the same unbranched three-carbon chain, so C_3H_8 has one arrangement only. **21** a zig-zag of four lines meeting at five carbon positions, with OH written at one end; all 5 carbon atoms and the 11 hydrogen atoms bonded to carbon are implied — only the $-OH$ group (and its hydrogen) is drawn.

Fully-worked solutions

Question 1 a. Counting the atoms in $CH_3CH_2CH_3$: 3 C and $3+2+3=8$ H, so the molecular formula is C_3H_8. b. The skeletal formula of propane is a zig-zag of **two lines**, drawn with no atom symbols at all. Each line represents a carbon–carbon bond, and each vertex or free line end represents a carbon atom — here the two free line ends and the single vertex between them account for all three carbons. The hydrogen atoms bonded to those carbons (three on each end carbon, two on the middle carbon) are not drawn; they are understood to be present because every carbon must form four bonds. c. Propane is **saturated**: all three carbon–carbon bonds are single bonds, so the molecule holds the maximum possible number of hydrogen atoms (there is no $C=C$ or $C\equiv C$).

Question 2 a. Ethene: 2 C, 4 H $\rightarrow C_2H_4$. Propene: 3 C, 6 H $\rightarrow C_3H_6$. But-1-ene: 4 C, 8 H $\rightarrow C_4H_8$. b. The pattern C : H is $2:4$, $3:6$, $4:8$, i.e. $H = 2n$ for n carbons, so the general formula is C_nH_{2n}. c. Every member contains one carbon–carbon double bond ($C=C$), the functional group of the alkenes; each successive member has one more CH_2 unit than the one before.

Question 3 a. The two isomers are the straight chain butane, $CH_3CH_2CH_2CH_3$, and the branched 2-methylpropane, $CH_3CH(CH_3)CH_3$. b. Butane: $3+2+2+3=10$ H with 4 C $\rightarrow C_4H_{10}$. 2-methylpropane: the central carbon carries 1 H and the three CH_3 groups carry $3\times3=9$ H, giving 10 H with 4 C $\rightarrow C_4H_{10}$. Both are C_4H_{10}. c. Although they have the same molecular formula, their atoms are connected differently (one is an unbranched chain, the other is branched). This different arrangement makes them distinct substances with different physical and chemical properties — they are structural isomers.

Question 4 a. $CH_3CH_2CH_2OH$: 3 C, $3+2+2+1=8$ H and 1 O → C_3H_8O. b. Every alcohol carries one hydroxyl group on a saturated carbon chain, so for n carbon atoms there are $2n+2$ hydrogen atoms and one oxygen atom: the general formula is $C_nH_{2n+2}O$. Check with propan-1-ol: $n=3$ gives $2(3)+2=8$ hydrogens and 1 oxygen, i.e. C_3H_8O, as found in part a. c. The functional group is the **hydroxyl** group, $-OH$. All the carbon–carbon bonds are single bonds, so the molecule is **saturated**.

Question 5 a. For $n=6$: $H=2(6)+2=14$, so the molecular formula is C_6H_{14}. b. Set $2n+2=20$, so $2n=18$ and $n=9$. The molecule has 9 carbon atoms and molecular formula C_9H_{20}. c. A homologous series is a family of organic compounds that contain the same functional group and can be described by one general formula. Successive members differ by a CH_2 unit, so they have similar chemical properties and show a gradual change in physical properties (such as boiling and melting point) as the chain lengthens.

Question 6 a. Ethane (C_2H_6) is **saturated**; ethene (C_2H_4) and ethyne (C_2H_2) are **unsaturated**. b. Ethane has a carbon–carbon **single** bond; ethene has a **double** bond ($C=C$); ethyne has a **triple** bond ($C\equiv C$). c. A fully saturated two-carbon compound is C_2H_6. Removing two hydrogens to form C_2H_4 introduces one carbon–carbon double bond (one degree of unsaturation); removing two more to form C_2H_2 introduces a second, making the bond a triple bond (two degrees of unsaturation). Each pair of hydrogens lost corresponds to one further degree of unsaturation.

Question 7 $CH_3CH_2CH_2CH_3$: 4 C and $3+2+2+3=10$ H → molecular formula C_4H_{10}. The four carbon atoms form an unbranched chain, so they are joined by **3 carbon–carbon bonds**. Every hydrogen atom is bonded to a carbon atom, so the 10 hydrogens give **10 carbon–hydrogen bonds**. (Check: each of the 4 carbons forms 4 bonds, giving $4\times4=16$ bond positions in all; each of the 3 carbon–carbon bonds uses two of them, leaving $16-6=10$ positions for carbon–hydrogen bonds.)

Question 8 An alkene has the general formula C_nH_{2n}. For $n=5$: $H=2(5)=10$, so the molecular formula is C_5H_{10}. It contains a carbon–carbon double bond, so it is **unsaturated**.

Question 9 $CH_3CH_2CH(CH_3)CH_2CH_3$ has a five-carbon main chain plus one CH_3 branch, i.e. 6 carbon atoms. Hydrogens: $3+2+1+3+2+3=14$. The molecular formula is C_6H_{14}.

Question 10 For an alkane, $2n+2=12$, so $2n=10$ and $n=5$. The molecule contains 5 carbon atoms and has molecular formula C_5H_{12}.

Question 11 Work through the two possible carbon skeletons, placing the hydroxyl group in each distinct position on each.

An **unbranched four-carbon chain** allows the $-OH$ on an end carbon or on an inner carbon: - $CH_3CH_2CH_2CH_2OH$ — butan-1-ol (hydroxyl on C1); - $CH_3CH_2CH(OH)CH_3$ — butan-2-ol (hydroxyl on C2).

A **branched skeleton** — a three-carbon chain carrying a methyl branch on its middle carbon — allows the $-OH$ on an end carbon or on the branched carbon itself: - $CH_3CH(CH_3)CH_2OH$ — 2-methylpropan-1-ol; - $(CH_3)_3COH$ — 2-methylpropan-2-ol.

(Placing the hydroxyl on C3 or C4 of the straight chain gives butan-2-ol and butan-1-ol again, counted from the other end.) Each of the four contains 4 C, 10 H and 1 O, yet the atoms are connected differently, so all four are structural isomers of $C_4H_{10}O$.

Question 12 a. Each vertex and free line end is a carbon, so the chain has 6 carbon atoms; the drawing shows one carbon–carbon double bond. Adding hydrogens to complete four bonds at each carbon gives C_6H_{12} (equivalently, an alkene C_nH_{2n} with $n=6$). b. It is **unsaturated**, because it contains a carbon–carbon double bond; a saturated six-carbon molecule would be C_6H_{14}, which has two more hydrogens.

Question 13 Benzene is **unsaturated**. A saturated compound with six carbons would be the alkane C_6H_{14}; benzene has only 6 hydrogen atoms, a deficiency of 8 H. A hydrogen deficiency of 8 corresponds to four degrees of unsaturation, made up of the ring plus carbon–carbon double-bond character within it. Because the carbon atoms are not each bonded to the maximum number of hydrogens, the molecule is unsaturated.

Question 14 There are more organic compounds than compounds of any other element because of several properties of the carbon atom acting together: - carbon has four valence electrons, so each carbon atom forms **four covalent bonds**; - carbon atoms **catenate** — they bond strongly and stably to one another, building chains, branches and rings of almost unlimited size; - carbon forms **stable bonds to many other elements** (H, O, N and the halogens), allowing a wide range of functional groups; - carbon can form **double and triple bonds**, adding unsaturated compounds to the saturated ones; and - a single molecular formula can be arranged in different ways, giving **structural isomers**, and the number of isomers grows rapidly with the number of carbon atoms. Together these features generate the millions of known organic compounds.

Question 15 Heptane is an alkane, so it follows the general formula $\mathrm{C}_n\mathrm{H}_{2n+2}$. For $n=7$: $\mathrm{H}=2(7)+2=16$, giving the molecular formula $\mathrm{C}_7\mathrm{H}_{16}$.

Its molar mass is therefore

$$M=7(12.0)+16(1.0)=84.0+16.0=100.0\ \mathrm{g\ mol^{-1}}$$

and the mass of $0.150\ \mathrm{mol}$ follows from $m=n\times M$:

$$m=0.150\ \mathrm{mol}\times 100.0\ \mathrm{g\ mol^{-1}}=15.0\ \mathrm{g}$$

$\therefore$ heptane is $\mathrm{C}_7\mathrm{H}_{16}$, $M=100.0\ \mathrm{g\ mol^{-1}}$, and $0.150\ \mathrm{mol}$ has a mass of $15.0\ \mathrm{g}$ (3 significant figures, matching the data).

Question 16 A **structural (fully displayed) formula** shows every atom in the molecule and every bond between them, so the complete connectivity is drawn out. A **semi-structural (condensed) formula** shortens this by grouping together the atoms bonded to each carbon and leaving the C–H and C–C bonds implied, so it fits on a single line. For propane the semi-structural formula is $\mathrm{CH_3CH_2CH_3}$; the structural formula would instead draw each of the three carbons joined to its neighbours and show all eight C–H bonds explicitly. Both describe the same molecule, but the structural formula shows the bonding in full while the semi-structural formula is a compact summary.

Question 17 But-1-ene and but-2-ene both have four carbons in a chain and one carbon–carbon double bond, but the **position** of that double bond differs: in but-1-ene it lies between carbons 1 and 2 ($\mathrm{CH_2=CHCH_2CH_3}$), whereas in but-2-ene it lies between carbons 2 and 3 ($\mathrm{CH_3CH=CHCH_3}$). Because their atoms are connected differently they are structural isomers of $\mathrm{C_4H_8}$. A further isomer of the same molecular formula is 2-methylprop-1-ene, $\mathrm{CH_2=C(CH_3)CH_3}$ (the ring compound cyclobutane is also acceptable).

Question 18 a. Substituting $n=1,2,3$ into $\mathrm{C}_n\mathrm{H}_{2n}\mathrm{O}$ gives $\mathrm{CH_2O}$ (methanal), $\mathrm{C_2H_4O}$ (ethanal) and $\mathrm{C_3H_6O}$ (propanal). b. The boiling point **rises** as the series is ascended. Each additional $\mathrm{CH_2}$ unit makes the molecule larger and gives it more electrons, so the dispersion forces between molecules become stronger and more energy is needed to separate them. (The full treatment of these intermolecular-force trends is developed in subtopic 8E.)

Question 19 Counting the atoms in $\mathrm{CH_3CH_2OH}$: 2 C, $3+2+1=6$ H and 1 O, so the molecular formula is $\mathrm{C_2H_6O}$.

Complete combustion converts every carbon atom to carbon dioxide and every hydrogen atom to water. The 2 carbon atoms give $2\,\mathrm{CO_2}$ and the 6 hydrogen atoms give $3\,\mathrm{H_2O}$. Counting oxygen atoms on the right: $2(2)+3=7$. One of these is supplied by the ethanol itself, so the remaining 6 must come from oxygen gas, i.e. $3\,\mathrm{O_2}$:

$$\mathrm{CH_3CH_2OH(l)+3\,O_2(g)\rightarrow 2\,CO_2(g)+3\,H_2O(l)}$$

Checking each element: C, 2 on each side; H, 6 on each side; O, $1+6=7$ on the left and $4+3=7$ on the right. Ethanol is a liquid at 25 °C, oxygen and carbon dioxide are gases, and the water produced is a liquid once the products cool to 25 °C.

Question 20 The number of compounds sharing a molecular formula is the number of genuinely different ways the carbon atoms can be connected.

With **four** carbon atoms there are two skeletons. All four may be joined in an unbranched row, giving butane, $\mathrm{CH_3CH_2CH_2CH_3}$; or three may be joined in a row with the fourth attached as a methyl branch on the middle carbon,

giving 2-methylpropane, $CH_3CH(CH_3)CH_3$. These two skeletons cannot be superimposed by rotating or re-numbering the molecule, so they are different compounds — structural isomers — each with its own physical and chemical properties.

With **three** carbon atoms the only skeleton is the row of three, propane, $CH_3CH_2CH_3$. The alternative — a two-carbon chain carrying the third carbon as a branch — is not a different molecule at all: a two-carbon chain has no inner carbon, so the branch can only go onto an end carbon, which simply lengthens the chain back to propane. Only one arrangement therefore exists, and C_3H_8 describes a single compound.

Question 21 In a skeletal formula the carbon skeleton is drawn as a zig-zag of lines, and only atoms other than carbon and hydrogen — together with the hydrogens attached to those atoms — are written in.

Pentan-1-ol has 5 carbon atoms in an unbranched chain, so the drawing is a zig-zag of **four lines** meeting at five carbon positions (three vertices and two free line ends), with OH written at the end of the chain that carries the hydroxyl group.

The molecular formula is $C_5H_{12}O$. Of the 12 hydrogen atoms, one is bonded to the oxygen and is drawn as part of the OH label; the other 11 are bonded to carbon and are left implied.

$\therefore$ the drawing leaves **all 5 carbon atoms** and **11 hydrogen atoms** implied, showing explicitly only the $-OH$ group.

Chapter 8 Structure and properties of organic compounds — 8B Hydrocarbons

Theory

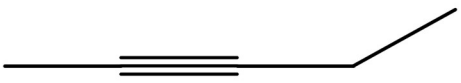
A **hydrocarbon** is an organic compound built from carbon and hydrogen only. Because a carbon atom has four valence electrons it forms four covalent bonds, and because carbon–carbon bonds are strong and stable, carbon atoms link into chains, branches and rings of almost unlimited variety. Hydrocarbons are grouped into families, and within each family the members form a **homologous series** — compounds with the same general formula that differ by successive CH_2 units and so share very similar chemical behaviour.

Alkanes. Alkanes contain only single carbon–carbon bonds. Every carbon is bonded to as many hydrogen atoms as possible, so alkanes are described as **saturated**. Their general formula is C_nH_{2n+2}: methane CH_4, ethane C_2H_6, propane C_3H_8, and so on. The name is built from a stem that states the number of carbons in the longest chain, followed by the suffix **-ane**.

n	Stem	Alkane C_nH_{2n+2}	Alkene C_nH_{2n}
1	meth	methane	—
2	eth	ethane	ethene
3	prop	propane	propene
4	but	butane	but-1-ene
5	pent	pentane	pent-1-ene
6	hex	hexane	hex-1-ene
7	hept	heptane	hept-1-ene
8	oct	octane	oct-1-ene

Alkenes. An **alkene** contains one carbon–carbon double bond, $C=C$. An alkene is **unsaturated** — it holds fewer hydrogen atoms than the alkane with the same number of carbons, because forming a double bond removes two hydrogens. The general formula is C_nH_{2n} and the suffix is **-ene**. A number (a *locant*) is placed in the name to show which carbon the double bond starts from, for example hex-2-ene, $CH_3CH=CHCH_2CH_2CH_3$.

