An introduction to A Level organic chemistry

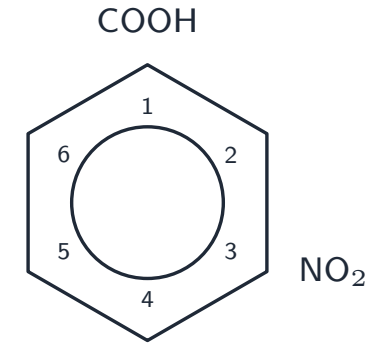
A-Level Chemistry

New functional groups and naming

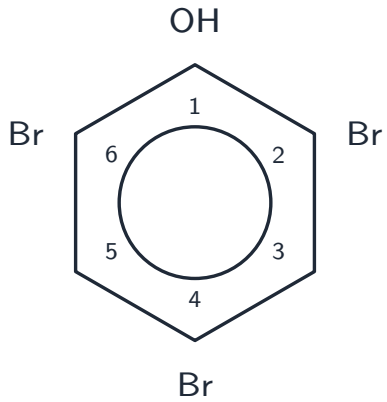
At A Level you meet more **functional group** 官能团 families, including the **amide** 酰胺 group and **aromatic** 芳香 compounds (those built on a benzene ring). As before, the functional group decides the properties, and you read it from the general, structural, displayed or skeletal formula.

Naming aromatic compounds

A **benzene** 苯 molecule is a ring of six carbons. When you name an aromatic compound, use the **benzene ring** 苯环 as the parent and number the positions of the substituents. For example, 3-nitrobenzoic acid has a $–NO_2$ group on carbon 3, and 2,4,6-tribromophenol has three bromine atoms on a phenol ring. You can also name cyclic compounds with a single ring of up to six carbons.



3-nitrobenzoic acid



2,4,6-tribromophenol

Number the ring from the principal group (carbon 1); the substituent positions then give the name

Two new types of mechanism

- **electrophilic substitution** 亲电取代: an electrophile replaces a hydrogen atom on a benzene ring (this is how benzene reacts).
- **addition–elimination** 加成消去: a molecule first adds on, then a small molecule is removed (seen with 2,4-DNPH and with acyl chlorides).

electrophilic substitution
an electrophile replaces an H
on a benzene ring

addition–elimination
a molecule adds on, then
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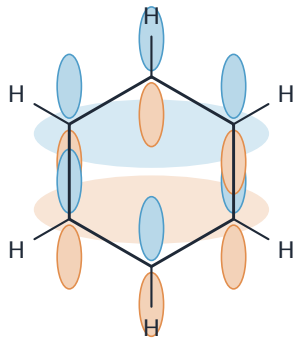
Two aromatic mechanisms: electrophilic substitution and addition-elimination

The shape of benzene

Benzene is a flat, regular hexagon. Each carbon is **sp²** hybridised, using its three **hybridisation** 杂化 orbitals to make **sigma bonds** σ 键 to two neighbouring carbons and one hydrogen. This gives the ring of σ bonds.

Each carbon also has one electron left in a p orbital, standing up at right angles to the ring. These p orbitals overlap sideways all the way round, making a single **delocalised** 离域 **pi bond** π 键 system —a ring of electrons above and below the plane. Because the electrons are shared evenly, all six C–C bonds are the same length, and benzene is very stable.

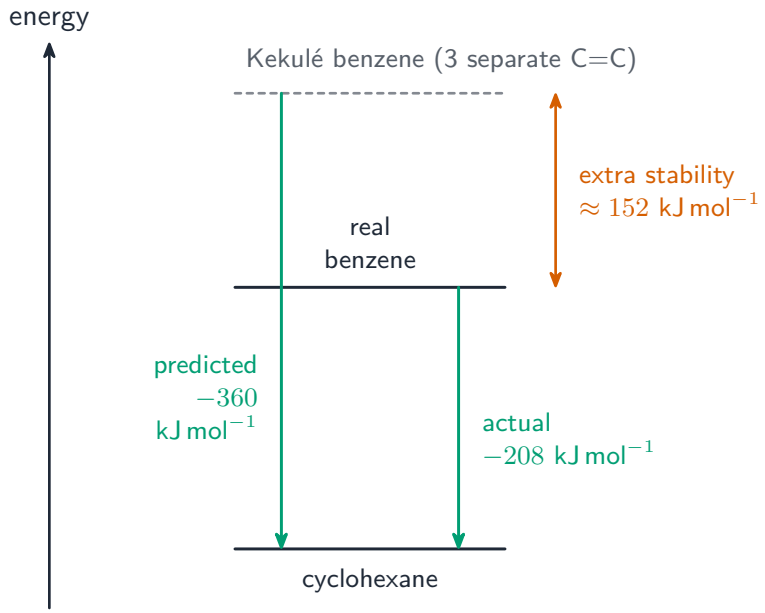


one **delocalised** π system
above and below the ring

sp^2 σ framework;
all six C–C bonds equal

Benzene's bonding: an sp^2 σ framework makes the flat hexagon, while the p orbitals overlap into one delocalised π system above and below the ring

