An introduction to A Level organic chemistry

Naming and formulas for the A Level functional groups including aromatic compounds, electrophilic substitution and addition–elimination, the structure of benzene, and optical isomerism and its importance for drugs.

29.1 Formulas, functional groups and the naming of organic compounds

The A Level adds these functional groups to those of the AS Level:

Class	Functional group	Example
Arene	benzene ring	methylbenzene
Phenol	–OH on a benzene ring	phenol, C_6H_5OH
Acyl chloride	–COCl	ethanoyl chloride
Amide	$–CONH_2$ (or –CONHR)	ethanamide
Phenylamine	$–NH_2$ on a benzene ring	phenylamine
Amino acid	$–NH_2$ and –COOH	2-aminoethanoic acid (glycine)
Azo compound	–N=N–	an azo dye

Rules for naming: for compounds with a **benzene ring** and substituents, number the ring from the principal functional group (position 1) so that the other groups get the **lowest numbers**: 3-nitrobenzoic acid, 2,4,6-tribromophenol, 4-nitromethylbenzene. For esters and amides, the chain can be up to six carbons plus six (straight chains only for esters). Cyclic compounds with a single ring of up to six carbons (cyclohexane, cyclohexene) are named with the prefix **cyclo-**.

Distinguish groups that look similar in a condensed formula

An OH directly bonded to an aromatic carbon is phenolic; OH on a side-chain CH_2 is an alcohol. C_6H_5OH is phenol, while $C_6H_5CH_2OH$ is phenylmethanol and undergoes ordinary primary-alcohol reactions at that side chain. Similarly, an amine has nitrogen attached without an adjacent carbonyl, whereas an amide has an N–C=O linkage. This difference changes basicity and hydrolysis chemistry.

Worked example: $C_6H_5CONHCH_3$ is an N-substituted amide, not a phenylamine. Nitrogen is attached to a carbonyl carbon, and the N-methyl substituent belongs to the nitrogen side of the amide.

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$C_6H_5NHCH_3$ has no carbonyl and is an amine. Read every connecting atom rather than classifying from the presence of N alone.

For an aromatic acid such as C_6H_5COOH, the carboxyl carbon is outside the six-membered ring, so the molecule has seven carbons. When counting a substituted aromatic molecular formula, begin with benzene and replace each ring hydrogen once for each substituent. This avoids accidentally retaining six ring hydrogens after substitution.

> TRY IT
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> Give the molecular formula of 4-hydroxybenzoic acid and identify both functional groups.

Answer: $C_7H_6O_3$. It contains a phenol OH and a carboxylic acid. Two substituents replace two benzene hydrogens, leaving four ring hydrogens plus one hydrogen on each OH-containing group.

29.2 Characteristic organic reactions

Two further mechanism types are used.

- **Electrophilic substitution:** an electrophile replaces a hydrogen on the benzene ring (nitration, halogenation, Friedel–Crafts reactions).
- **Addition–elimination:** a nucleophile adds to a C=O carbon and then a small molecule is lost, as in the reactions of acyl chlorides with water, alcohols, ammonia and amines.

Arene substitution versus acyl substitution

Electrophilic aromatic substitution starts with electron donation from a ring pi system to an electrophile. Loss of a proton then restores aromaticity. Nucleophilic addition–elimination begins with donation to an acyl carbonyl carbon, followed by reformation of C=O and loss of a leaving group. The word “substitution” appears in both overall descriptions, but the attacking species and electron-flow sequence differ.

Worked comparison: nitration replaces a ring H with NO_2 through an electrophile. Ethanol reacting with ethanoyl chloride replaces acyl Cl with an alkoxy group through nucleophilic attack. A mechanism answer should identify the electron-rich donor and electron-deficient acceptor before drawing arrows; copying an alkene addition mechanism into a benzene question misses aromaticity restoration.

> TRY IT
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> Why is an acyl chloride reaction with ammonia not electrophilic substitution even though one group is replaced?

Answer: Ammonia is the attacking nucleophile, donating a lone pair to the carbonyl carbon. A tetrahedral intermediate forms and chloride leaves. Electrophilic substitution refers to a different attack on an

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electron-rich aromatic system.

29.3 Shapes of aromatic organic molecules; σ and π bonds

Benzene, C_6H_6, is a **planar** hexagon of carbon atoms with all bond angles **120°**. Each carbon is sp^2 **hybridised** and forms three σ bonds (two to carbon, one to hydrogen). The remaining p orbital on each carbon, perpendicular to the plane, overlaps sideways with its neighbours to form a **delocalised π system** (a ring of electron density above and below the plane) containing **six electrons**.

