Functional groups: classification of organic compounds

Structure 3.2 · SL and AHL

Same formula, different connections

> Molecular formula alone does not determine structure or properties.

- Ethanol and methoxymethane share C_2H_6O.
- An O–H donor changes interactions between pure molecules.

Interconvert formula types

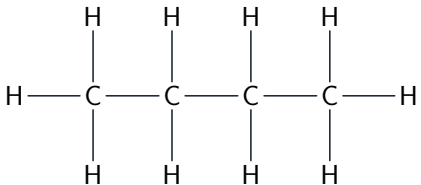
molecular

C_4H_{10}

condensed

$CH_3CH_2CH_2CH_3$

full structural



skeletal



Count carbon corners and ends; retain heteroatoms and their attached H.

Build a three-dimensional carbon model

A flat connectivity drawing need not show the actual bond angles.

- An sp^3 carbon has four approximately tetrahedral bond directions.
- C=C centres are approximately planar; a C≡C region is linear.

Recognize whole functional groups

Connection	**Class**
R–OH	alcohol
R–CHO / R–C(=O)–R	aldehyde / ketone
R–COOH / R–COOR	acid / ester
R–O–R / R–C(=O)–NH_2	ether / **primary** amide

Distinguish addition and substitution

Addition

$\mathrm{CH_2{=}CH_2 + H_2 \rightarrow CH_3CH_3}$

Ni catalyst and heat: C=C becomes C–C; two C–H bonds form.

Substitution

$\mathrm{C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-}$

Aqueous hydroxide and heat: C–Br is replaced by C–O.

Distinguish oxidation and polymerization

Oxidation

$\mathrm{CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O}$

Acidified dichromate; distil ethanal. Carbon loses C–H and gains a second bond to O.

Addition polymerization

$\mathrm{n CH_2{=}CH_2 \rightarrow [-CH_2 - CH_2-]_n}$

Suitable initiator/catalyst: C=C opens; new C–C links join monomers without a small product.

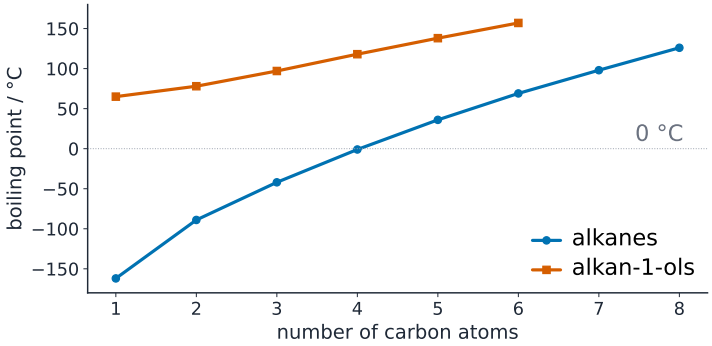
AHL track a two-step synthesis

1. **Hydrate.** Ethene $\rightarrow$ ethanol: steam, phosphoric-acid catalyst, elevated temperature and pressure.
2. **Oxidize.** Ethanol $\rightarrow$ ethanoic acid: excess acidified dichromate, heat under reflux.
3. **Check.** $\mathrm{CH_3CH_2OH} + 2[\mathrm{O}] \rightarrow \mathrm{CH_3COOH} + \mathrm{H_2O}$; hydrogenation would instead give ethane.

Use a general formula with its conditions

Simple acyclic series	**General formula**
alkanes	C_nH_{2n+2}
monoalkenes	C_nH_{2n}
monohydric alcohols	$C_nH_{2n+1}OH$
monocarboxylic acids	$C_nH_{2n}O_2$

Explain the normal boiling-point trend



Comparable longer chains have stronger dispersion; alcohols also hydrogen-bond.

Melting requires a packing explanation

> Do not transfer an exact boiling-point order to melting points.

- Crystal packing and symmetry affect the solid.
- Branching can change packing as well as intermolecular contact.

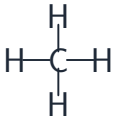
Name a branched parent chain

1. **Structure.** $CH_3CH_2CH(CH_3)CH_3$.
2. **Parent.** Four-carbon chain: butane.
3. **Locant.** Number from the nearer branch: 2-methylbutane.

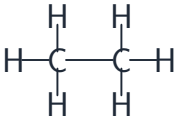
Decision

Include the characteristic group in the parent and apply its locant priority.

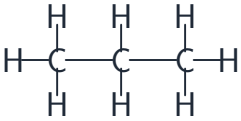
A homologous series



methane
CH_4



ethane
C_2H_6



propane
C_3H_8

each step adds a CH_2 unit

general formula C_nH_{2n+2}

The same general formula, C_nH_{2n+2}

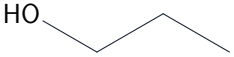
Distinguish structural isomer types

chain



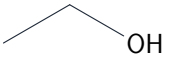
butane

position

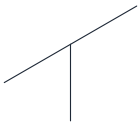


propan-1-ol

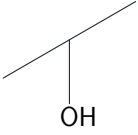
functional group



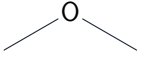
ethanol



2-methylpropane



propan-2-ol



methoxymethane

Same formula; different connectivity.

