

An introduction to AS Level organic chemistry

A-Level Chemistry

Formulas, functional groups and naming



Crude oil is a complex mixture of hydrocarbons – the feedstock for organic chemistry.

A **hydrocarbon** is a compound of only carbon and hydrogen. **Alkanes** are the simplest hydrocarbons and have no functional group.

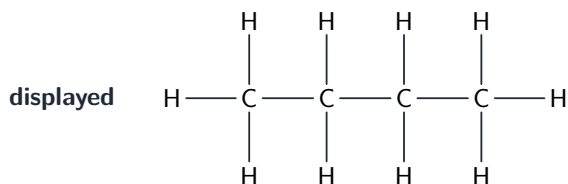
A **functional group** is the reactive part of a molecule. It decides the physical and chemical properties of the compound, so molecules with the same functional group behave alike (for example the -OH group in alcohols).

■ Types of formula

Formula	What it shows
general formula	the pattern for a whole family, e.g. alkanes are C_nH_{2n+2}
molecular formula	the actual number of each atom, e.g. C_4H_{10}
structural formula	the groups in order, e.g. $CH_3CH_2CH_2CH_3$
displayed formula	every atom and every bond drawn out
skeletal formula	lines for bonds; carbons at corners, hydrogens on carbon not shown

molecular C_4H_{10}

structural $CH_3CH_2CH_2CH_3$



skeletal



The same molecule (butane) shown four ways – molecular, structural, displayed and skeletal – each hiding more detail than the last

You can read off the **empirical formula** (simplest ratio) from any of these.

■ Naming

Use systematic **nomenclature** : a stem for the number of carbons (meth-, eth-, prop-, but-, pent-, hex- for 1 to 6), an ending for the functional group, and numbers to show where groups are.

Characteristic organic reactions

■ Some key terms

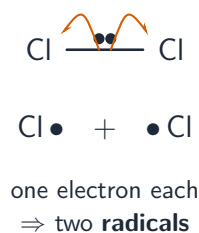
- a **homologous series** is a family of compounds with the same functional group and general formula, where successive members differ by CH_2 .
- a **saturated** compound has only single C–C bonds; an **unsaturated** compound has a C=C double bond (or a triple bond).

■ Breaking bonds

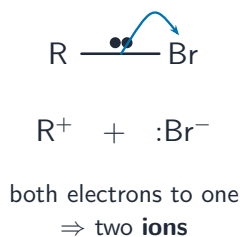
A covalent bond can break in two ways:

- **homolytic fission** : the bond splits evenly, one electron to each atom. This makes two **free radicals** (species with an unpaired electron).
- **heterolytic fission** : the bond splits unevenly, both electrons going to one atom. This makes two ions.

homolytic fission



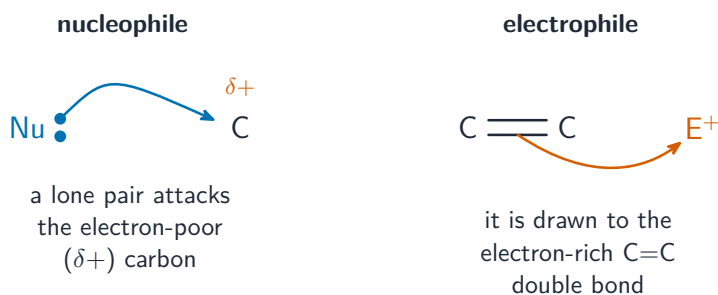
heterolytic fission



Homolytic fission gives one electron to each atom (two radicals); heterolytic fission gives both electrons to one atom (two ions)

■ Attacking species

- a **nucleophile** is an electron-pair donor: it uses a lone pair to form a bond to an electron-poor centre. A nucleophile can be neutral, such as ammonia, or negative, such as hydroxide.
- an **electrophile** is an electron-pair acceptor: it accepts a pair from an electron-rich region, such as the pi bond of C=C.



A nucleophile uses its lone pair to attack an electron-poor centre; an electrophile is drawn to an electron-rich one such as a $C=C$ bond

■ Types of reaction

Reaction	What happens
addition	two molecules join to make one
substitution	one atom or group is swapped for another
elimination	a small molecule is removed, making a double bond
hydrolysis	a molecule is split apart by water
condensation	two molecules join and a small molecule (such as water) is lost

For organic redox, the symbol [O] stands for one oxygen atom from an oxidising agent, and [H] for one hydrogen atom from a reducing agent.

