A-LEVEL CHEMISTRY • EXERCISE SHEET

29.4 Optical isomerism

Name: ______________ Class: __________ Date: ____________ **Total: 29 marks**

KEY WORDS optically active 旋光活性 • enantiomers 对映体 • plane-polarised light 平面偏振光 • racemic mixture 外消旋混合物 • chirality 手性

Objective

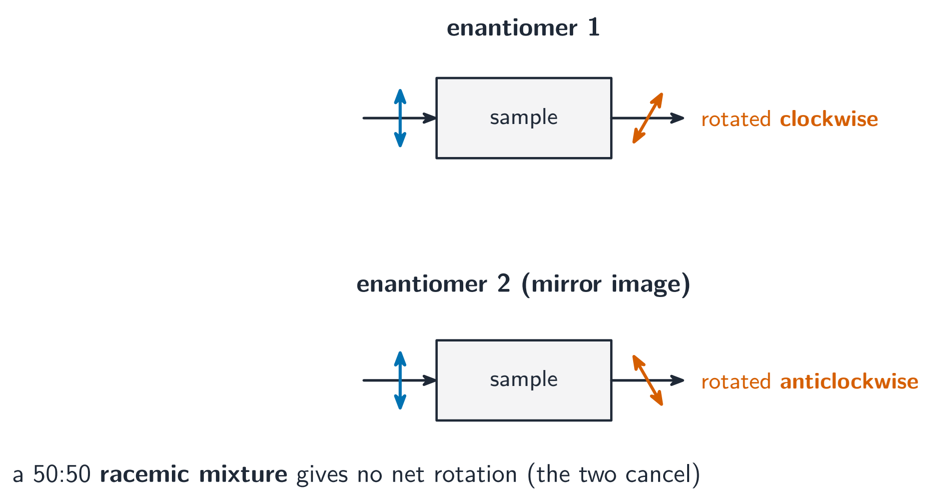
Build the skills to answer exam questions on **optical isomerism** 旋光异构 — **chiral centres** 手性中心, **enantiomers** 对映体, **plane-polarised light** 平面偏振光 and **racemic mixtures** 外消旋混合物.

You must be able to:

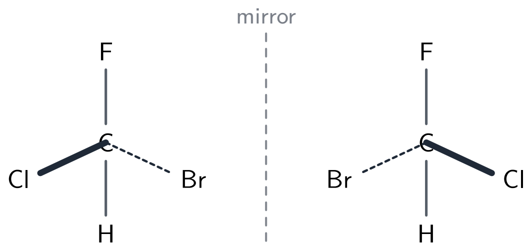
- identify a chiral centre (4 different groups on one carbon)
- describe how enantiomers differ (rotation of plane-polarised light; biological activity)
- explain why a racemic mixture is optically inactive

1 Worked examples

■ Chirality and optical activity



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



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

Optical isomers are non-superimposable mirror images

- a **chiral centre** is a carbon with **four different** groups → two non-superimposable mirror images (enantiomers).
- enantiomers are identical in all properties **except**: they rotate plane-polarised light in **opposite** directions, and may have different biological effects.
- a **racemic mixture** (50:50) shows **no** net rotation — the two opposite rotations cancel.

Drugs: one enantiomer may cure while the other harms — so makers use a chiral catalyst or separate the enantiomers.

■ Finding a chiral centre, and what optical activity actually means

A **chiral centre** 手性中心 is a carbon with **four different groups** attached. Such a molecule is **not superimposable on its mirror image**, and the two mirror images are **enantiomers** 对映异构体.

Testing for chirality — go carbon by carbon. At each carbon, list its four attachments; if any two are identical, that carbon is not chiral. Watch for the trap where two groups look different but are the same, for example two CH_3 groups written at different angles.

What differs between enantiomers, and what does not:

- **Identical**: melting point, boiling point, density, solubility, and every ordinary chemical reaction with a non-chiral reagent.
- **Different**: they rotate the plane of **plane-polarised light** by equal amounts in **opposite directions**, and they react differently with other **chiral** molecules — which is why one enantiomer of a drug can be therapeutic and the other inactive or harmful.

A **racemic mixture** 外消旋混合物 is an equal mixture of both enantiomers. It shows **no optical rotation**, because the two rotations cancel exactly.

Why a mechanism predicts which you get — the examinable link:

- $\mathbf{S_N2}$: the nucleophile attacks from the opposite side to the leaving group, so the configuration is **inverted** and a single enantiomer gives a single, opposite enantiomer.

- **S_N1**: the intermediate is a **planar carbocation**, so the nucleophile attacks either face with equal probability, giving a **racemic mixture**.
- Adding HCN to an aldehyde or unsymmetrical ketone likewise attacks a planar $C=O$ from both faces, so the hydroxynitrile is racemic.

Worked example. $CH_3CH(OH)COOH$ (lactic acid): identify the chiral centre and state what a 50:50 mixture of its enantiomers would do to plane-polarised light.

1. The middle carbon carries $-H$, $-OH$, $-CH_3$ and $-COOH$: four different groups, so it is the chiral centre.
2. A 50:50 mixture is racemic, so the equal and opposite rotations cancel and there is **no net rotation**.

2 Practice

2.1 State what feature a molecule must have to show optical isomerism. [1]

2.2 State why a racemic mixture does not rotate plane-polarised light. [1]

2.3 State the two features that make a molecule optically active. [2]

2.4 Explain why a racemic mixture shows no optical rotation. [2]

2.5 State one property in which two enantiomers differ, and one in which they are identical. [2]

3 Exam-style questions

3.1 A chiral carbon atom is bonded to: [1]

A | B
C | D

A four identical groups
B two identical and two different groups
C four different groups
D three different groups and one H, with a double bond

3.2 Two enantiomers of a molecule always have the **same**: [1]

A | B
C | D

A rotation of plane-polarised light
B boiling point
C effect in the body
D direction of optical rotation

3.3 The molecule $CH_3CH(OH)COOH$ (lactic acid) is optically active.

(a) Mark the chiral centre and state how many enantiomers it has. [2]

(b) State the two ways in which the enantiomers differ. [2]

3.4 Explain why drug manufacturers often want a single enantiomer rather than a racemic mixture. [2]

3.5 2-bromobutane, $CH_3CHBrCH_2CH_3$, is hydrolysed by aqueous sodium hydroxide.

(a) Identify the chiral centre in 2-bromobutane and explain your choice. [2]

(b) Draw the two enantiomers of 2-bromobutane as three-dimensional structures. [2]

(c) A single enantiomer of 2-bromobutane is hydrolysed by an S_N2 mechanism. State what is observed about the optical activity of the product and explain why. [3]

(d) A tertiary halogenoalkane hydrolyses by S_N1. Explain why the product is optically inactive. [3]

(e) HCN is added to butanone. Explain why the hydroxynitrile formed is a racemic mixture. [3]