Classify at the correct atom

Alcohol and halogenoalkane

Propan-2-ol: the OH carbon has two carbon neighbours.

2-Bromopropane: the Br carbon also has two.

Amine

CH_3NH_2 **primary**; $(CH_3)_2NH$ **secondary**.

$(CH_3)_3N$ is **tertiary** despite having no N–H bond.

Check a full structural drawing

1. **Formula.** Butan-1-ol: $C_4H_{10}O$.
2. **Atoms.** $4 + 10 + 1 = 15$ atoms.
3. **Bonds.** A connected acyclic all-single-bond drawing has 14 bonds.

Decision

Its four-carbon skeletal chain has two corners and two ends.

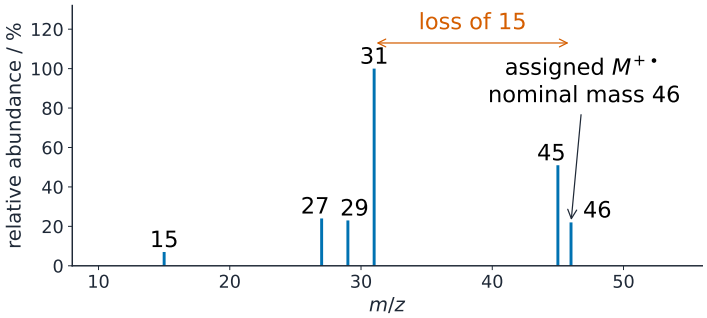
AHL: Use IHD as supporting evidence

1. **Given.** Neutral $C_4H_8O_2$ with usual valences.
2. **Calculate.** IHD $= (2\times4 + 2 - 8)/2 = 1$.
3. **Interpret.** One ring or double bond before other evidence is applied.

Decision

IHD alone does not tell you that the unsaturation must be a carbonyl.

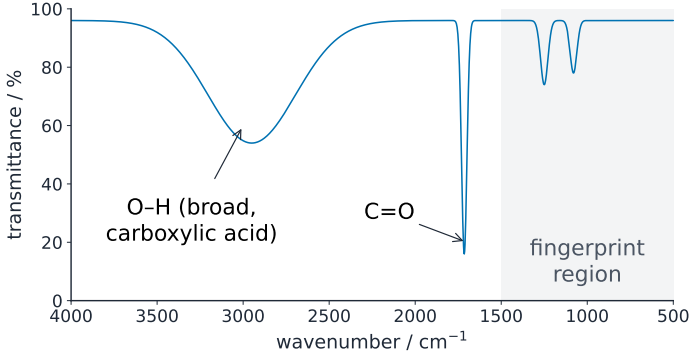
AHL: Assign the molecular ion carefully



Illustrative EI pattern; isotope peaks omitted

Assigned $M^{+\bullet}$ at 46 supports nominal mass; isotope peaks may lie above it.

AHL: Interpret an IR transmittance spectrum



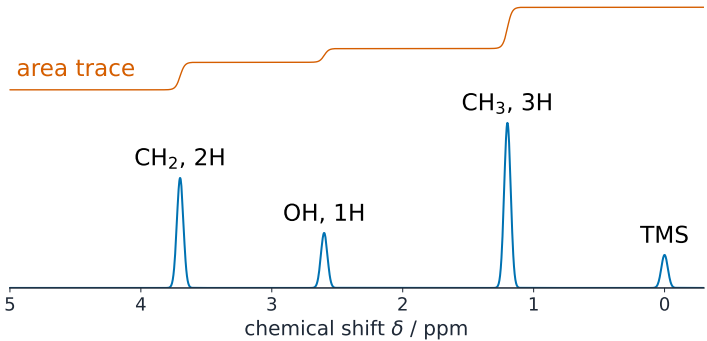
Schematic bands support functional groups; use a reference table and other evidence.

AHL: Why CO_2 can absorb infrared

> No permanent dipole does not mean no IR-active vibration.

- IR activity requires a vibration that changes dipole moment.
- CO_2 bending and asymmetric stretching can be IR active.

AHL: Signals and integrated areas



Total areas give H ratios; an OH shift depends strongly on conditions.