Worked classification. Ethene plus HBr makes bromoethane by addition; bromoethane plus hydroxide replaces Br with OH by substitution; ethanol losing water to make ethene is elimination. Ester plus water giving acid and alcohol is hydrolysis, while acid plus alcohol giving ester and water is condensation. Classify from the structural change and the role of water.

■ Types of mechanism

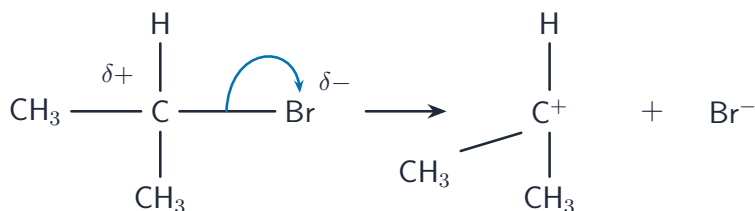
A free-radical reaction happens in three steps: **initiation** (radicals are made), **propagation** (radicals react and make new radicals), and **termination** (two radicals join and stop the chain).

The main mechanisms you meet are **free-radical substitution** (alkanes), **electrophilic addition** (alkenes), **nucleophilic substitution** (halogenoalkanes) and **nucleophilic addition** (carbonyls). In mechanisms, a full **curly arrow** shows a pair of electrons moving; it starts at a bond or a lone pair.

■ Follow the electron pair in a substitution

A full curly arrow starts on a bond or a lone pair and shows **two** electrons moving. A half-headed arrow shows one electron moving in a radical step. Do not start an arrow at a positive charge.

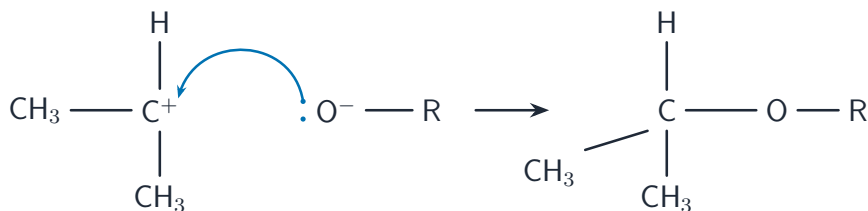
Original application: 9701/24 N25 Q3(b)(ii). The question states an S_N1 mechanism for 2-bromopropane with $(\text{CH}_3)_2\text{CHO}^-$. Follow the stated mechanism. First show the $\delta+$ carbon and $\delta-$ bromine, then move the C–Br pair to bromine. This gives a carbocation and Br^- .



Bond pair moves to Br; the carbon intermediate has a positive charge.

Full curly arrow from the C–Br bond to Br; the intermediate carbon has a positive charge.

Next, move a lone pair on the nucleophile's oxygen to the positive carbon. A new C–O bond forms. In the figure, R means $\text{CH}(\text{CH}_3)_2$.



An oxygen lone pair forms the C–O bond. Here $\text{R} = \text{CH}(\text{CH}_3)_2$.

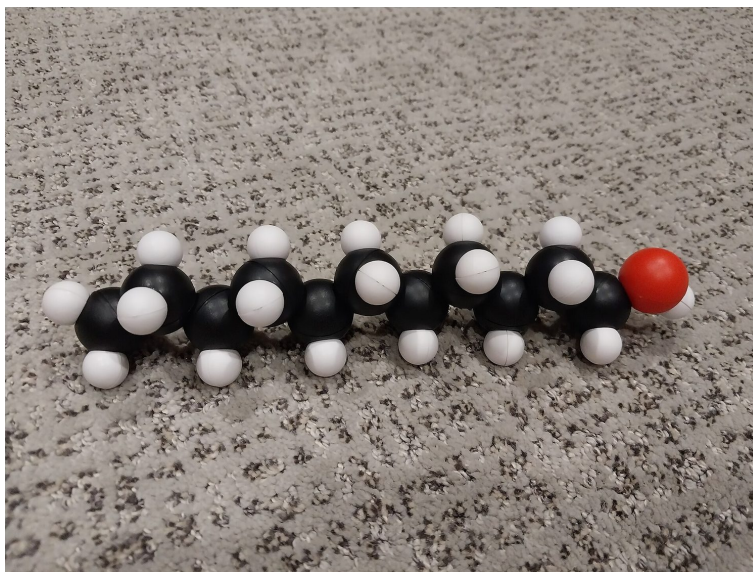
The arrow begins at the lone pair; it shows electron movement, not the movement of an entire molecule.