Extension — alkynes. *Alkynes appear nowhere in the VCE Chemistry Units 3 & 4 study design and are never assessed in this course. They are set out here only because they complete the pattern of the hydrocarbon families; the practice items tagged "Extension" use them and may be skipped.* An **alkyne** contains one carbon–carbon triple bond, $C\equiv C$. Forming a triple bond removes four hydrogens from the alkane of the same carbon number, so the general formula is C_nH_{2n-2} and the suffix is **-yne**: ethyne, propyne, but-1-yne, pent-1-yne, hex-1-yne. Locants are placed exactly as they are for alkenes — pent-2-yne is $CH_3C\equiv CCH_2CH_3$. The two carbons of a triple bond and the two atoms bonded to them lie in a straight line, so a skeletal structure draws the $C\equiv C$ unit and its immediate neighbours along one axis rather than on the zig-zag.



Representing structures. The same molecule may be written as a **molecular formula** (C_5H_{12}), a **semi-structural (condensed) formula** that groups the hydrogens with each carbon ($CH_3CH_2CH_2CH_2CH_3$), or a **skeletal structure** in which each line is a bond and each vertex or line-end is a carbon atom, with the hydrogen atoms on the chain left implied. When you write a condensed formula, show the terminal groups correctly — write CH_3CH_2OH-style groups the right way round, not reversed.

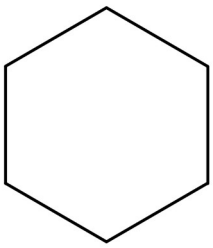
IUPAC nomenclature. Systematic names are assigned by the International Union of Pure and Applied Chemistry (IUPAC) rules. To name a structure:

1. Find the **longest continuous carbon chain** — this is the *parent* chain and sets the stem and suffix. The longest chain is not always drawn in a straight line, so trace every path.
2. **Number the chain** from the end that gives the **lowest locants**. A double or triple bond takes priority for the lowest number; where there is no multiple bond, number to give the substituents (branches) the lowest set of locants.
3. Name each **branch** as an alkyl substituent — a CH_3- branch is *methyl*, a C_2H_5- branch is *ethyl* — and give each a locant.
4. List the substituents **alphabetically** (ethyl before methyl); use the multiplying prefixes *di-, tri-* for repeated identical branches (these prefixes are ignored when alphabetising). Separate numbers with commas and numbers from words with hyphens, for example 2,3-dimethylhexane.

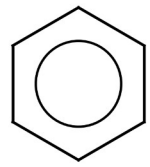
To draw a structure from a name, work backwards: lay out the parent chain, place the multiple bond at its locant, attach each branch at its locant, then add hydrogens so that every carbon has four bonds.

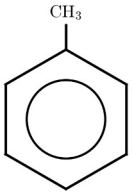
Structural isomers. Structural isomers are different compounds that share the same molecular formula but differ in the way their atoms are connected. Two important types occur among hydrocarbons. **Chain isomers** differ in how the carbon skeleton is branched — for example hexane (a straight chain) and 2,2-dimethylbutane (a branched chain), which share the molecular formula C_6H_{14}. **Position isomers** differ in the position of a feature such as a double bond along the same chain — for example but-1-ene and but-2-ene. Isomers must have the *same* molecular formula: two compounds with different molecular formulae (such as C_3H_8 and C_3H_6) are not isomers of each other.

Cyclic hydrocarbons. Carbon atoms can also join into a ring. A **cycloalkane** is a saturated ring named with the prefix *cyclo-*; cyclohexane is a six-membered ring, C_6H_{12}. Closing a chain into a ring removes two hydrogens, so a cycloalkane has the general formula C_nH_{2n} — the same as an alkene. A ring and a double bond each strip the same two hydrogens from the parent alkane, so a molecular formula that fits C_nH_{2n} does not by itself say which of the two features the molecule carries.



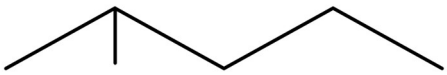
The aromatic ring: benzene. Benzene, C_6H_6, is a flat six-membered ring in which the bonding electrons are spread evenly (delocalised) around the ring rather than fixed as alternating single and double bonds. It is drawn as a hexagon with an inner circle to represent this delocalisation, and it is unusually stable as a result. Benzene is the parent of the **aromatic** hydrocarbons, the compounds built around a benzene ring; replacing one ring hydrogen with a methyl group gives **methylbenzene**, $C_6H_5CH_3$ (molecular formula C_7H_8), drawn below. Note that the four IUPAC rules above apply to non-cyclic hydrocarbons: the names of ring compounds such as cyclohexane, benzene and methylbenzene are learnt rather than built up from a parent chain, and you are never asked to derive them.





Worked examples

Worked Example 1 — Name the alkane whose skeletal structure is shown, and give its molecular formula.



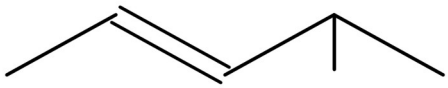
Working	Comment
Longest continuous chain $=5$ carbons $\rightarrow$ parent **pentane**.	Each vertex and line-end is a carbon; trace the longest path.
One branch, a CH_3- group $\rightarrow$ **methyl** substituent.	The single stub off the chain is a methyl branch.
Number from the end nearer the branch: it sits on C2 (numbering from the other end would call it C4).	The lowest locant is chosen, so 2 not 4.
Name: **2-methylpentane**.	Locant–hyphen–substituent–stem–suffix.
Molecular formula C_6H_{14}; check C_nH_{2n+2} with $n=6$: $2(6)+2=14$.	5 chain + 1 branch $=6$ carbons; saturated alkane.

Worked Example 2 — Draw the skeletal structure of 4-methylpent-2-ene, and give its semi-structural and molecular formulae.

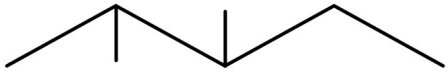
Working	Comment
Parent **pent-2-ene**: a 5-carbon chain with a $C=C$ between C2 and C3.	The stem *pent* fixes five carbons; the locant 2 fixes the double bond.
Add a **methyl** branch on C4.	The prefix 4-methyl places a CH_3- on the fourth carbon.
Semi-structural formula: $CH_3CH=CHCH(CH_3)CH_3$.	Read C1 to C5 along the chain; the branch is bracketed on C4.
Molecular formula C_6H_{12}; check C_nH_{2n} with $n=6$:	5 chain + 1 branch $=6$ carbons; one double bond $\rightarrow$

Working	Comment
$2(6)=12$.	alkene.

The drawn skeletal structure is shown below.



Worked Example 3 — Name the branched alkane whose skeletal structure is shown, and give its molecular formula.

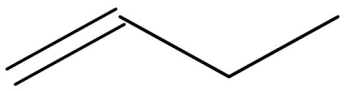


The longest continuous chain contains 5 carbons, so the parent is pentane. There are two CH_3- branches. Numbering from the left-hand end places them on C2 and C3, giving the locant set $\{2,3\}$; numbering from the right-hand end would give $\{3,4\}$, which is higher. The lowest set $\{2,3\}$ is therefore used, and the two identical methyl branches are collected as *dimethyl*.

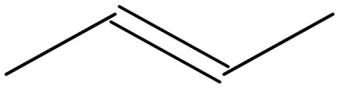
$\therefore$ the compound is **2,3-dimethylpentane**, molecular formula C_7H_{16} (7 carbons, an alkane, so C_nH_{2n+2} gives $2(7)+2=16$ hydrogens).

Worked Example 4 — Draw and name every open-chain structural isomer of the alkene C_4H_8, and state the type of isomerism in each case.

An alkene C_4H_8 has four carbons and one double bond. Keeping all four carbons in one chain, the double bond can sit between C1–C2 or between C2–C3, giving two **position isomers**:

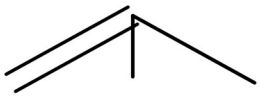


but-1-ene, $CH_2=CHCH_2CH_3$



but-2-ene, $CH_3CH=CHCH_3$

Branching the carbon skeleton instead gives a three-carbon chain carrying a methyl branch, a **chain isomer**:



2-methylprop-1-ene, $CH_2=C(CH_3)CH_3$

$\therefore$ there are three open-chain structural isomers of C_4H_8 — but-1-ene and but-2-ene (position isomers) and 2-methylprop-1-ene (a chain isomer). All three share the molecular formula C_4H_8 but differ in the connectivity of their atoms.

Practice questions

Question 1 — For each molecular formula, state whether the compound is an alkane or an alkene, and give the general formula of that family.

a. C_3H_8
b. C_4H_8
c. C_7H_{14}

Question 2 — Give the IUPAC name of each compound.

a. $CH_3CH_2CH_3$
b. $CH_3CH=CH_2$
c. $CH\equiv CCH_2CH_3$ *(Extension)*

Question 3 — Give the semi-structural formula of each compound named.

a. octane
b. hept-3-ene
c. but-2-yne *(Extension)*

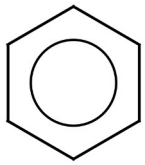
Question 4 — Consider the branched alkane $CH_3CH(CH_3)CH_2CH_2CH_2CH_3$.

a. Give its IUPAC name.
b. Give its molecular formula.
c. Draw and name a chain isomer of this compound.

Question 5 — The molecular formula C_4H_{10} has two structural isomers.

a. Draw and name both isomers.
b. State whether they are chain isomers or position isomers.
c. Explain how two compounds can share the same molecular formula yet be different substances.

Question 6 — This question concerns cyclic and aromatic hydrocarbons. The ring drawn below is an aromatic hydrocarbon.



a. Draw cyclohexane and give its molecular formula.
b. Name the compound shown, and state what the circle drawn inside the ring represents.
c. Explain why the compound shown is classified as unsaturated.

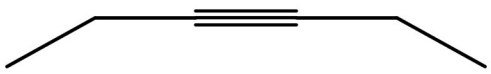
Question 7 — Give the IUPAC name of $CH_3CH_2CH_2CH_2CH_2CH_3$.

Question 8 — Draw the skeletal structure of 3-methylpentane and give its molecular formula.

Question 9 — Give the IUPAC name of $CH_3CH(CH_3)CH(CH_2CH_3)CH_2CH_3$.

Question 10 *(Extension)* — Draw the semi-structural formula of pent-1-yne and give its molecular formula.

Question 11 *(Extension)* — Give the IUPAC name of the compound whose skeletal structure is shown.



Question 12 — Draw and name the three structural isomers of C_5H_{12}.

Question 13 — There are two position isomers of pentene (a five-carbon chain with one double bond and no branches).

a. Draw and name both.
b. Explain why they are described as *position* isomers rather than chain isomers.

Question 14 — Explain, with reference to their molecular formulae, why C_4H_{10} and C_4H_8 are *not* isomers of each other.

Question 15 — Give the IUPAC name and molecular formula of $CH_3CH(CH_3)CH(CH_3)CH_3$.

Question 16 — Give the IUPAC name and molecular formula of $CH_2{=}C(CH_3)CH_2CH_3$.

Question 17 — The skeletal structure of a hydrocarbon is shown.

a. Give its semi-structural formula and its IUPAC name.
b. Give its molecular formula and name the homologous series to which it belongs.

Question 18 — Cyclohexane and hex-1-ene both have the molecular formula C_6H_{12}.

a. Identify the structural feature in each compound that accounts for this shared formula.
b. State whether the two compounds are isomers, and justify your answer.

Question 19 *(Extension)* — A hydrocarbon has the molecular formula C_6H_{10} and contains one carbon–carbon triple bond.

a. Show that this formula fits the general formula of the alkynes.
b. Draw and name one possible structure.

Question 20 — Draw the skeletal structure of 2,4-dimethylpentane and give its molecular formula.

Question 21 — A student names a compound "2-ethylpentane".

a. Draw the structure the student intended, and give its correct IUPAC name.
b. Explain the naming error the student has made.

Answers

1 a alkane, C_nH_{2n+2}; b alkene, C_nH_{2n}; c alkene, C_nH_{2n}. **2** a propane; b prop-1-ene (propene); c but-1-yne. **3** a $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$; b $CH_3CH_2CH=CHCH_2CH_2CH_3$; c $CH_3C\equiv CCH_3$. **4** a 2-methylhexane; b C_7H_{16}; c heptane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ (chain isomer). **5** a butane $CH_3CH_2CH_2CH_3$ and 2-methylpropane $(CH_3)_2CHCH_3$; b chain isomers; c same atoms, different connectivity. **6** a cyclohexane, C_6H_{12}; b benzene — the circle stands for the delocalised ring electrons; c C_6H_6 holds far fewer hydrogens than the saturated C_6H_{14}, so it is unsaturated. **7** hexane. **8** 3-methylpentane, C_6H_{14}. **9** 3-ethyl-2-methylpentane. **10** $CH\equiv CCH_2CH_2CH_3$, C_5H_8. **11** hex-3-yne. **12** pentane, 2-methylbutane, 2,2-dimethylpropane (all C_5H_{12}). **13** a pent-1-ene and pent-2-ene; b the chain is unchanged — only the position of the double bond differs. **14** They have different molecular formulae (different numbers of H), so by definition they cannot be isomers. **15** 2,3-dimethylbutane, C_6H_{14}. **16** 2-methylbut-1-ene, C_5H_{10}. **17** a $CH_2=CHCH(CH_3)CH_2CH_2CH_3$, 3-methylhex-1-ene; b C_7H_{14}, the alkenes (C_nH_{2n}). **18** a cyclohexane has a ring, hex-1-ene has a $C=C$ double bond — each removes two H from C_6H_{14}; b yes, they are isomers (same molecular formula C_6H_{12}, different connectivity). **19** a with $n=6$, $2n-2=10$, so C_6H_{10} fits C_nH_{2n-2}; b e.g. hex-2-yne, $CH_3C\equiv CCH_2CH_2CH_3$. **20** 2,4-dimethylpentane, C_7H_{16}. **21** a the intended structure is $CH_3CH(CH_2CH_3)CH_2CH_2CH_3$ — correctly named **3-methylhexane**; b the longest chain (six carbons) was not chosen as the parent.

Fully-worked solutions

Question 1 The family is read from the ratio of H to C. a. C_3H_8: with $n=3$, $2n+2=8$, so it fits C_nH_{2n+2} — an **alkane**. b. C_4H_8: with $n=4$, $2n=8$, so it fits C_nH_{2n} — an **alkene**. c. C_7H_{14}: with $n=7$, a saturated chain would carry $2n+2=16$ hydrogens, but $2n=14$, so it fits C_nH_{2n} — an **alkene**.

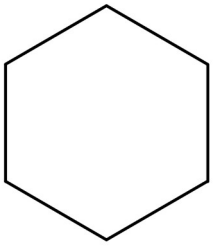
Question 2 a. Three carbons, all single bonds → **propane**. b. Three carbons with a double bond from C1 → **prop-1-ene** (commonly propene; with only three carbons the double bond can only begin at C1). c. Four carbons with a triple bond from C1 → **but-1-yne**.

Question 3 a. octane is an eight-carbon alkane: $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$. b. hept-3-ene is a seven-carbon chain with the double bond between C3 and C4: $CH_3CH_2CH=CHCH_2CH_2CH_3$. c. but-2-yne has the triple bond between C2 and C3: $CH_3C\equiv CCH_3$.