How do we know benzene really is delocalised? One strong piece of evidence is its **enthalpy change of hydrogenation** 氢化焓变. Adding hydrogen to one C=C double bond (as in cyclohexene) releases about 120 kJ mol^{-1}, so a Kekulé ring of three separate double bonds should release about $3 \times 120 = 360$ kJ mol^{-1}. Real benzene releases only 208 kJ mol^{-1} —it is about 152 kJ mol^{-1} **more stable** than the model predicts.



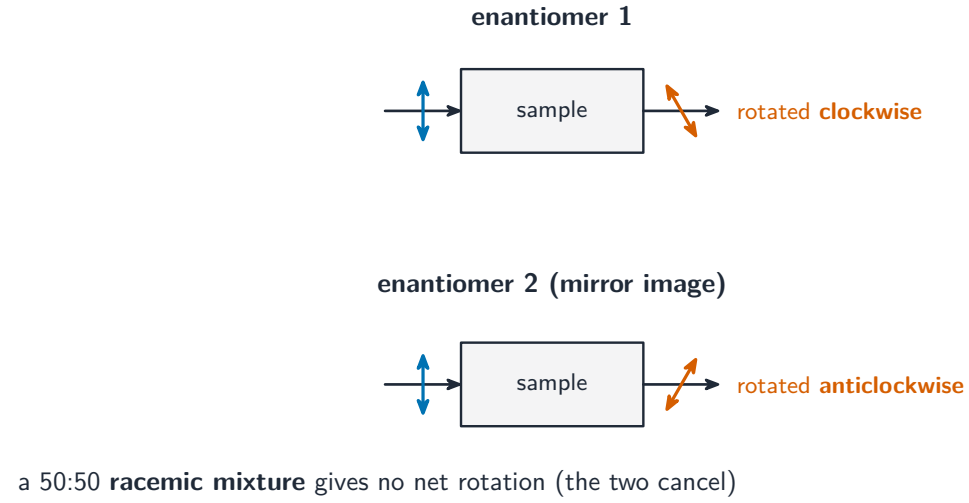
Evidence for delocalisation: real benzene releases far less on hydrogenation ($-208\ kJ\,mol^{-1}$) than the Kekulé model predicts ($-360 = 3\times$ cyclohexene), so it is about $152\ kJ\,mol^{-1}$ more stable than expected

Optical isomerism

Two **enantiomers** 对映体 (mirror-image isomers) have **identical** physical and chemical properties, with two exceptions:

- they rotate **plane polarised light** 平面偏振光 in opposite directions. A substance that does this is **optically active** 旋光活性.
- they may have different effects in living things (biological activity).

A **racemic mixture** 外消旋混合物 is a 50:50 mix of the two enantiomers. It does **not** rotate plane polarised light, because the two opposite rotations cancel out.



The two enantiomers rotate plane-polarised light in opposite directions; a 50:50 racemic mixture gives no net rotation

Why chirality matters for drugs

Chirality 手性 is important when making medicines. A molecule with a **chiral centre** 手性中心 has two enantiomers, and they can behave very differently in the body —one may cure while the other does harm. So drug makers either:

- separate a racemic mixture into the two pure enantiomers, or
- use a **chiral catalyst** 手性催化剂 to make just the single enantiomer they want.

Worked example. Which of butan-1-ol, butan-2-ol and 2-methylpropan-2-ol is **chiral**? A molecule is chiral if it has a carbon carrying **four different** groups. Take the carbons one at a time. In butan-2-ol, $CH_3CH(OH)CH_2CH_3$, carbon 2 carries OH, H, CH_3 and C_2H_5 - four different groups, so it is a **chiral centre** and butan-2-ol exists as two optical isomers. Butan-1-ol's carbon 1 carries **two hydrogens**, and the central carbon of 2-methylpropan-2-ol carries **two identical methyl** groups, so neither is chiral. It takes only **one** repeated group on a carbon to destroy the chirality there - and compare groups properly: CH_3 and C_2H_5 differ, but only once you look past the first atom.

Exam tips

- **Optical isomers** need a **chiral carbon** (four different groups); they are non-superimposable mirror images that rotate plane-polarised light oppositely.
- A **racemic mixture** forms when a **planar intermediate** (carbocation or C = O) is attacked equally from both sides.
- Benzene's **delocalised** ring (equal bond lengths, planar) explains its stability versus the Kekulé model.
- Learn the two new mechanisms —electrophilic substitution of arenes, and nucleophilic addition-elimination.