The evidence: all six C–C bonds are the **same length** (0.140 nm, between a single 0.154 and a double 0.134), and the molecule is **more stable than expected** for three isolated double bonds (the hydrogenation enthalpy, −208 kJ mol^{-1}, is much less exothermic than three times that of cyclohexene, −360). It does not decolourise bromine water. The delocalisation (**aromatic stabilisation**) is why benzene prefers **substitution** (which keeps the ring) over addition (which would destroy it).

Use evidence to assess the benzene model

Three isolated C=C bonds would predict alternating bond lengths and a hydrogenation enthalpy about three times that of a comparable isolated double bond. Benzene instead has equal carbon–carbon distances and releases less energy on hydrogenation than that hypothetical structure. Its starting state is therefore lower in energy and more stable through delocalisation.

Worked calculation: if one isolated-double-bond hydrogenation is −120 kJ mol^{-1}, three would predict −360. An observed benzene value of approximately −208 gives a stabilisation difference of $360 - 208 = 152$ kJ mol^{-1}. This is an energy comparison between models, not an extra reagent energy that must be added to every benzene reaction equation.

The circle-in-hexagon representation emphasises delocalisation; alternating-bond drawings can represent contributing structures rather than a molecule rapidly switching between physically distinct short and long bonds. All carbons are approximately planar and sp^2, with overlapping p orbitals perpendicular to the ring. The pi electrons are delocalised **above and below** the ring, not collected in a hole at its centre.

> **TRY IT**
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> Why does substitution usually preserve benzene's stabilisation better than an alkene-like addition across the ring?

Answer: After electrophile attack, proton loss restores the continuous delocalised pi system. Addition would leave a less extensively delocalised ring, losing aromatic stabilisation.

29.4 Isomerism: optical

Enantiomers are non-superimposable mirror images, arising from a **chiral centre** (a carbon with four different groups). They have **identical physical and chemical properties** (melting point, boiling point,

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reactions with achiral reagents) **apart from**:

- their effect on **plane-polarised light**: one rotates it clockwise and the other by an equal amount anticlockwise, so each is **optically active**;
- their reaction with other chiral molecules, which gives **different biological activity**.

A **racemic mixture** (racemate) contains equal amounts of the two enantiomers, and is **not optically active** because the rotations cancel.

Importance for drugs

- The two enantiomers may have **different biological activity**: one may be the active drug and the other less active or harmful (thalidomide is the standard example).
- Making a chiral compound by ordinary synthesis from achiral starting materials usually gives a **racemic mixture**, so the mixture must be **separated** into pure enantiomers (which is costly and wasteful).
- A **chiral catalyst** or enzyme can favour one enantiomer, sometimes very selectively. Enantiomeric purity must be measured rather than assumed to be 100% solely because a chiral catalyst was used.

> **A reaction that forms a chiral centre by attack of a nucleophile on a planar group (a C=O or a carbocation) from either face gives a racemic mixture: for example HCN adding to ethanal, or SN1 hydrolysis of a chiral tertiary halogenoalkane.**

Decide chirality by comparing whole groups

A tetrahedral carbon bearing H, OH, methyl and ethyl is chiral because all four groups differ. A carbon bearing two methyl groups is not chiral. Two substituents beginning with carbon may still differ beyond their first atom, so trace each chain until a difference appears. A flat structural formula can hide chirality; mark the candidate centre and list its four attachments.

Worked example: $CH_3CH(OH)CH_2CH_3$ has one chiral carbon at C-2. Propan-2-ol does not, because its OH carbon has two methyl groups. Ethanal plus HCN creates OH, H, methyl and CN attachments and therefore a pair of enantiomers, whereas propanone plus HCN has two methyl groups and does not create the analogous centre.

Optical activity and racemates

Plane-polarised light has its electric-field vibrations in one plane. An enantiomer can rotate that plane, with its mirror partner giving equal and opposite rotation under matched conditions. Optical inactivity of an equal mixture arises from cancellation, not because each molecule has stopped being chiral. The

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direction of rotation is measured experimentally; it cannot be read directly from an arbitrary wedge-and-dash drawing.

Worked example: equal concentrations of two enantiomers are mixed in equal volumes. Their opposing rotations cancel in a polarimeter. Mixing unequal amounts leaves a net rotation. Absence of observed rotation could indicate a racemate **or** an achiral substance, so optical inactivity alone does not prove either explanation.

> **TRY IT**
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> Why can two enantiomers behave differently with an enzyme although they react similarly with achiral laboratory reagents?

Answer: The enzyme has a chiral binding environment. The two mirror-image substrates form different spatial interactions and may bind or react differently. An achiral environment does not provide the same distinction.

Chapter check: identify attachment points in aromatic functional groups, distinguish the two new mechanism types, use benzene evidence quantitatively, and separate molecular chirality from the optical activity of a bulk mixture.

References and further reading

Scope follows section 29 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

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