Question 4 a. The longest chain is six carbons (hexane), with a methyl branch on C2, so the name is **2-methylhexane**. b. There are $6+1=7$ carbons and it is a saturated alkane, so the molecular formula is C_7H_{16} ($2(7)+2=16$). c. A chain isomer keeps the formula C_7H_{16} but rearranges the skeleton into an unbranched chain: **heptane**, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$.

Question 5 a. The two isomers are the straight chain **butane**, $CH_3CH_2CH_2CH_3$, and the branched **2-methylpropane**, $(CH_3)_2CHCH_3$ (a three-carbon chain with a methyl branch on C2). b. They differ in the branching of the carbon skeleton, so they are **chain isomers**. c. Both molecules are made from the same atoms — four carbons and ten hydrogens — but those atoms are joined together in a different order (a continuous chain versus a branched chain). Different connectivity produces different molecular shapes and therefore different physical properties, even though the molecular formula is identical.

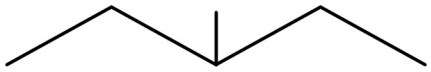
Question 6 a. Cyclohexane is a six-membered saturated carbon ring; each carbon carries two hydrogens, giving C_6H_{12}.



b. The ring drawn is **benzene**, C_6H_6. The circle inside the hexagon stands for the bonding electrons that are spread evenly (delocalised) around the ring rather than being fixed as three alternating double bonds.
c. Benzene is unsaturated because it does not hold the maximum possible number of hydrogen atoms for six carbons: a saturated six-carbon chain would be C_6H_{14}, whereas benzene is C_6H_6. The eight "missing" hydrogens reflect the ring closure (two) and the delocalised, multiple-bond character of the ring bonding (six).

Question 7 Six carbons in an unbranched saturated chain make the compound **hexane**.

Question 8 3-methylpentane is a five-carbon (pentane) chain with a methyl branch on the central carbon (C3); condensed form $CH_3CH_2CH(CH_3)CH_2CH_3$. Its molecular formula is C_6H_{14} ($5+1=6$ carbons; alkane, $2(6)+2=14$).



Question 9 The longest continuous chain is five carbons (pentane). It carries an **ethyl** branch on C3 and a **methyl** branch on C2. Numbering from the left gives the locant set $\{2,3\}$ (from the right it would be $\{3,4\}$), so the lower set is used. Listing substituents alphabetically (ethyl before methyl) gives **3-ethyl-2-methylpentane**.

Question 10 pent-1-yne is a five-carbon chain with a triple bond beginning at C1: $CH\equiv CCH_2CH_2CH_3$. With five carbons and one triple bond it is an alkyne, C_nH_{2n-2}, giving C_5H_8 ($2(5)-2=8$).

Question 11 The chain has six carbons with a triple bond between C3 and C4 — numbering from either end gives the locant 3 — so the compound is **hex-3-yne**. Note that the drawing keeps the four carbons C2 to C5 in a straight line, because the two triple-bonded carbons and their neighbours are collinear.

Question 12 Every isomer has five carbons and the formula C_5H_{12} (a saturated alkane). Rearranging the carbon skeleton gives exactly three:

- **pentane**, $CH_3CH_2CH_2CH_2CH_3$ (unbranched);
- **2-methylbutane**, $CH_3CH(CH_3)CH_2CH_3$ (a four-carbon chain with one methyl branch);
- **2,2-dimethylpropane**, $C(CH_3)_4$ (a three-carbon chain with two methyl branches on the central carbon).

Question 13 a. The two isomers are **pent-1-ene**, $CH_2=CHCH_2CH_2CH_3$, and **pent-2-ene**, $CH_3CH=CHCH_2CH_3$.
b. Both keep the same unbranched five-carbon chain; only the position of the double bond changes (between C1–C2 versus C2–C3). Because the carbon skeleton is unchanged and only the location of a feature differs, they are **position isomers**.

Question 14 Isomers must have the *same* molecular formula. C_4H_{10} contains ten hydrogens (a saturated alkane), whereas C_4H_8 contains only eight (an unsaturated alkene or a cyclic compound). Because the two formulae differ in

the number of hydrogen atoms, the compounds are not simply rearrangements of the same set of atoms, and so they cannot be isomers of each other.

Question 15 The longest chain is four carbons (butane), carrying methyl branches on C2 and C3. The locant set is $\{2,3\}$ either way the chain is numbered, so the name is **2,3-dimethylbutane**. With $4+2=6$ carbons and a saturated skeleton, the molecular formula is C_6H_{14}.

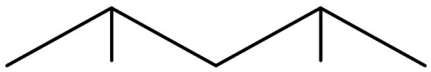
Question 16 The longest chain that includes the double bond is four carbons, with the double bond starting at C1 and a methyl branch on C2, giving **2-methylbut-1-ene**. With $4+1=5$ carbons and one double bond it is an alkene, C_nH_{2n}, so the molecular formula is C_5H_{10}.

Question 17 a. Each vertex and line-end is a carbon. The longest continuous chain that carries the double bond is six carbons, the double bond runs from the first of them, and a single methyl stub sits on the third, so the semi-structural formula is $CH_2=CHCH(CH_3)CH_2CH_2CH_3$. Numbering from the double-bond end gives it the lowest locant (1) and places the branch on C3, so the name is **3-methylhex-1-ene**. b. There are $6+1=7$ carbons and one $C=C$, so C_nH_{2n} with $n=7$ gives C_7H_{14} — a member of the **alkenes**.

Question 18 a. Cyclohexane owes its formula to its **ring**: closing a six-carbon chain into a ring removes two hydrogen atoms. Hex-1-ene owes its formula to its **carbon–carbon double bond**, which likewise removes two hydrogen atoms. Starting from the saturated C_6H_{14}, each feature reduces the count to C_6H_{12}. b. Because both compounds have the identical molecular formula C_6H_{12} but connect their atoms differently (a ring versus an open chain with a double bond), they **are structural isomers** of each other.

Question 19 a. For six carbons, $2n-2=2(6)-2=10$, which is exactly the hydrogen count given, so C_6H_{10} matches the general formula C_nH_{2n-2}. Counting from the saturated alkane C_6H_{14}, the one triple bond removes four hydrogens: $14-4=10$. b. One valid structure is **hex-2-yne**, $CH_3C\equiv CCH_2CH_2CH_3$ — a six-carbon chain with a triple bond between C2 and C3.

Question 20 2,4-dimethylpentane is a five-carbon (pentane) chain with a methyl branch on C2 and a methyl branch on C4; condensed form $CH_3CH(CH_3)CH_2CH(CH_3)CH_3$. With $5+2=7$ carbons and a saturated skeleton the molecular formula is C_7H_{16}.



Question 21 a. The student built pentane (five carbons) and attached an ethyl group to C2, giving $CH_3CH(CH_2CH_3)CH_2CH_2CH_3$. Now trace the longest continuous chain out through the "ethyl" group: its terminal CH_3, its CH_2, then C2, C3, C4 and C5 of the pentane — a chain of **six** carbons (a hexane), leaving the original C1 as a single methyl branch. Numbering that hexane chain from the ethyl end puts the branch on C3 (from the other end it would be C4), so the correct IUPAC name is **3-methylhexane** (C_7H_{16}). b. The error is a failure to identify the longest continuous carbon chain: the student named a five-carbon parent when a six-carbon chain is present. An ethyl branch on C2 can never be correct — an ethyl group attached to the second carbon of any chain always extends that chain by one carbon, so a name beginning "2-ethyl" always signals that the parent chosen was too short.

Chapter 8 Structure and properties of organic compounds — 8C Functional groups: haloalkanes, amines and alcohols

Theory

A **functional group** is an atom or group of atoms that gives an organic molecule its characteristic chemical behaviour. The remainder of the molecule — the hydrocarbon "skeleton" of C–C and C–H bonds — is comparatively unreactive, so it is the functional group that identifies the *family* to which a compound belongs. Because every member of a family carries the same functional group, they form a **homologous series**: successive members differ by a $-CH_2-$ unit, share one general formula, and are named with the same characteristic suffix or prefix. This subtopic deals with three families defined by their functional group — **haloalkanes**, **primary amines** and **alcohols** — and with the systematic (IUPAC) rules for naming a structure and drawing a structure from its name.

Systematic naming — the common steps. Naming these families extends the rules used for hydrocarbons in subtopic 8B. Identify the **longest continuous carbon chain** to fix the parent stem (meth-, eth-, prop-, but-, pent-, …), then **number the chain from the end that gives the principal functional group the lowest locant**. Each substituent is cited with its locant; prefixes are listed in **alphabetical order**, locants are joined to words by hyphens and to one another by commas, and repeated identical groups take the multiplying prefixes di-, tri- and tetra-.

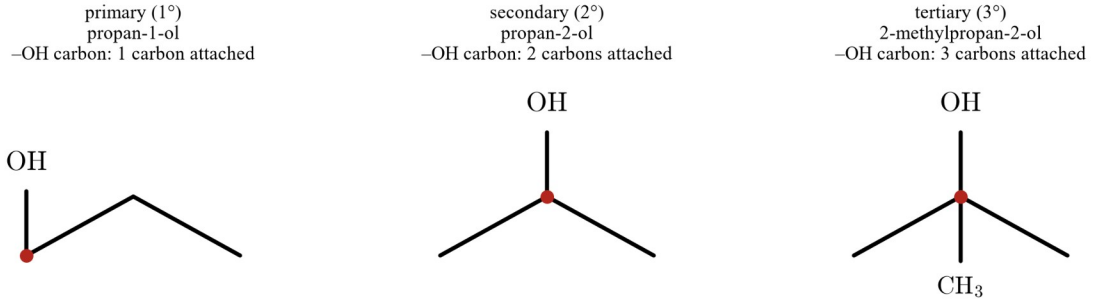
Haloalkanes. A haloalkane is an alkane in which one or more hydrogen atoms have been replaced by a **halogen atom** — X = F, Cl, Br or I — producing a **carbon–halogen (C–X) bond**. The halogen is *always* named as a **prefix**: fluoro-, chloro-, bromo- or iodo-, placed before the parent stem with a locant. For example $CH_3CHClCH_3$ is **2-chloropropane** and $BrCH_2CH_2Br$ is **1,2-dibromoethane**. A saturated haloalkane bearing a single halogen has the general formula $C_nH_{2n+1}X$.

Primary amines. An amine contains a **nitrogen atom bonded to a carbon chain**. In a **primary amine** the nitrogen is joined to exactly **one** carbon atom, giving the group $R–NH_2$ (the amino group, $–NH_2$). Primary amines are named in two ways: as a **suffix** by replacing the final -e of the parent alkane with **-amine** and citing the locant of the nitrogen — for example $CH_3CH_2CH_2NH_2$ is **propan-1-amine** — or, where another group takes priority for the suffix, as the **prefix** amino-. A saturated primary amine has the general formula $C_nH_{2n+3}N$. Note that "primary" here refers to the nitrogen being bonded to one carbon; it does **not** depend on where along the chain that carbon sits, so $CH_3CH(NH_2)CH_3$ (**propan-2-amine**) is also a primary amine.

Alcohols. An alcohol contains the **hydroxyl group,** $–OH$, bonded to a carbon atom (R–OH). Alcohols are named with the **suffix -ol**, again formed by replacing the final -e of the parent alkane and citing the locant of the carbon carrying the $–OH$: methanol, ethanol, **propan-1-ol**, **butan-2-ol**, and so on. A saturated alcohol with one hydroxyl group has the general formula $C_nH_{2n+2}O$.

Classifying alcohols as primary, secondary or tertiary. Alcohols are further classified by the number of **other carbon atoms bonded to the carbon that carries the $–OH$ group**:

- a **primary (1°)** alcohol has the $–OH$ carbon bonded to **one** other carbon (or, in methanol, to none);
- a **secondary (2°)** alcohol has the $–OH$ carbon bonded to **two** other carbons;
- a **tertiary (3°)** alcohol has the $–OH$ carbon bonded to **three** other carbons.

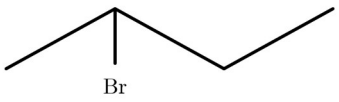


The classification depends only on the immediate surroundings of the –OH carbon, not on the length of the chain: propan-1-ol and butan-1-ol are both primary, while propan-2-ol and pentan-3-ol are both secondary. A tertiary alcohol is only possible once the –OH carbon carries a branch, the simplest being **2-methylpropan-2-ol**.

Molecules with two functional groups. The study design allows names for molecules carrying **up to two** functional groups. When two are present, one is chosen as the **principal group** (named as the suffix) and the other becomes a prefix. Among the groups met here, the **hydroxyl group (-ol) takes priority over the amino group** for the suffix, while **halogens are never a suffix** — they are always prefixes. Thus $HOCH_2CH_2NH_2$ is **2-aminoethan-1-ol** (the –OH fixes the suffix -ol and the numbering; the amine becomes the amino- prefix), and $ClCH_2CH_2CH_2OH$ is **3-chloropropan-1-ol**. To *recognise* a functional group within a larger structure, look for the tell-tale atom or group — a C–X bond (haloalkane), an $-NH_2$ group (primary amine) or an –OH group (alcohol) — regardless of the rest of the molecule.

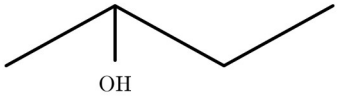
Worked examples

Worked Example 1 — Name the haloalkane shown below and give its molecular formula.



Working	Comment
The longest continuous chain has four carbons → parent **butane**.	Fix the parent stem first (subtopic 8B).
The only substituent is a bromine atom → prefix **bromo-**.	A halogen is always named as a prefix.
Numbering from the left-hand end places Br on carbon 2; from the right it would be carbon 3.	Choose the numbering giving the lowest locant.
Name: **2-bromobutane**.	Locant–hyphen–prefix–stem.
Butane is C_4H_{10}; replacing one H by Br gives C_4H_9Br.	General form $C_nH_{2n+1}X$.

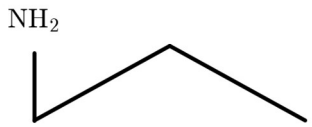
Worked Example 2 — Name the alcohol shown below, classify it as primary, secondary or tertiary, and give its molecular formula.



Working	Comment
Longest chain = four carbons → parent **but-**; the –OH group gives the suffix **-ol**.	Alcohols end in -ol.
Number so that the –OH carbon has the lowest locant: carbon 2. Name **butan-2-ol**.	The principal group takes the lowest locant.

Working	Comment
The carbon carrying –OH (carbon 2) is bonded to two other carbons (carbons 1 and 3).	Count the carbons on the –OH carbon.
Two carbons ⇒ **secondary (2°)** alcohol.	1 → 1°, 2 → 2°, 3 → 3°.
Butane C_4H_{10}, replace one H by –OH (add one O): $C_4H_{10}O$.	General form $C_nH_{2n+2}O$.

Worked Example 3 — The compound below is a member of the amine family. Name it, state whether it is a primary amine and justify your answer, and give its molecular formula.



The longest chain is three carbons, so the parent stem is **propan-**, and the $-NH_2$ group gives the suffix **-amine**. The nitrogen is on the end carbon, carbon 1, so the name is **propan-1-amine**. The nitrogen atom is bonded to only **one** carbon atom, which is the definition of a primary amine, so it is indeed primary. Propane is C_3H_8; replacing one H by $-NH_2$ removes one H and adds NH_2, a net gain of one N and one H, giving C_3H_9N.