For the worksheet's 2-bromo-2-methylpropane case, the same two-stage pattern gives a tertiary carbocation, then attack by OH^- . Three alkyl groups help stabilise the positive charge by their electron-releasing effect. A primary carbocation is much less stable. In the worksheet's 1-bromobutane S_N2 case, attack and C–Br breaking occur together in one stage, without a carbocation intermediate. Draw both pair-moving arrows in that stage.

■ Identify radical stages from what they do

For methane and chlorine under UV light: initiation $\text{Cl}_2 \rightarrow 2\text{Cl}\cdot$ makes radicals. Propagation $\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{HCl} + \cdot\text{CH}_3$, followed by $\cdot\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$, consumes and regenerates one radical in each step. Termination $\cdot\text{CH}_3 + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$ consumes two radicals without making a new radical.

Shapes of organic molecules



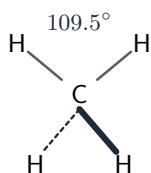
Organic molecules have definite three-dimensional shapes.

Organic molecules can be straight-chained, branched or **cyclic** (in a ring).

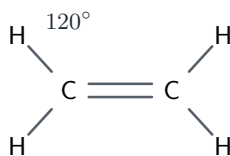
The shape around a carbon depends on its **hybridisation** :

Hybridisation	Bonds	Shape	Angle
sp^3	4 single	tetrahedral	109.5°
sp^2	1 double + 2 single	planar (flat)	120°
sp	1 triple (or 2 doubles)	linear	180°

Every single bond is a **sigma bond** σ , made by direct overlap. A double bond is one sigma bond plus one **pi bond** π , made by sideways overlap of p orbitals. Ethene is planar because of its sp^2 carbons.



sp³: 4 single bonds
tetrahedral

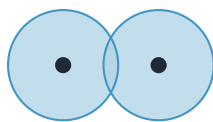


sp²: 1 double + 2 single
planar (flat)

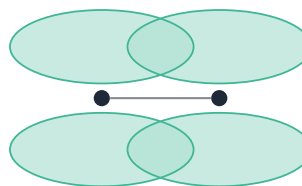


sp: 1 triple bond
linear

The shape at a carbon follows from its hybridisation: sp³ is tetrahedral (109.5°), sp² is planar (120°), sp is linear (180°)



σ bond:
head-on overlap



π bond: sideways overlap
of p orbitals

Sigma density lies on the internuclear axis; pi density is on both sides of it.

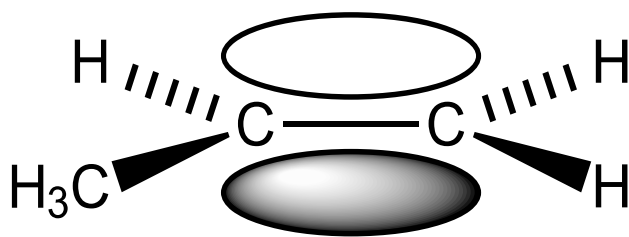
■ Work locally, then count the whole molecule

Original application: 9701/14 N25 Q6. In propyne, $\text{CH}_3\text{--C}\equiv\text{CH}$, the methyl carbon has four bonding regions: sp³, tetrahedral, 109.5°. Each triple-bond carbon has two regions: sp, linear, 180°. A multiple bond counts as one region for shape. The molecule therefore contains sp and sp³ carbons, not sp².

For bond counts, each bonded atom pair contributes one σ bond. A double bond adds one π ; a triple bond adds two π bonds. Methane has four σ and no π bonds. Ethene has **five** σ (four C–H and one C–C) and **one** π . Ethyne has three σ and two π bonds. Include the C–H bonds when counting the whole molecule.

Original application: 9701/12 N25 Q25. Methanal, $\text{H}_2\text{C=O}$, has three bonding regions around carbon: sp², trigonal planar, approximately 120°. All four atoms are in a plane. It has three σ bonds (two C–H and one C–O) plus one π bond. Both original statements are correct: answer A.

Orbital drawing: 9701/24 N25 Q3(a)(iv). The original scheme shows the π overlap above and below the propene framework:



Sideways overlap of parallel p orbitals forms one pi bond with two regions of density; the regions are not separate pi bonds.

Transfer to a non-organic molecule: 9701/12 N25 Q5. The question states that each N in N₂ is sp hybridised. Of its two sp orbitals, one holds a lone pair and one forms a head-on sp–sp σ overlap. The two remaining p orbitals form two π bonds by sideways overlap. The original answer is B.