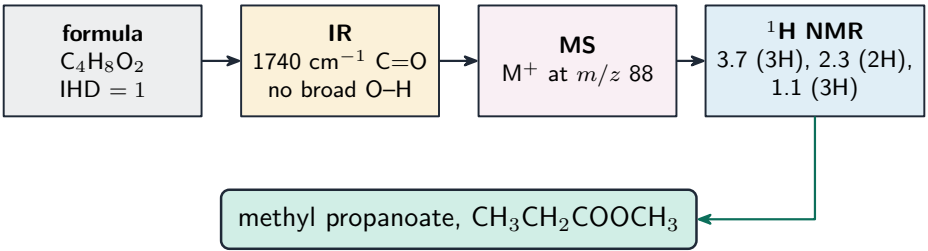
AHL: Reconcile all the data

1. **Invented data.** $C_4H_8O_2$; assigned M at 88; IR C=O, no broad OH.
2. **NMR.** 3.7 ppm (3H), 2.3 (2H), 1.1 (3H): total 8H.
3. **Assignment.** OCH_3, CH_2CO and terminal CH_3 fit methyl propanoate.
4. **Count.** $CH_3CH_2COOCH_3$ has 4C, 8H, 2O; nominal mass 88.

Decision

A formula $C_3H_6O_2$ or mass 74 would contradict these data.

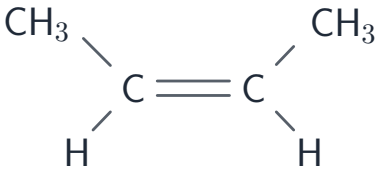
Identifying a compound from its spectra



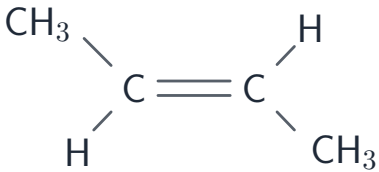
each technique narrows the options (invented data)

Together: methyl propanoate

AHL: Cis and trans need reference groups



cis: both CH_3 on the same side



trans: CH_3 on opposite sides

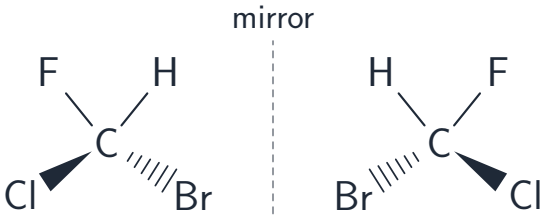
But-2-ene has identical methyl groups to compare across the restricted C=C.

AHL: Constrained small-ring faces

A conformation change need not change the **stereoisomer**.

- Cis substituents lie on the same ring face; trans on opposite faces.
- Cyclobutane can pucker without converting cis to trans.

AHL: Read tapered and hashed wedges



solid: towards viewer; hashed: away
mirror images cannot be superimposed

Four different groups around one carbon give a non-superimposable mirror pair.

AHL: Explain optical inactivity carefully

> No net rotation does not prove that all molecules are achiral.

- Enantiomers rotate equally and oppositely under identical conditions.
- A 1:1 racemate cancels rotations while retaining **chiral** molecules.

AHL: Apply the simple n + 1 rule

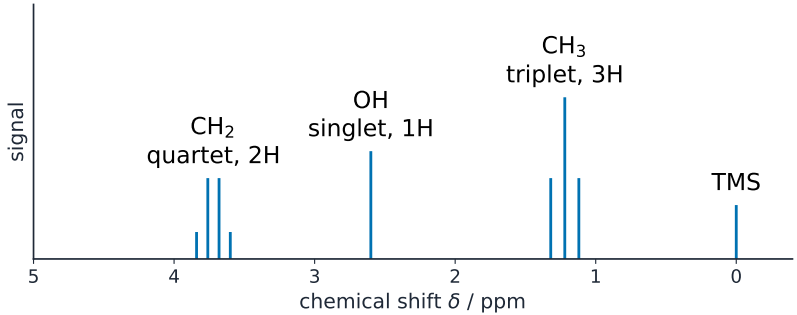


singlet $n = 0$ **doublet** $n = 1$ **triplet** $n = 2$ **quartet** $n = 3$

n equivalent neighbours split a peak into $n + 1$ lines

One set of n equivalent coupled neighbours gives n + 1 lines in first-order examples.

AHL: Read the ethanol multiplets



n+1 rule · integration 3 : 2 : 1 · TMS = 0 ppm

CH_3 triplet area 3; CH_2 quartet area 2; OH often unsplit with rapid exchange.

AHL: Recognize a supported ethyl assignment

Multiplicity, **integration**, shifts and formula must agree.

- A compatible 3H triplet and 2H quartet supports CH_3CH_2–.
- A quartet is four lines within one signal, not four proton environments.

Exam tips

> Check structure and atom counts before interpreting a property.

- Count corners and ends, complete valences and classify at the correct atom.
- Use a parent, locants and explicit reaction or measurement conditions.

Check yourself

Apply the model

Give all four alcohol constitutional isomers of $C_4H_{10}O$.

Compare amine and alcohol classification; explain an ether's hydrogen-bond acceptor role.

Explain why a general formula cannot alone distinguish an alkene from a cycloalkane.

AHL. Reconcile the invented mass-88 ester data and distinguish signals, split lines and areas.