∴ the compound is **propan-1-amine**, a primary amine, molecular formula C_3H_9N.

Worked Example 4 — Classify each of butan-1-ol, butan-2-ol and 2-methylpropan-2-ol as a primary, secondary or tertiary alcohol.

The class of an alcohol is decided solely by the number of carbon atoms bonded to the carbon that carries the –OH group (see the figure in the Theory).

- **butan-1-ol**, $CH_3CH_2CH_2CH_2OH$: the –OH carbon (carbon 1) is bonded to one other carbon → **primary (1°)**.
- **butan-2-ol**, $CH_3CH_2CH(OH)CH_3$: the –OH carbon (carbon 2) is bonded to two other carbons → **secondary (2°)**.
- **2-methylpropan-2-ol**, $(CH_3)_3COH$: the –OH carbon is bonded to three other carbons (three methyl groups) → **tertiary (3°)**.

∴ they are primary, secondary and tertiary respectively — all three share the molecular formula $C_4H_{10}O$, so they are structural isomers that differ only in the position and surroundings of the hydroxyl group.

Practice questions

Question 1 — Consider the haloalkane $CH_3CHClCH_3$.

a. Write its IUPAC name.
b. Give its molecular formula.
c. Name a positional isomer of this compound (a haloalkane with the same molecular formula but the halogen on a different carbon).

Question 2 — Consider the alcohol $CH_3CH_2CH_2CH_2OH$.

a. Write its IUPAC name.

b. Classify it as a primary, secondary or tertiary alcohol.
c. Give its molecular formula.

Question 3 — Consider the primary amine ethanamine.

a. Write its semi-structural (condensed) formula.
b. Name the functional group present and state whether the amine is primary.
c. Give its molecular formula.

Question 4 — Draw a structural or skeletal formula for each of the following.

a. 2-chlorobutane
b. propan-2-ol
c. propan-1-amine

Question 5 — Three alcohols are propan-1-ol, propan-2-ol and 2-methylpropan-2-ol.

a. Classify each as primary, secondary or tertiary.
b. State which one is the tertiary alcohol and give its semi-structural formula.
c. Explain how the structure of an alcohol determines whether it is classified as primary, secondary or tertiary.

Question 6 — Consider the molecule $\mathrm{BrCH_2CH_2CH_2CH_2OH}$, which contains two functional groups.

a. Identify the two functional groups present and name each.
b. Write the IUPAC name of the molecule.
c. Give its molecular formula.

Question 7 — Write the IUPAC name of the haloalkane $\mathrm{CH_3CH_2CH_2CHBrCH_2CH_3}$.

Question 8 — Write the IUPAC name and molecular formula of the compound $\mathrm{BrCH_2CH_2CH_2Br}$.

Question 9 — Draw a structural formula for 2-fluoropropane and give its molecular formula.

Question 10 — For the alcohol $\mathrm{(CH_3)_2CHCH_2OH}$, write its IUPAC name, classify it as primary, secondary or tertiary, and give its molecular formula.

Question 11 — For the alcohol $\mathrm{CH_3CH_2CH(OH)CH_2CH_3}$, write its IUPAC name, classify it as primary, secondary or tertiary, and give its molecular formula.

Question 12 — Draw butan-2-ol, then draw and name a positional isomer of it that is a *primary* alcohol.

Question 13 — Propan-2-amine has the semi-structural formula $\mathrm{CH_3CH(NH_2)CH_3}$. Explain why this compound is classified as a *primary* amine even though the amino group is on the middle carbon of the chain.

Question 14 — Draw a structural formula for propan-2-amine and give its molecular formula.

Question 15 — The molecule $\mathrm{HOCH_2CH_2CH_2NH_2}$ contains two functional groups. Identify and name each functional group, write the IUPAC name of the molecule, and give its molecular formula.

Question 16 — Determine the molecular formula of (a) pentan-1-ol and (b) 1-chloropentane.

Question 17 — Monobromopropane has two positional isomers. Draw and name each, and give the molecular formula they share.

Question 18 — A compound X has the semi-structural formula $\mathrm{CH_3CH(OH)CH_2CH_2CH_3}$.

a. Write the IUPAC name of X.
b. Classify X as a primary, secondary or tertiary alcohol.
c. Give the molecular formula of X.
d. Identify the functional group present in X.

e. Draw and name a structural isomer of X that is a tertiary alcohol.

Answers

1 a 2-chloropropane; b C_3H_7Cl; c 1-chloropropane. **2** a butan-1-ol; b primary (1°); c $C_4H_{10}O$. **3** a $CH_3CH_2NH_2$; b the amino group $-NH_2$; primary (N bonded to one carbon); c C_2H_7N. **4** a $CH_3CHClCH_2CH_3$; b $CH_3CH(OH)CH_3$; c $CH_3CH_2CH_2NH_2$. **5** a propan-1-ol 1°, propan-2-ol 2°, 2-methylpropan-2-ol 3°; b 2-methylpropan-2-ol, $(CH_3)_3COH$; c count the carbons bonded to the –OH carbon (1 → primary, 2 → secondary, 3 → tertiary). **6** a hydroxyl group –OH (alcohol) and a C–Br bond (bromo substituent); b 4-bromobutan-1-ol; c C_4H_9BrO. **7** 3-bromohexane. **8** 1,3-dibromopropane; $C_3H_6Br_2$. **9** CH_3CHFCH_3; C_3H_7F. **10** 2-methylpropan-1-ol; primary (1°); $C_4H_{10}O$. **11** pentan-3-ol; secondary (2°); $C_5H_{12}O$. **12** butan-2-ol $CH_3CH(OH)CH_2CH_3$; primary positional isomer = butan-1-ol $CH_3CH_2CH_2CH_2OH$. **13** the classification of an amine depends on the number of carbons bonded to the **nitrogen** (one here), not on the position of the group along the chain — so it is primary. **14** $CH_3CH(NH_2)CH_3$; C_3H_9N. **15** hydroxyl group –OH (alcohol) and amino group $-NH_2$ (primary amine); 3-aminopropan-1-ol (3-aminopropanol); C_3H_9NO. **16** a $C_5H_{12}O$; b $C_5H_{11}Cl$. **17** 1-bromopropane $CH_3CH_2CH_2Br$ and 2-bromopropane $CH_3CHBrCH_3$; C_3H_7Br. **18** a pentan-2-ol; b secondary (2°); c $C_5H_{12}O$; d hydroxyl group –OH; e 2-methylbutan-2-ol $CH_3CH_2C(CH_3)_2OH$ (tertiary).

Fully-worked solutions

Question 1 a. The parent chain is propane (three carbons); the chlorine is on the middle carbon. Numbering from either end places it on carbon 2, so the name is **2-chloropropane**. b. Propane is C_3H_8; replacing one H by Cl gives C_3H_7Cl. c. Moving the chlorine to an end carbon gives **1-chloropropane**, $CH_3CH_2CH_2Cl$, which has the same molecular formula C_3H_7Cl but the halogen on a different carbon.

Question 2 a. The longest chain is four carbons and the –OH is on carbon 1, so the name is **butan-1-ol**. b. The –OH carbon (carbon 1) is bonded to only one other carbon, so the alcohol is **primary (1°)**. c. Butane C_4H_{10} with one H replaced by –OH (adding one O) gives $C_4H_{10}O$.

Question 3 a. Ethanamine has a two-carbon chain with $-NH_2$ on the end carbon: $CH_3CH_2NH_2$. b. The functional group is the **amino group,** $-NH_2$. The nitrogen is bonded to a single carbon atom, so the amine is **primary**. c. Ethane C_2H_6; replacing one H by $-NH_2$ (net gain of one N and one H) gives C_2H_7N.

Question 4 a. **2-chlorobutane** — a four-carbon chain with Cl on carbon 2: $CH_3CHClCH_2CH_3$. b. **propan-2-ol** — a three-carbon chain with –OH on the middle carbon: $CH_3CH(OH)CH_3$. c. **propan-1-amine** — a three-carbon chain with $-NH_2$ on carbon 1: $CH_3CH_2CH_2NH_2$.

Question 5 a. In **propan-1-ol** the –OH carbon is bonded to one other carbon → primary; in **propan-2-ol** the –OH carbon is bonded to two other carbons → secondary; in **2-methylpropan-2-ol** the –OH carbon is bonded to three other carbons → tertiary. b. The tertiary alcohol is **2-methylpropan-2-ol**, $(CH_3)_3COH$: its central carbon carries an –OH and three methyl groups. c. First locate the carbon atom bonded to the hydroxyl group. Then count how many *other carbon atoms* are directly bonded to that carbon. If it is bonded to one carbon the alcohol is primary, if to two carbons it is secondary, and if to three carbons it is tertiary; only the immediate neighbours of the –OH carbon matter, not the total length of the chain.

Question 6 a. The molecule contains a **hydroxyl group (–OH)**, which makes it an alcohol, and a **carbon–bromine (C–Br) bond**, a bromo substituent. b. The hydroxyl group is the principal group and takes the suffix -ol, so it fixes the numbering: the –OH is on carbon 1 and the bromine on carbon 4. The name is **4-bromobutan-1-ol**. c. Butane C_4H_{10}: replace one H by –OH (add one O) and one H by Br (remove one H), giving C_4H_9BrO.

Question 7 The longest continuous chain has six carbons, so the parent is hexane. Numbering from the right-hand end of the formula as written places the bromine on carbon 3; from the left it would be carbon 4, so the lowest locant is 3. The name is **3-bromohexane**.

Question 8 A three-carbon chain (propane) carries a bromine on each end carbon. The locants are 1 and 3 and there are two bromines, so the name is **1,3-dibromopropane**. Propane C_3H_8 with two H replaced by Br gives $C_3H_6Br_2$.

Question 9 2-fluoropropane is a three-carbon chain with a fluorine on the middle carbon: CH_3CHFCH_3. Propane C_3H_8 with one H replaced by F gives C_3H_7F.

Question 10 The longest continuous chain is three carbons (propane), with a methyl branch on one of them. Numbering so that the –OH carbon gets the lowest locant puts the –OH on carbon 1 and the methyl branch on carbon 2, so the name is **2-methylpropan-1-ol**. The –OH carbon (carbon 1) is bonded to only **one** other carbon, so the alcohol is **primary (1°)** — the branch elsewhere in the molecule does not affect the classification, which depends only on the immediate neighbours of the –OH carbon. Its molecular formula is that of a four-carbon alcohol, $C_4H_{10}O$.

Question 11 The longest chain is five carbons (pentane) with the –OH on the central carbon, carbon 3, giving **pentan-3-ol**. That carbon is bonded to two other carbons, so the alcohol is **secondary (2°)**. Pentane C_5H_{12} with one H replaced by –OH gives $C_5H_{12}O$.

Question 12 Butan-2-ol is $CH_3CH(OH)CH_2CH_3$ (a four-carbon chain, –OH on carbon 2). Moving the hydroxyl group to an end carbon gives the primary positional isomer **butan-1-ol**, $CH_3CH_2CH_2CH_2OH$; both have the molecular formula $C_4H_{10}O$.

Question 13 The class of an amine (primary, secondary or tertiary) is decided by the number of carbon atoms bonded directly to the **nitrogen** atom, not by the position of the amino group along the carbon chain. In $CH_3CH(NH_2)CH_3$ the nitrogen is bonded to just one carbon atom (the central carbon), so — despite that carbon being in the middle of the chain — the compound is a **primary** amine. (This contrasts with alcohols, whose 1°/2°/3° classification *is* based on the carbon bearing the group.)

Question 14 Propan-2-amine is a three-carbon chain with the $-NH_2$ on the middle carbon: $CH_3CH(NH_2)CH_3$. Propane C_3H_8 with one H replaced by $-NH_2$ gives C_3H_9N.

Question 15 The molecule contains a **hydroxyl group (**–OH**)**, making it an alcohol, and an **amino group (**$-NH_2$**)**, making it a primary amine. Because the hydroxyl group outranks the amine for the suffix, the parent is propan-1-ol and the amine is cited as the prefix amino- on carbon 3: the name is **3-aminopropan-1-ol** (commonly 3-aminopropanol). Propane C_3H_8: replace one H by –OH (add one O) and one H by $-NH_2$ (net gain of one N and one H), giving C_3H_9NO.

Question 16 a. Pentan-1-ol is a five-carbon alcohol: pentane C_5H_{12} with one H replaced by –OH gives $C_5H_{12}O$. b. 1-chloropentane is a five-carbon haloalkane: pentane C_5H_{12} with one H replaced by Cl gives $C_5H_{11}Cl$.

Question 17 On a three-carbon chain a single bromine can sit either on an end carbon or on the middle carbon:

- **1-bromopropane**, $CH_3CH_2CH_2Br$ (Br on carbon 1);
- **2-bromopropane**, $CH_3CHBrCH_3$ (Br on carbon 2).

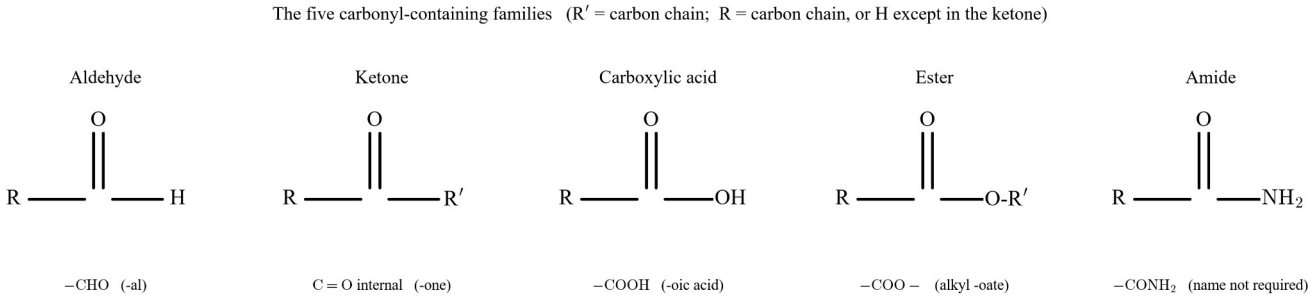
Both are C_3H_7Br and differ only in the position of the halogen, so they are positional isomers.

Question 18 a. The longest chain is five carbons (pentane) and the –OH is on carbon 2 (numbering from the nearer end gives 2 rather than 4), so X is **pentan-2-ol**. b. The –OH carbon (carbon 2) is bonded to two other carbons, so X is a **secondary (2°)** alcohol. c. Pentane C_5H_{12} with one H replaced by –OH gives $C_5H_{12}O$. d. The functional group is the **hydroxyl group,** –OH. e. A structural isomer with the same formula $C_5H_{12}O$ whose –OH carbon is bonded to three other carbons is **2-methylbutan-2-ol**, $CH_3CH_2C(CH_3)_2OH$: its carbon 2 carries the –OH plus a methyl branch and two chain carbons, making it a tertiary alcohol.