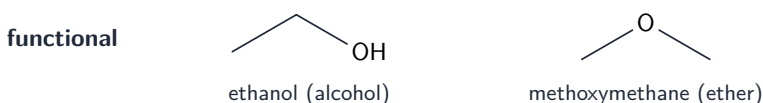
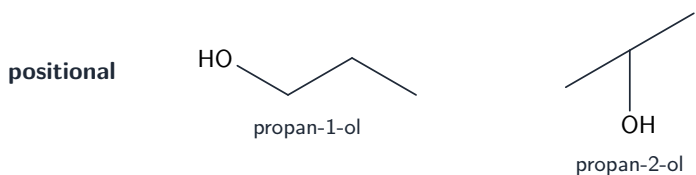
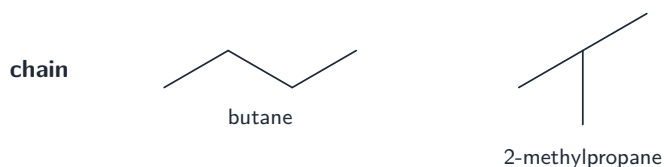
Isomerism

Isomers are compounds with the same molecular formula but a different arrangement of atoms. This is called **isomerism**.

■ Structural isomerism

In **structural isomerism** the atoms are joined in a different order. There are three kinds:

- **chain isomerism** : the carbon chain is branched in different ways.
- **positional isomerism** : the functional group is on a different carbon.
- **functional group isomerism** : the atoms form a different functional group (for example an alcohol and an ether).

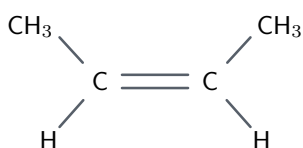


The three kinds of structural isomerism – chain, positional and functional-group – each pair sharing the same molecular formula

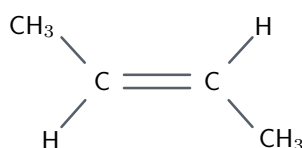
■ Stereoisomerism

In **stereoisomerism** the atoms are joined in the same order but point in different directions in space.

- **geometrical isomerism** (cis/trans) happens at a C=C double bond. The pi bond stops the two carbons rotating (**restricted rotation**), so groups are fixed on the same side (**cis**) or opposite sides (**trans**).



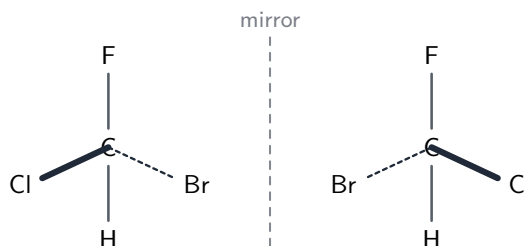
cis: both CH₃ on the same side



trans: CH₃ on opposite sides

Cis-trans isomerism at a C=C bond: the methyl groups are fixed on the same side (cis) or opposite sides (trans) because the bond cannot rotate

- **optical isomerism** happens at a **chiral** carbon – a **chiral centre** is a carbon with four different groups attached. Such a carbon gives two mirror-image forms called **enantiomers**. A molecule may have more than one chiral centre.



enantiomers: mirror images that cannot be superimposed
(the central carbon has 4 different groups)

Optical isomerism: a carbon with four different groups gives two mirror-image forms (enantiomers) that cannot be superimposed

From a molecular formula you can deduce the possible isomers by trying different chains, positions and functional groups.

Worked example. Explain why but-2-ene shows **cis-trans** (E/Z) isomerism but but-1-ene does not. Stereoisomerism at a C=C needs two things: restricted rotation about the double bond (both alkenes have that), **and** two **different** groups on **each** of the two double-bond carbons. In but-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$, each double-bond carbon carries an H and a CH_3 - different, so the methyl groups can sit on the same side (**cis** / **Z**) or on opposite sides (**trans** / **E**). In but-1-ene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$, the first carbon carries **two hydrogens** - identical, so swapping them changes nothing and only one form exists. Test **each** double-bond carbon separately: two identical groups on **either** carbon kills the isomerism, however different the other carbon may be.

Exam tips

- Know the difference between **general**, **molecular**, **structural**, **displayed** and **skeletal** formulas – questions ask for a specific one.
- Name systematically: longest chain, lowest locants, substituents alphabetical; a wrong locant loses the mark.
- Classify each reaction by **type and reagent** (addition, substitution, elimination, oxidation).
- **E/Z isomerism** needs restricted rotation about a C = C **and** two different groups on each carbon.