Chapter 8 Structure and properties of organic compounds — 8D Functional groups: aldehydes, ketones, carboxylic acids, esters and amides

Theory

Five of the organic families in this course are built around the **carbonyl group** — a carbon atom joined to an oxygen atom by a double bond, $C=O$. What separates the families is the set of atoms attached to that carbonyl carbon: an aldehyde, a ketone, a carboxylic acid, an ester and an amide each place a different partner alongside the $C=O$. Recognising a family in a structure is therefore a matter of finding the carbonyl carbon and reading off what else is bonded to it.



Aldehydes. An aldehyde carries the carbonyl group at the **end** of the carbon chain, so the carbonyl carbon also holds at least one hydrogen atom; the functional group is written –CHO. Aldehydes are named by taking the parent alkane and replacing the final *-e* with *-al*. The carbonyl carbon is numbered C1, and because a terminal group can occupy only that position, no locant is written. Examples are methanal $HCHO$, ethanal CH_3CHO and propanal CH_3CH_2CHO. In a semi-structural formula the group is written …CHO (the terminal group last, never OHC…), with the doubly-bonded oxygen understood.

Ketones. A ketone carries the carbonyl group **inside** the chain, bonded to two other carbon atoms; it can never sit at a chain end. Ketones are named with the suffix *-one* together with a locant giving the position of the carbonyl carbon, the chain being numbered from whichever end gives the lower locant. The smallest ketone is propan-2-one, CH_3COCH_3 (still commonly called propanone). From five carbons onwards positional isomers appear: pentan-2-one and pentan-3-one share the molecular formula $C_5H_{10}O$ and differ only in where the carbonyl lies along the chain. A locant is required for a ketone (unlike an aldehyde) precisely because the internal carbonyl can occupy more than one position.

Carboxylic acids. A carboxylic acid carries the **carboxyl** group –COOH — a carbonyl and a hydroxyl on the **same** terminal carbon. Carboxylic acids are named with the suffix *-oic acid*, the carboxyl carbon being C1. Examples are methanoic acid $HCOOH$, ethanoic acid CH_3COOH and propanoic acid CH_3CH_2COOH.

Esters. An ester contains the linkage –COO– joining two carbon-containing groups: $R-CO-O-R'$. An ester's name has **two words**, read from the two parts on either side of the linkage. The part on the carbonyl side (the **acyl** group, $R-CO-$) comes from a **carboxylic acid** and is named as the *…anoate* — this gives the second word. The part on the single-bonded-oxygen side (the **alkyl** group, $-R'$) comes from an **alcohol** and gives the first word. So the acid supplies the second word and the alcohol supplies the first: butan-1-ol and ethanoic acid give **butyl ethanoate**, $CH_3COOCH_2CH_2CH_2CH_3$. The carbonyl always lies on the acid side of the linking oxygen, which is how the two ends are told apart. (The esterification reaction that actually forms an ester is met in Chapter 9; here the acid-and-alcohol pairing is used only to build the name.) This course treats non-branched esters only. Because an ester and a carboxylic acid can share the same molecular formula — for example methyl methanoate $HCOOCH_3$ and ethanoic acid CH_3COOH are both $C_2H_4O_2$ — the two are structural isomers and must be distinguished from the arrangement around the carbonyl.

Amides. A primary amide carries the carbonyl carbon bonded to an $-NH_2$ group, giving the functional group –$CONH_2$. The carbonyl carbon is C1 of the chain, and the three smallest primary amides are $HCONH_2$, CH_3CONH_2 and $CH_3CH_2CONH_2$. The wider amide linkage $-CO-NH-$ also joins amino-acid units in proteins. In this course an amide is identified from its **structure**: find the carbonyl carbon and look for the $-NH_2$ attached to it.

Extension — the *-amide* suffix. *Systematic amide names are not on the study design's IUPAC-naming list and are not assessed in this course. They are set out here only so that you can read them when you meet them; every amide name used in this subtopic is supplied to you, and no graded item asks you to produce one.* Primary amides are named by replacing the *-oic acid* ending of the parent carboxylic acid with *-amide*, so $HCONH_2$ is methanamide, CH_3CONH_2 is ethanamide and $CH_3CH_2CONH_2$ is propanamide. The naming list runs only to non-cyclic hydrocarbons, haloalkanes, primary amines, alcohols, aldehydes, ketones, carboxylic acids and non-branched esters, and the Data Book's nomenclature table carries no amide row.

Reading a family from a structure. Find the carbonyl carbon and identify its remaining partner: a hydrogen at a chain end means an **aldehyde**; two carbons means a **ketone**; a hydroxyl –OH means a **carboxylic acid**; a single-bonded oxygen leading on to another carbon (–O–R′) means an **ester**; an $-NH_2$ means a primary **amide**. The saturated general formulas are a useful cross-check: aldehydes and ketones are both $C_nH_{2n}O$ (and so are isomers of each other); carboxylic acids and non-branched esters are both $C_nH_{2n}O_2$; primary amides are $C_nH_{2n+1}NO$. A molecular formula can be built from a name by counting the carbons in the parent chain (from the stem meth-, eth-, prop-, but-, pent-, hex-, hept-, oct-) plus any branch, then applying the family formula — or simply by counting every atom in the semi-structural formula.

Reading a skeletal structure. The same reading works on a **skeletal structure**, in which each line is a bond and every vertex and free line end is a carbon atom, with the hydrogens on those carbons left implied. The carbonyl appears as a short double bond drawn from a chain carbon to an O, and the only other atoms written in are the ones that fix the family: the ester's single-bonded O sitting *within* the chain, the acid's –OH, the amide's $-NH_2$. A carbonyl at a free line end with nothing else attached is therefore an **aldehyde**, and one at a vertex between two carbons is a **ketone**. To convert a skeleton to a semi-structural formula, walk along the chain, giving each carbon the hydrogens needed to bring it to four bonds.

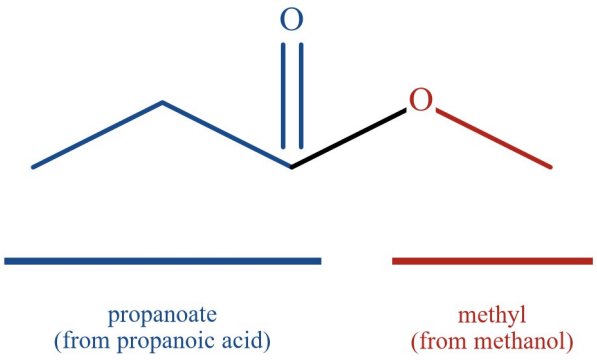
Worked examples

Worked Example 1 — Name each compound and give its molecular formula: (i) $CH_3CH_2CH_2CHO$; (ii) $CH_3CH_2CH_2CH_2COOH$.

Working	Comment
(i) The carbonyl carbon is at the chain end and carries an H: terminal –CHO.	A terminal carbonyl means an **aldehyde**, suffix *-al*.
Longest chain including the carbonyl carbon $= 4$ C → stem but-; carbonyl is C1.	The aldehyde carbon is always C1, so no locant is needed.
Name: **butanal**.	
Atoms: C 4, H 8, O 1 → C_4H_8O.	Fits $C_nH_{2n}O$ with $n = 4$.
(ii) Terminal –COOH (a carbonyl and a hydroxyl on one carbon): **carboxylic acid**, suffix *-oic acid*.	
Chain including the carboxyl carbon $= 5$ C → stem pent-; carboxyl is C1.	
Name: **pentanoic acid**.	
Atoms: C 5, H 10, O 2 → $C_5H_{10}O_2$.	Fits $C_nH_{2n}O_2$ with $n = 5$.

Worked Example 2 — (i) Name the ester formed from propanoic acid and methanol, and draw its semi-structural formula. (ii) Ethyl ethanoate has the formula $CH_3COOC_2H_5$; identify the carboxylic acid and the alcohol from which it is derived.

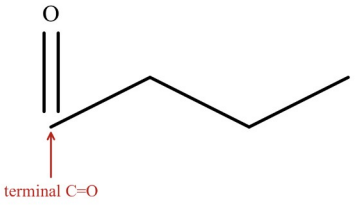
methyl propanoate $CH_3CH_2COOCH_3$



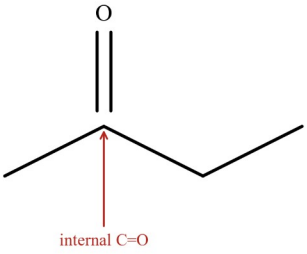
Working	Comment
(i) Acid = propanoic acid → acyl group CH_3CH_2CO- → named as the *...anoate*: propanoate.	The acid supplies the **second** word.
Alcohol = methanol → alkyl group CH_3- → methyl.	The alcohol supplies the **first** word.
Name: **methyl propanoate**.	
Structure: $CH_3CH_2COOCH_3$.	Carbonyl on the acid side; the $-OCH_3$ comes from methanol.
(ii) Split at the –COO– linkage. Acyl side CH_3CO- → ethanoate → **ethanoic acid**.	The *...anoate* names the parent acid.
Alkyl side $-C_2H_5$ → ethyl → **ethanol**.	The first word names the alcohol.
∴ ethyl ethanoate is derived from ethanoic acid and ethanol.	

Worked Example 3 — A compound has molecular formula C_4H_8O. Draw and name one aldehyde and one ketone with this formula, and explain how the position of the carbonyl group differs.

butanal (C_4H_8O)



butan-2-one (C_4H_8O)



The formula C_4H_8O fits $C_nH_{2n}O$ with $n=4$, the general formula shared by aldehydes and ketones, so a four-carbon example of each is possible.

Aldehyde: the carbonyl must sit at a chain end, giving **butanal**, $CH_3CH_2CH_2CHO$ — its carbonyl carbon (C1) is bonded to one hydrogen and one carbon.

Ketone: the carbonyl must sit inside the chain, giving **butan-2-one**, $CH_3COCH_2CH_3$ — its carbonyl carbon (C2) is bonded to two carbons.

Both molecules contain four carbons, eight hydrogens and one oxygen, so both are C_4H_8O; they are structural isomers that differ only in whether the carbonyl group is **terminal** (aldehyde) or **internal** (ketone).

∴ butanal and butan-2-one are the aldehyde and the ketone of formula C_4H_8O.

Worked Example 4 — (i) Identify the functional-group family of $CH_3CH_2CONH_2$ and give its molecular formula. (ii) From CH_3CH_2CHO, CH_3COOCH_3, $CH_3CH_2CONH_2$ and CH_3COCH_3, identify the ester and the amide, stating the feature used.

(i) The carbonyl carbon is bonded to an $-NH_2$ group, so the compound is a primary **amide** (functional group –CONH₂). The chain, including the carbonyl carbon as C1, has three carbons. Counting atoms: C 3, H 7, N 1, O 1 $\rightarrow C_3H_7NO$ (consistent with $C_nH_{2n+1}NO$, $n=3$).

(ii) Read each carbonyl's partner:

- CH_3COOCH_3 — the carbonyl carbon is joined through a single-bonded oxygen to a second carbon group (–COO–), so this is the **ester**, methyl ethanoate.
- $CH_3CH_2CONH_2$ — the carbonyl carbon is bonded to $-NH_2$ (–CONH₂), so this is the primary **amide**.
- (CH_3CH_2CHO is an aldehyde and CH_3COCH_3 a ketone.)

∴ the ester is methyl ethanoate and the amide is $CH_3CH_2CONH_2$.

Practice questions

Question 1 — Consider the aldehyde $CH_3CH_2CH_2CH_2CHO$.

a. Write its IUPAC name.
b. Give its molecular formula.
c. Draw the semi-structural formula of propanal.

Question 2 — Consider the two ketones $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$.

a. Name the first compound.
b. Name the second compound.
c. Explain why a ketone requires a locant in its name whereas an aldehyde does not.

Question 3 — Consider the carboxylic acid $CH_3CH_2CH_2COOH$.

a. Write its IUPAC name.
b. Give its molecular formula.
c. Draw the semi-structural formula of ethanoic acid.

Question 4 — Esters can be named from the acid and alcohol that form them.

a. Name the ester formed from ethanoic acid and propan-1-ol.
b. Draw its semi-structural formula.
c. Name the carboxylic acid and the alcohol from which methyl butanoate is derived.

Question 5 — Consider the amide $CH_3CH_2CH_2CONH_2$.

a. Give its molecular formula.
b. Draw the semi-structural formula of the primary amide that contains two carbon atoms.
c. Show that both of these amides fit the general formula $C_nH_{2n+1}NO$.

Question 6 — For each of the following, identify the functional-group family present.

a. CH_3CHO
b. $CH_3CH_2COOCH_2CH_2CH_3$
c. $CH_3CH_2CH_2CH_2CONH_2$

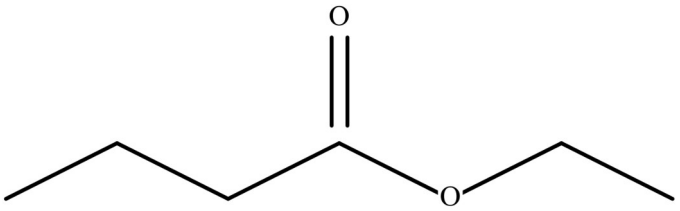
Question 7 — Write the IUPAC name of $CH_3CH_2CH_2CH_2CH_2CHO$.

Question 8 — Draw the semi-structural formula of hexan-3-one, and draw its skeletal structure, stating which atoms your skeletal drawing leaves implied.

Question 9 — Write the IUPAC name of $CH_3CH_2CH_2CH_2CH_2CH_2COOH$.

Question 10 — Name the ester $CH_3CH_2COOCH_2CH_3$, and state the carboxylic acid and the alcohol from which it is derived.

Question 11 — Write the semi-structural formula, the IUPAC name and the molecular formula of the ester whose skeletal structure is shown below.



Question 12 — Give the molecular formula of (a) hexan-2-one and (b) hexanoic acid.

Question 13 — Two compounds each have the molecular formula C_3H_6O; one is an aldehyde and the other a ketone. Draw and name each, and state how the position of the $C=O$ group differs between them.

Question 14 — Which one of the following is an ester? Justify your choice.

A CH_3CH_2COOH B $CH_3COOCH_2CH_3$ C CH_3COCH_3 D $CH_3CH_2CONH_2$

Question 15 — Which one of the following contains an amide functional group? Justify your choice.

A CH_3CH_2CHO B $CH_3CH_2COOCH_3$ C CH_3CONH_2 D $CH_3COCH_2CH_3$

Question 16 — Draw the semi-structural formula of ethyl methanoate, and show that it is a structural isomer of propanoic acid.

Question 17 — Name the ester $HCOOCH_2CH_2CH_2CH_3$, and draw the semi-structural formulas of the carboxylic acid and the alcohol from which it is made.

Question 18 — Write the IUPAC name of $(CH_3)_2CHCHO$.

Question 19 — Write the IUPAC name of $(CH_3)_2CHCH_2COOH$.

Question 20 — Write the IUPAC name of $CH_3COCH_2CH(CH_3)CH_3$.

Question 21 — A compound has the molecular formula $C_4H_8O_2$. Explain how you could decide whether it is a carboxylic acid or an ester, and give one named example of each.

Answers

1 a pentanal; b $C_5H_{10}O$; c CH_3CH_2CHO. **2** a pentan-2-one; b pentan-3-one; c the aldehyde carbonyl is fixed at the terminal C1, so no locant is needed; a ketone carbonyl can occupy different internal positions, so a locant is required. **3** a butanoic acid; b $C_4H_8O_2$; c CH_3COOH. **4** a propyl ethanoate; b $CH_3COOCH_2CH_2CH_3$; c butanoic acid and methanol. **5** a C_4H_9NO; b CH_3CONH_2; c C_4H_9NO has $n=4$ ($2n+1=9$) and C_2H_5NO has $n=2$ ($2n+1=5$). **6** a aldehyde; b ester (propyl propanoate); c primary amide (–$CONH_2$). **7** hexanal. **8** $CH_3CH_2COCH_2CH_2CH_3$; skeletal — a zig-zag of five lines meeting at six carbon positions, with an O drawn as a double bond from the third carbon along; all 6 carbon atoms and the 12 hydrogen atoms bonded to carbon are implied, only the carbonyl oxygen being drawn. **9** heptanoic acid. **10** ethyl propanoate; from propanoic acid and ethanol. **11** $CH_3CH_2CH_2COOCH_2CH_3$; ethyl butanoate; $C_6H_{12}O_2$. **12** a $C_6H_{12}O$; b $C_6H_{12}O_2$. **13** propanal CH_3CH_2CHO (terminal $C=O$, C1) and propan-2-one CH_3COCH_3 (internal $C=O$, C2). **14** B, $CH_3COOCH_2CH_3$ (ethyl ethanoate) — the only compound with a –COO– ester linkage. **15** C, CH_3CONH_2 — the only compound with a –$CONH_2$ amide group. **16** $HCOOCH_2CH_3$; it and propanoic acid CH_3CH_2COOH are both $C_3H_6O_2$, so they are structural isomers. **17** butyl methanoate; from methanoic acid $HCOOH$ and butan-1-ol $CH_3CH_2CH_2CH_2OH$. **18** 2-methylpropanal. **19** 3-methylbutanoic acid. **20** 4-methylpentan-2-one. **21** $C_4H_8O_2$ fits $C_nH_{2n}O_2$ ($n=4$), shared by acids and esters; a carboxylic acid has –COOH (carbonyl carbon bearing an –OH), an ester has –COO– (the carbonyl carbon joined through a single-bonded oxygen to a second carbon); e.g. butanoic acid $CH_3CH_2CH_2COOH$ and methyl propanoate $CH_3CH_2COOCH_3$ (structural isomers).

Fully-worked solutions

Question 1 a. The terminal –CHO group makes this an aldehyde (suffix *-al*). The chain, counted from the carbonyl carbon (C1), has five carbons → **pentanal**. b. Counting atoms in $CH_3CH_2CH_2CH_2CHO$: C 5, H 10, O 1 → $C_5H_{10}O$ (fits $C_nH_{2n}O$). c. Propanal has three carbons with the –CHO at the end: CH_3CH_2CHO.

Question 2 a. The carbonyl is internal; numbering from the nearer end places it at C2, in a five-carbon chain → **pentan-2-one**. b. Here the carbonyl sits at the centre of the five-carbon chain (C3) → **pentan-3-one**. c. In an aldehyde the carbonyl group is always at the terminal carbon, C1, so its position is fixed and needs no locant. In a ketone the carbonyl is internal and can lie at different positions along the chain (for example C2 or C3 in a five-carbon chain); a locant is therefore required to state exactly where it is.

Question 3 a. The terminal –COOH group makes this a carboxylic acid (suffix *-oic acid*). Counting from the carboxyl carbon (C1) gives a four-carbon chain → **butanoic acid**. b. Atoms in $CH_3CH_2CH_2COOH$: C 4, H 8, O 2 → $C_4H_8O_2$ (fits $C_nH_{2n}O_2$). c. Ethanoic acid has two carbons, the second being the carboxyl carbon: CH_3COOH.

Question 4 a. The acid (ethanoic acid) gives the *…anoate* second word, ethanoate; the alcohol (propan-1-ol) gives the alkyl first word, propyl → **propyl ethanoate**. b. The acyl part is CH_3CO- and the alkyl part is $-CH_2CH_2CH_3$: $CH_3COOCH_2CH_2CH_3$. c. Methyl butanoate: the *butanoate* second word comes from **butanoic acid**; the *methyl* first word comes from **methanol**.

Question 5 a. Counting atoms in $CH_3CH_2CH_2CONH_2$: C 4, H 9, N 1, O 1 → C_4H_9NO. b. A primary amide places the $-CONH_2$ group on C1, so the two-carbon member is a CH_3- group joined to that carbon: CH_3CONH_2. (Its atoms are C 2, H 5, N 1, O 1 → C_2H_5NO.) c. For C_4H_9NO, $n=4$ and $2n+1=9$, which matches the nine hydrogens; for C_2H_5NO, $n=2$ and $2n+1=5$, which matches the five hydrogens. Both therefore fit $C_nH_{2n+1}NO$.

Question 6 a. The carbonyl carbon carries a hydrogen at the chain end (–CHO) → **aldehyde** (ethanal). b. The carbonyl carbon is joined through a single-bonded oxygen to a second carbon group (–COO–) → **ester** (propyl propanoate). c. The carbonyl carbon is bonded to $-NH_2$ (–$CONH_2$) → primary **amide**.

Question 7 The terminal –CHO group is an aldehyde. Counting from the carbonyl carbon (C1) gives a six-carbon chain → **hexanal** ($C_6H_{12}O$).

Question 8 Hexan-3-one is a six-carbon ketone with the carbonyl at C3, so two carbons lie on one side of it and three on the other: $CH_3CH_2COCH_2CH_2CH_3$. (Numbering from the other end would place the carbonyl at C4, so C3 is the correct, lower locant.) The skeletal structure is a zig-zag of five lines meeting at six carbon positions, with the carbonyl oxygen drawn as a double bond rising from the third carbon along. Every vertex and free line end is a carbon, so all 6 carbon atoms and the 12 hydrogen atoms bonded to them are left implied; the single O is the only atom written in.

Question 9 The terminal –COOH group is a carboxylic acid. Counting from the carboxyl carbon (C1) gives a seven-carbon chain → **heptanoic acid** ($C_7H_{14}O_2$).

Question 10 Splitting $CH_3CH_2COOCH_2CH_3$ at the –COO– linkage: the acyl side CH_3CH_2CO- gives *propanoate*, and the alkyl side $-CH_2CH_3$ gives *ethyl* → **ethyl propanoate**. It is derived from **propanoic acid** and **ethanol**.

Question 11 Every vertex and free line end in the skeleton is a carbon atom, and the hydrogens on those carbons are implied. Reading from the left: three carbons, then the carbon carrying the double-bonded O, then the single-bonded O written into the chain, then two more carbons — that is $CH_3CH_2CH_2COOCH_2CH_3$. The carbonyl lies to the left of the linking oxygen, so the acyl side is the acid-derived part: four carbons give *butanoate* (from butanoic acid), while the two-carbon alkyl side gives *ethyl* (from ethanol) → **ethyl butanoate**. Counting atoms: C 6, H 12, O 2 → $C_6H_{12}O_2$ (fits $C_nH_{2n}O_2$ with $n=6$).

Question 12 a. Hexan-2-one is a six-carbon ketone, $CH_3COCH_2CH_2CH_2CH_3$: C 6, H 12, O 1 → $C_6H_{12}O$. b. Hexanoic acid is a six-carbon acid, $CH_3CH_2CH_2CH_2CH_2COOH$: C 6, H 12, O 2 → $C_6H_{12}O_2$.

Question 13 C_3H_6O fits $C_nH_{2n}O$ ($n=3$). The aldehyde must have the carbonyl at a chain end: **propanal**, CH_3CH_2CHO, with the $C=O$ at the terminal carbon C1. The ketone must have the carbonyl inside the chain: **propan-2-one**, CH_3COCH_3, with the $C=O$ at the internal carbon C2. They are structural isomers: the carbonyl is **terminal** in the aldehyde and **internal** in the ketone.

Question 14 B is the ester. In $CH_3COOCH_2CH_3$ the carbonyl carbon is joined through a single-bonded oxygen to a second carbon group, the –COO– ester linkage (it is ethyl ethanoate). By contrast, A (CH_3CH_2COOH) has a –COOH carboxyl group with an O–H; C (CH_3COCH_3) has an internal carbonyl with no oxygen bridge, a ketone; and D ($CH_3CH_2CONH_2$) has a –$CONH_2$ amide group.

Question 15 C contains the amide group. In CH_3CONH_2 the carbonyl carbon is bonded to $-NH_2$, the –$CONH_2$ primary-amide group. A (CH_3CH_2CHO) is an aldehyde; B ($CH_3CH_2COOCH_3$) is an ester; and D ($CH_3COCH_2CH_3$) is a ketone — none contains nitrogen.

Question 16 Ethyl methanoate is the ester of methanoic acid and ethanol: the acyl part is $HCO-$ (methanoate) and the alkyl part is $-CH_2CH_3$ (ethyl), giving $HCOOCH_2CH_3$. Counting atoms: C 3, H 6, O 2 → $C_3H_6O_2$. Propanoic acid, CH_3CH_2COOH, also has C 3, H 6, O 2 → $C_3H_6O_2$. The two compounds have the same molecular formula but different arrangements of atoms (an ester linkage versus a carboxyl group), so they are structural isomers.

Question 17 Splitting $HCOOCH_2CH_2CH_2CH_3$ at the –COO– linkage: the acyl side $HCO-$ gives *methanoate*, and the alkyl side $-CH_2CH_2CH_2CH_3$ gives *butyl* → **butyl methanoate**. It is made from the acid HCOOH (methanoic acid) and the alcohol $CH_3CH_2CH_2CH_2OH$ (butan-1-ol).

Question 18 The –CHO group is an aldehyde, so the carbonyl carbon is C1. The longest chain through it is three carbons (propanal), and a methyl branch sits on C2: **2-methylpropanal**. (Molecular formula C_4H_8O, an isomer of butanal.)

Question 19 The –COOH group is a carboxylic acid, so the carboxyl carbon is C1. The longest chain through it is four carbons (butanoic acid), with a methyl branch on C3: **3-methylbutanoic acid**. (Molecular formula $C_5H_{10}O_2$, an isomer of pentanoic acid.)

Question 20 The internal carbonyl is a ketone. Numbering the five-carbon parent chain from the end nearer the carbonyl places it at C2 (pentan-2-one), with a methyl branch on C4: **4-methylpentan-2-one**. (Molecular formula $C_6H_{12}O$, an isomer of hexan-2-one.)

Question 21 $C_4H_8O_2$ fits the general formula $C_nH_{2n}O_2$ with $n = 4$, which is shared by carboxylic acids and non-branched esters, so both families are possible for this formula. To decide between them, examine the arrangement around the carbonyl carbon. A **carboxylic acid** has the –COOH group: the carbonyl carbon carries a hydroxyl (–OH), sits at a chain end, and its O–H makes the molecule acidic. An **ester** has the –COO– linkage: the carbonyl carbon is joined through a single-bonded oxygen to a second carbon group, so there is no O–H and the carbonyl always lies on the acid-derived side of that oxygen. A named acid of this formula is **butanoic acid**, $CH_3CH_2CH_2COOH$; a named ester of this formula is **methyl propanoate**, $CH_3CH_2COOCH_3$. The two are structural isomers of one another.

Chapter 8 Structure and properties of organic compounds — 8E Physical properties of organic compounds

Theory

The physical properties of an organic compound — its **melting point**, **boiling point** and **viscosity** — are decided almost entirely by the **intermolecular forces** acting *between* its molecules, not by the strong covalent bonds *within* them. When a molecular substance melts or boils, the molecules are pulled apart from one another; the covalent bonds inside each molecule stay intact. The stronger the intermolecular forces, the more kinetic energy the molecules need in order to separate, and so the higher the melting and boiling points. To rank or compare compounds you must identify the **type** of intermolecular force present, weigh its **strength**, and take account of **molecular size**.

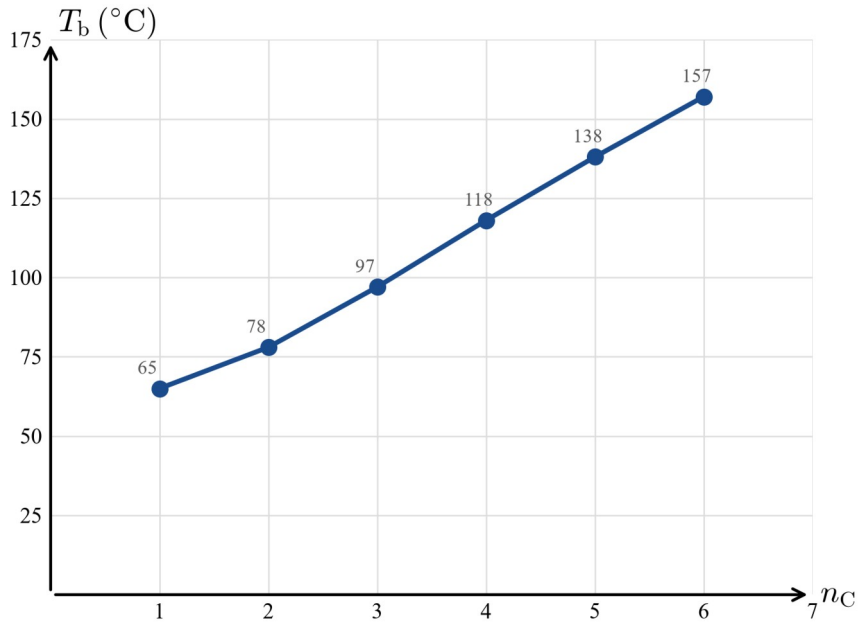
The three intermolecular forces, weakest to strongest. Three types of attraction operate between the molecules of the organic families studied in this course.

- **Dispersion forces** (also called London forces) act between *all* molecules. They arise from the constant, random motion of electrons, which creates instantaneous dipoles that induce matching dipoles in neighbours. Dispersion forces strengthen as the molecule gains electrons and presents a larger surface over which to make contact — that is, they increase with **molar mass**, **chain length** and **surface area**. They are the *only* force between non-polar molecules such as the alkanes.
- **Dipole–dipole forces** act between **polar** molecules — those with a permanent dipole because a polar bond is not cancelled by symmetry. They occur in the haloalkanes (the polar C–halogen bond) and in the carbonyl compounds — the aldehydes, ketones and esters (the polar C=O bond). For molecules of similar size, dipole–dipole attraction is stronger than dispersion alone.
- **Hydrogen bonding** is the strongest of the three. It occurs only when a hydrogen atom is bonded directly to a small, highly electronegative atom — in this course an **O–H** or **N–H** bond. Hydrogen bonding therefore operates in the **alcohols**, **carboxylic acids**, **amines** and **amides**. A hydrogen bond is much stronger than a dipole–dipole force, so molecules that can hydrogen-bond have markedly higher melting and boiling points than molecules of similar size that cannot.

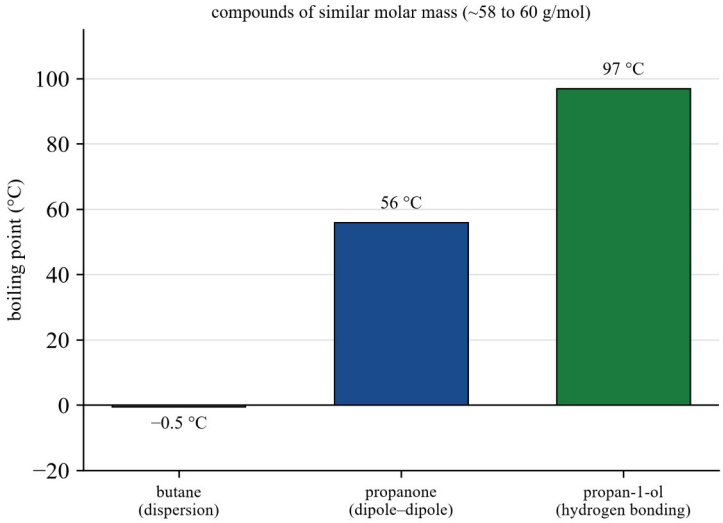
For molecules of similar size the order of boiling point therefore follows the order of intermolecular-force strength: **dispersion < dipole–dipole < hydrogen bonding**.

A special case: the carboxylic acids. A carboxylic acid molecule carries both an O–H group and a C=O group. Two acid molecules can lock together through *two* hydrogen bonds to form a cyclic **dimer**. This especially extensive hydrogen bonding makes the carboxylic acids boil higher than alcohols of the same molar mass.

Trend 1 — within a homologous series. Along a homologous series every member has the *same* functional group, so the *type* of intermolecular force is unchanged from one member to the next. What changes is size: each successive member gains a CH_2 group, so molar mass, chain length and surface area all increase, and the **dispersion forces strengthen**. Boiling point therefore rises steadily as the chain lengthens. For example, the straight-chain primary alcohols boil at 65 °C (methanol), 78 °C (ethanol), 97 °C (propan-1-ol), 118 °C (butan-1-ol), 138 °C (pentan-1-ol) and 157 °C (hexan-1-ol) — a rise of roughly 20 °C for each additional CH_2 group (a little less between the two smallest members).



Trend 2 — between families of similar size. When compounds of *similar molar mass* but *different functional groups* are compared, the dispersion contribution is roughly the same for all of them, so the boiling point is governed by the strongest force type each can form. For three molecules of almost equal molar mass ($M \approx 58$–$60\ \text{g mol}^{-1}$), the boiling point climbs steeply as the dominant force changes from dispersion to hydrogen bonding: butane (dispersion only) boils at −0.5 °C, propanone (dipole–dipole) at 56 °C, and propan-1-ol (hydrogen bonding) at 97 °C. The comparison is only this clean while the molecules are of *similar size*. When one molecule is much the larger, the two factors pull in opposite directions and size can win: octane, with dispersion forces only, boils at 126 °C, well above ethanol's 78 °C, because its far greater surface of contact more than makes up for the weaker *type* of force. Force type settles the order only once the dispersion contributions are comparable.



Melting point. Melting also requires molecules to be pulled apart, so it follows the same logic: within a homologous series the melting point generally rises with chain length as the dispersion forces strengthen, and molecules that can hydrogen-bond melt higher than similar-sized molecules that cannot. Melting point is a little more sensitive than boiling point to how neatly the molecules pack into the solid lattice, so its rise along a series is less smooth than that of boiling point.

Viscosity. Viscosity is a liquid's resistance to flow. A liquid flows less easily when its molecules attract one another more strongly, so viscosity increases with both chain length (stronger dispersion forces, and longer chains that tangle) and the number of hydrogen bonds a molecule can form. Molecules with several O–H groups, such as ethane-1,2-diol and propane-1,2,3-triol (glycerol), build an extensive hydrogen-bonded network and are very viscous.

Branching and molecular shape. Two structural isomers have the same molecular formula and molar mass, and therefore the same number of electrons, so any difference in their melting and boiling points must come from the

shape of the molecule. A straight-chain molecule can lie alongside its neighbours along its whole length, giving a large surface of contact and relatively strong dispersion forces. A branched isomer is compact and closer to spherical, so it touches its neighbours over a smaller area, its dispersion forces are weaker, and it boils lower. Shape matters where hydrogen bonding is present too: bulky groups crowded around an O–H keep neighbouring molecules further apart, so a branched alcohol boils below its straight-chain isomer.

Answering ranking and comparison questions. A complete answer always gives the reasoning **chain**, never just the order. For each compound: (1) identify the strongest intermolecular force it can form, from its functional group; (2) compare the strength of those forces (hydrogen bonding > dipole–dipole > dispersion); and (3) where the compounds are of different size, account for the dispersion contribution using molar mass, chain length or surface area. State the direct comparison — do not describe only one compound.

Worked examples

Worked Example 1 — Arrange propane (C_3H_8, $M = 44\ g\ mol^{-1}$), ethanal (CH_3CHO, $M = 44\ g\ mol^{-1}$) and ethanol (CH_3CH_2OH, $M = 46\ g\ mol^{-1}$) in order of increasing boiling point, and justify your order.

Working	Comment
The three molecules have almost the same molar mass, so their dispersion forces are comparable; the boiling-point order is set by the *type* of intermolecular force.	At similar size, dispersion is roughly equal, so the strongest force type each molecule can form decides the order.
Propane is non-polar, so its only intermolecular force is dispersion.	No polar bond and no O–H or N–H, so neither dipole–dipole nor hydrogen bonding operates — the weakest attractions.
Ethanal has a polar C=O group, giving dipole–dipole forces (plus dispersion), but no O–H, so it cannot hydrogen-bond.	Dipole–dipole is stronger than dispersion alone.
Ethanol has an O–H group and so forms hydrogen bonds (plus weaker dipole–dipole and dispersion).	Hydrogen bonding is the strongest force of the three.
Increasing boiling point: propane (−42 °C) < ethanal (20 °C) < ethanol (78 °C).	The boiling point rises with force strength: dispersion < dipole–dipole < hydrogen bonding.

Worked Example 2 — The straight-chain alkanes methane, ethane, propane and butane boil at −162 °C, −89 °C, −42 °C and −0.5 °C respectively. Explain this trend with reference to structure and bonding.

Working	Comment
Every alkane is non-polar, so the only intermolecular force present is dispersion.	No polar bonds and no O–H or N–H, so dipole–dipole and hydrogen bonding are both absent.
Along the series each successive molecule gains a CH_2 group, raising molar mass, chain length and surface area: methane 16, ethane 30, propane 44, butane $58\ g\ mol^{-1}$.	The functional "family" is unchanged; only molecular size changes.
More electrons and a larger surface of contact produce a larger, more polarisable electron cloud, so the dispersion forces become stronger.	Stronger instantaneous-dipole/induced-dipole attractions.
Stronger dispersion forces require more kinetic energy to overcome, so more thermal energy is needed to separate the molecules into the gas phase.	Hence the boiling point rises steadily along the series.
Boiling point increases: methane < ethane < propane < butane.	Within any homologous series, boiling point rises with chain length.

Worked Example 3 — Propane melts at −188 °C, propan-1-ol at −126 °C and propanoic acid at −21 °C, although each molecule is built on a three-carbon chain. Account for this order.

Melting, like boiling, separates whole molecules from one another — here it breaks down the ordered solid lattice — so the melting point is decided by the strength of the **intermolecular** forces and not by the covalent bonds inside each molecule. All three molecules are built on the same three-carbon skeleton, so their dispersion contributions are broadly comparable and the order is set by the type and extent of the other forces. Propane is non-polar, with no polar bond and no O–H, so **dispersion** is its only intermolecular force and its lattice collapses at the lowest temperature. Propan-1-ol carries an O–H group, so its molecules **hydrogen-bond** to one another; hydrogen bonds are much stronger than dispersion forces, and the melting point rises by more than 60 °C. Propanoic acid carries both an O–H and a C=O, so pairs of molecules lock together through **two** hydrogen bonds as cyclic dimers — the most extensive hydrogen bonding of the three — and it melts highest of all.

∴ the melting point rises propane < propan-1-ol < propanoic acid, following the strengthening of the intermolecular forces from dispersion, to hydrogen bonding, to the double hydrogen bonding of the acid dimer.

Worked Example 4 — Octane (C_8H_{18}, $M = 114\ \text{g mol}^{-1}$) and octan-1-ol ($C_8H_{17}OH$, $M = 130\ \text{g mol}^{-1}$) are both liquids at 25 °C, but their viscosities differ greatly: about $0.51\ \text{mPa s}$ for octane and about $7.3\ \text{mPa s}$ for octan-1-ol. Account for the difference.

Viscosity measures how strongly a liquid resists flow. For one layer of molecules to slide past another, the attractions between them must be pulled apart and remade over and over, so the stronger the intermolecular forces, the more viscous the liquid. Both molecules are built on an eight-carbon chain, so both have substantial **dispersion** forces and these are of similar strength (marginally greater in octan-1-ol, which is slightly heavier). Octane is non-polar, so dispersion is the *only* attraction between its molecules and they slip past one another readily. Octan-1-ol carries an O–H group, so its molecules also **hydrogen-bond** to one another; because hydrogen bonds are much stronger than dispersion forces, each molecule is held to its neighbours far more firmly and the layers shear past one another only with difficulty — some fourteen times less readily than in octane.

∴ octan-1-ol is far more viscous than octane because its hydroxyl group adds strong hydrogen bonding to the dispersion forces the two eight-carbon chains already share.

Practice questions

Question 1 — For each of the following compounds, state the strongest type of intermolecular force acting between its molecules.

a. hexane, C_6H_{14}
b. propanal, CH_3CH_2CHO
c. propan-1-ol, $CH_3CH_2CH_2OH$

Question 2 — Three compounds of similar molar mass are pentane (C_5H_{12}, $M = 72\ \text{g mol}^{-1}$), butanal ($C_3H_7CHO$, $M = 72\ \text{g mol}^{-1}$) and butan-1-ol ($C_4H_9OH$, $M = 74\ \text{g mol}^{-1}$).

a. Arrange the three compounds in order of increasing boiling point.
b. Justify your order by referring to the type and strength of the intermolecular forces present.
c. Identify the compound with the strongest intermolecular forces.

Question 3 — The boiling points of four straight-chain primary alcohols are methanol 65 °C, ethanol 78 °C, propan-1-ol 97 °C and butan-1-ol 118 °C.

a. Describe the trend in boiling point.
b. Explain the trend in terms of intermolecular forces and molecular size.
c. Estimate the boiling point of pentan-1-ol and justify your estimate.

Question 4 — The melting points of three compounds containing five carbon atoms are pentane −130 °C, pentan-1-ol −79 °C and pentanoic acid −34 °C.

a. Explain, in terms of intermolecular forces, why pentan-1-ol melts at a much higher temperature than pentane.
b. Pentanoic acid melts higher again. Identify the structural feature of a carboxylic acid responsible for this and explain its effect.

c. Explain why the melting point of a molecular substance depends on the strength of its intermolecular forces rather than on the strength of the covalent bonds within its molecules.

Question 5 — Butan-1-ol ($CH_3CH_2CH_2CH_2OH$) and 2-methylpropan-2-ol ($(CH_3)_3COH$) are structural isomers with molecular formula $C_4H_{10}O$ and $M = 74\ g\ mol^{-1}$.

a. Identify the strongest intermolecular force acting between the molecules of each compound.
b. Predict which isomer has the higher boiling point.
c. Justify your prediction.

Question 6 — Viscosity is a liquid's resistance to flow; stronger intermolecular forces produce a more viscous liquid.

a. Explain why propane-1,2,3-triol (glycerol) is far more viscous than propan-1-ol.
b. Explain why hexan-1-ol is more viscous than ethanol.
c. State and explain how the viscosity of the straight-chain alkanes changes as the chain length increases.

Question 7 — State the strongest type of intermolecular force acting between the molecules of each of the following compounds of the same carbon number: butane, butanal, butan-1-ol and butanoic acid.

Question 8 — Arrange hexane (C_6H_{14}, $M = 86\ g\ mol^{-1}$), pentanal (C_4H_9CHO, $M = 86\ g\ mol^{-1}$) and pentan-1-ol ($C_5H_{11}OH$, $M = 88\ g\ mol^{-1}$) in order of increasing boiling point, and justify your order in terms of intermolecular forces.

Question 9 — Explain, giving the full reasoning chain, why the boiling point increases along the series ethanal (20 °C), propanal (48 °C) and butanal (75 °C), even though every member of this series contains the same functional group.

Question 10 — Ethanol ($M = 46\ g\ mol^{-1}$) can form hydrogen bonds, whereas octane ($M = 114\ g\ mol^{-1}$) is non-polar and has only dispersion forces. Yet octane boils at 126 °C and ethanol at only 78 °C. Explain how the non-polar compound can have the higher boiling point.

Question 11 — Propan-1-amine (boiling point 48 °C) and propan-1-ol (boiling point 97 °C) have similar molar masses (59 and $60\ g\ mol^{-1}$) and both can form hydrogen bonds, yet the alcohol boils considerably higher. Explain why.

Question 12 — Butan-1-ol and propanoic acid both have molar mass $74\ g\ mol^{-1}$ and both form hydrogen bonds, yet propanoic acid (boiling point 141 °C) boils higher than butan-1-ol (boiling point 118 °C). Explain this difference.

Question 13 — Propanamide ($CH_3CH_2CONH_2$, $M = 73\ g\ mol^{-1}$, boiling point 213 °C) boils well above propanoic acid ($M = 74\ g\ mol^{-1}$, boiling point 141 °C), even though both compounds form hydrogen bonds. Explain this difference.

Question 14 — Pentane and 2,2-dimethylpropane are structural isomers with molecular formula C_5H_{12}. Pentane boils at 36 °C but 2,2-dimethylpropane at only 9.5 °C. Explain why the branched isomer has the lower boiling point.

Question 15 — Explain why both the melting point and the boiling point of the straight-chain alkanes increase as the number of carbon atoms in the molecule increases.

Question 16 — Ethane-1,2-diol ($M = 62\ g\ mol^{-1}$) is much more viscous than propan-1-ol ($M = 60\ g\ mol^{-1}$), despite their similar molar masses. Explain why.

Question 17 — Chloroethane (C_2H_5Cl, $M = 64.5\ g\ mol^{-1}$, boiling point 12 °C) and ethanol (C_2H_5OH, $M = 46\ g\ mol^{-1}$, boiling point 78 °C) each contain a polar bond. Compare the intermolecular forces present in the two liquids, and explain why ethanol has the higher boiling point despite its smaller molar mass.

Question 18 — An ester and a carboxylic acid can have the same molar mass. Ethyl ethanoate (an ester, $M = 88\ g\ mol^{-1}$) boils at 77 °C, whereas butanoic acid ($M = 88\ g\ mol^{-1}$) boils at 164 °C. Explain, in terms of intermolecular forces, why the ester is much more volatile than the acid.

Answers

1 a dispersion forces; b dipole–dipole; c hydrogen bonding. **2** a pentane < butanal < butan-1-ol; b dispersion (pentane, non-polar) < dipole–dipole (butanal, polar C=O) < hydrogen bonding (butan-1-ol, O–H); c butan-1-ol. **3** a boiling point increases with chain length (by roughly 20 °C per added carbon); b all form the same O–H hydrogen bonding, so the rise is due to strengthening dispersion forces as the chain lengthens; c about 138–140 °C (extrapolating one more CH_2 step, ≈ +20 °C; literature value 138 °C). **4** a pentan-1-ol's O–H lets its molecules hydrogen-bond, while non-polar pentane has dispersion forces only, so more energy is needed to break down the alcohol's lattice; b the carboxyl group provides both an O–H and a C=O, so pairs of molecules lock into cyclic dimers held by two hydrogen bonds — more extensive hydrogen bonding again; c melting separates whole molecules, so only the intermolecular forces are overcome — the covalent bonds inside each molecule stay intact. **5** a hydrogen bonding for both (each has an O–H); b butan-1-ol; c same force type and same molar mass, so shape decides: the straight chain of butan-1-ol makes contact over a larger surface area (stronger dispersion) and its O–H is unhindered, whereas the compact, near-spherical isomer has weaker dispersion forces. **6** a glycerol has three O–H groups, forming a far more extensive hydrogen-bonded network; b hexan-1-ol has a longer chain, giving stronger dispersion forces and more chain entanglement; c viscosity increases with chain length (stronger dispersion forces and greater entanglement). **7** butane dispersion; butanal dipole–dipole; butan-1-ol hydrogen bonding; butanoic acid hydrogen bonding (forming dimers). **8** hexane < pentanal < pentan-1-ol; dispersion < dipole–dipole < hydrogen bonding at similar molar mass. **9** all are aldehydes with the same polar C=O, so the force *type* (dipole–dipole) is unchanged; each added CH_2 raises molar mass, chain length and surface area, strengthening the dispersion forces, so the total attraction and the boiling point rise. **10** octane's molecules are far larger, with many more electrons and a much greater surface of contact, so its dispersion forces are strong enough to outweigh ethanol's hydrogen bonding; the type of force settles the order only for molecules of similar size. **11** nitrogen is less electronegative than oxygen, so N–H···N hydrogen bonds are weaker than O–H···O hydrogen bonds; the alcohol's stronger hydrogen bonding gives the higher boiling point. **12** carboxylic acid molecules form cyclic dimers held by two hydrogen bonds per pair, a more extensive hydrogen bonding than the alcohol's single O–H, so more energy is needed to separate them. **13** each amide molecule has two N–H bonds as well as a C=O, so it hydrogen-bonds to several neighbours at once in an extended network, whereas the acid forms closed cyclic dimers of two molecules; the greater number of hydrogen bonds per molecule outweighs the individually weaker N–H···O bond. **14** both are non-polar (dispersion only); branching makes the molecule compact and near-spherical, reducing the surface area of contact and so weakening the dispersion forces, giving the lower boiling point. **15** larger molecules have more electrons and a larger surface area, so dispersion forces strengthen; more energy is then needed both to break the solid lattice (melting) and to separate the molecules into a gas (boiling), so both rise. **16** ethane-1,2-diol has two O–H groups, so each molecule forms more hydrogen bonds, building a stronger, more extensive network that resists flow. **17** chloroethane is polar (dipole–dipole plus dispersion) but has no O–H, so it cannot hydrogen-bond; ethanol has an O–H and does hydrogen-bond; hydrogen bonding is strong enough that ethanol boils higher even though its molar mass is smaller. **18** the ester has a polar C=O (dipole–dipole plus dispersion) but no O–H, so it cannot hydrogen-bond, while the acid forms hydrogen-bonded dimers; the acid's much stronger intermolecular forces give it the far higher boiling point, so the ester is more volatile.

Fully-worked solutions

Question 1 a. Hexane is a non-polar alkane with no polar bond and no O–H or N–H, so the only intermolecular force is **dispersion**. b. Propanal has a polar carbonyl (C=O) group but no O–H, so its strongest force is **dipole–dipole**. c. Propan-1-ol has an O–H group, so its strongest force is **hydrogen bonding**.

Question 2 a. Increasing boiling point: pentane (36 °C) < butanal (75 °C) < butan-1-ol (118 °C). b. The three molecules have almost the same molar mass, so their dispersion forces are comparable and the boiling point is set by the strongest force type each can form. Pentane is non-polar, so it has only dispersion forces (weakest, lowest boiling point). Butanal has a polar C=O and so has dipole–dipole forces, which are stronger than dispersion alone. Butan-1-ol has an O–H group and so hydrogen-bonds, the strongest force, giving the highest boiling point. c. Butan-1-ol has the strongest intermolecular forces (hydrogen bonding).

Question 3 a. The boiling point rises as the chain lengthens, by roughly 20 °C for each additional carbon atom (65 → 78 → 97 → 118 °C; the first step, to ethanol, is a little smaller). b. Every member of this homologous series has the same O–H group, so the *type* of intermolecular force (hydrogen bonding) is the same for all of them. What changes down the series is molecular size: each added CH_2 increases the molar mass, chain length and surface area, which strengthens the **dispersion** forces. Stronger total attractions require more energy to overcome, so the boiling point

rises. c. Extrapolating the trend by one more CH_2 step (about +20 °C above butan-1-ol's 118 °C) predicts a boiling point of about **138–140 °C** for pentan-1-ol. This is justified because pentan-1-ol continues the same series, adding one CH_2 and so a similar increment of dispersion force. (The literature value is 138 °C.)

Question 4 a. Both molecules are built on a five-carbon chain, so their dispersion forces are comparable and the difference lies in the other forces. Pentane is non-polar, with no polar bond and no O–H, so **dispersion** is its only intermolecular force. Pentan-1-ol has an O–H group, so its molecules **hydrogen-bond** to one another as well. Hydrogen bonds are much stronger than dispersion forces, so far more energy is needed to break down the ordered lattice of pentan-1-ol, and it melts about 50 °C higher than pentane. b. The feature is the **carboxyl group**, which carries an O–H *and* a C=O on the same carbon. This allows two acid molecules to lock together through **two** hydrogen bonds as a cyclic dimer, hydrogen bonding that is more extensive than the single O–H of an alcohol. More energy is therefore needed to pull pentanoic acid molecules out of the lattice, so it melts higher than pentan-1-ol. c. Melting pulls whole molecules apart from one another so that they are no longer held in fixed positions in a lattice; the molecules themselves survive intact. Only the attractions *between* molecules — the intermolecular forces — have to be overcome, while the covalent bonds *within* each molecule are untouched. The melting point therefore measures the strength of the intermolecular forces, which is why molecular substances melt at far lower temperatures than covalent-network or ionic lattices, in which bonds must actually be broken.

Question 5 a. Both compounds have an O–H group, so for both the strongest intermolecular force is **hydrogen bonding**. b. Butan-1-ol has the higher boiling point (118 °C, against 82 °C for 2-methylpropan-2-ol). c. Because the two compounds are isomers, they have the same molar mass and the same number of electrons, and because both hydrogen-bond, the *type* of force is the same as well. The difference must therefore come from molecular **shape**. Butan-1-ol is an unbranched chain, so its molecules can lie alongside one another along their whole length, making contact over a large surface area and so producing relatively strong dispersion forces; its O–H group is also at the exposed end of the chain, so neighbouring molecules can approach it closely. In 2-methylpropan-2-ol the three methyl groups are packed around the carbon bearing the O–H, making the molecule compact and almost spherical: it presents a smaller surface of contact (weaker dispersion forces) and the bulky groups keep neighbouring molecules further from the hydroxyl group. Its total intermolecular attraction is therefore weaker and it boils lower.

Question 6 a. Glycerol (propane-1,2,3-triol) has **three** O–H groups per molecule, while propan-1-ol has only one. Each glycerol molecule can therefore form many more hydrogen bonds, creating an extensive three-dimensional hydrogen-bonded network that strongly resists flow, making the liquid far more viscous. b. Hexan-1-ol and ethanol both hydrogen-bond through one O–H, but hexan-1-ol has a much longer hydrocarbon chain. The longer chain has stronger dispersion forces and the chains tangle more, both of which resist flow, so hexan-1-ol is the more viscous. c. Viscosity **increases** with chain length. Longer alkane molecules have more electrons and a larger surface area, so their dispersion forces are stronger, and the longer chains become entangled; both effects make the liquid flow less easily.

Question 7 Butane is a non-polar alkane → **dispersion** forces only. Butanal has a polar C=O but no O–H → **dipole–dipole**. Butan-1-ol has an O–H → **hydrogen bonding**. Butanoic acid has both O–H and C=O and forms cyclic dimers → **hydrogen bonding** (the most extensive of the four). The four therefore boil in this increasing order for the same reason.

Question 8 Increasing boiling point: hexane (69 °C) < pentanal (103 °C) < pentan-1-ol (138 °C). The three compounds have almost the same molar mass, so their dispersion forces are comparable and the boiling point is decided by the strongest force type. Hexane is non-polar (dispersion only), pentanal is polar with a C=O (dipole–dipole, stronger than dispersion), and pentan-1-ol has an O–H (hydrogen bonding, the strongest), so the boiling point rises in that order.

Question 9 Ethanal, propanal and butanal are successive members of the aldehyde homologous series, so every one of them carries the same polar C=O group and none has an O–H or N–H. The *type* of intermolecular force is therefore identical throughout the series — dipole–dipole attraction acting alongside dispersion — and the rise in boiling point cannot be attributed to a change of force type. What does change is molecular size: each successive member gains a CH_2 group, so molar mass, chain length and surface area all increase (44, 58 and $72\,\mathrm{g\,mol^{-1}}$). A larger molecule has more electrons and a larger, more polarisable electron cloud presented over a greater area of contact, so its **dispersion** forces are stronger. The total attraction between molecules therefore grows along the series, more kinetic energy is needed to separate the molecules into the gas phase, and the boiling point rises steadily from 20 °C to 48 °C to 75 °C.

Question 10 Two factors set a boiling point: the *type* of intermolecular force and the *size* of the molecule, which fixes the dispersion contribution. Comparing force types alone is valid only when the molecules are of similar size, and here they are not. Ethanol is a small molecule ($M = 46\ \text{g mol}^{-1}$) with only two carbon atoms; its O–H group lets it hydrogen-bond, which is the strongest of the three forces, but it has few electrons and a small surface of contact, so its dispersion contribution is modest. Octane is a much larger molecule ($M = 114\ \text{g mol}^{-1}$) with an eight-carbon chain: although it is non-polar and dispersion is its only intermolecular force, it has far more electrons and a much greater surface over which neighbouring molecules make contact, so its dispersion forces are very much stronger than ethanol's. In this case the size advantage more than compensates for the weaker type of force, so octane's total intermolecular attraction is the greater and it boils 48 °C higher.

Question 11 Both molecules hydrogen-bond and are of similar molar mass, so the difference lies in the strength of their hydrogen bonds. Hydrogen-bond strength depends on the electronegativity of the atom bonded to hydrogen. Nitrogen is less electronegative than oxygen, so the N–H bond in the amine is less polar than the O–H bond in the alcohol, and the resulting N–H···N hydrogen bonds are weaker than the alcohol's O–H···O hydrogen bonds. The alcohol therefore has stronger intermolecular forces and the higher boiling point.

Question 12 Both molecules have the same molar mass (so comparable dispersion forces) and both hydrogen-bond, so the difference comes from *how much* hydrogen bonding each can do. Butan-1-ol has a single O–H group. A carboxylic acid molecule has an O–H **and** a C=O, and two acid molecules lock together through **two** hydrogen bonds to form a cyclic dimer. This more extensive hydrogen bonding means more energy is needed to separate propanoic acid molecules, so it boils higher than butan-1-ol.

Question 13 The two compounds have effectively the same molar mass, so their dispersion forces are comparable, and both hydrogen-bond; the difference must therefore lie in *how much* hydrogen bonding each can do. Propanoic acid has a single O–H, so two molecules pair up through two hydrogen bonds to form a closed cyclic dimer; once that pair is complete, the dimers are held to one another only by the weaker dipole–dipole and dispersion forces. Propanamide has **two** N–H hydrogens as well as a C=O oxygen to accept hydrogen bonds, so each molecule can hydrogen-bond to several neighbours at once, building an extended three-dimensional network rather than closing off in pairs. An individual N–H···O hydrogen bond is weaker than an O–H···O one, because nitrogen is less electronegative than oxygen, but the amide forms enough more of them that its total intermolecular attraction is much the greater. Far more energy is therefore needed to separate propanamide molecules, so it boils 72 °C higher than propanoic acid.

Question 14 Both isomers are non-polar, so the only intermolecular force is dispersion, and both have the same molar mass and so the same number of electrons. Dispersion-force strength also depends on the surface area over which molecules can make contact. Pentane is an unbranched chain that can lie alongside its neighbours over a large surface area, giving relatively strong dispersion forces. 2,2-Dimethylpropane is highly branched and compact — almost spherical — so it presents a smaller surface area of contact, giving weaker dispersion forces. Weaker forces need less energy to overcome, so the branched isomer has the lower boiling point.

Question 15 Both melting and boiling require the molecules to be pulled apart from one another, so both depend on the intermolecular-force strength. The straight-chain alkanes are non-polar, so their only intermolecular force is dispersion. As the number of carbon atoms increases, molar mass and surface area increase, giving a larger, more polarisable electron cloud and therefore stronger dispersion forces. More energy is then needed both to break down the solid lattice (raising the melting point) and to separate the molecules into a gas (raising the boiling point), so both rise along the series.

Question 16 Both molecules hydrogen-bond and have almost the same molar mass, so the difference is the *number* of O–H groups. Propan-1-ol has one O–H, but ethane-1,2-diol has two. Each diol molecule can therefore form more hydrogen bonds to its neighbours, building a stronger and more extensive hydrogen-bonded network. A liquid whose molecules are more strongly linked resists flow more, so ethane-1,2-diol is much more viscous.

Question 17 Both molecules are polar, so both have dipole–dipole and dispersion forces. The key difference is that chloroethane's polar bond is C–Cl: it has no hydrogen bonded to a small, highly electronegative atom, so it **cannot** form hydrogen bonds, and its strongest force is dipole–dipole. Ethanol has an O–H group and so **can** form hydrogen bonds, which are much stronger than dipole–dipole forces. Although chloroethane has the larger molar mass (and therefore somewhat stronger dispersion forces), ethanol's hydrogen bonding more than makes up for this, so ethanol has the higher boiling point.

Question 18 Both compounds have the same molar mass, so their dispersion forces are comparable, and the difference lies in the other forces. Ethyl ethanoate is an ester: it has a polar C=O group (dipole–dipole plus dispersion) but no O–H, so its molecules cannot hydrogen-bond to one another. Butanoic acid has an O–H group and forms cyclic dimers held together by hydrogen bonds. The acid's much stronger intermolecular forces mean far more energy is needed to separate its molecules, giving it the higher boiling point. The ester, held only by weaker forces, evaporates more readily and so is the more volatile.