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

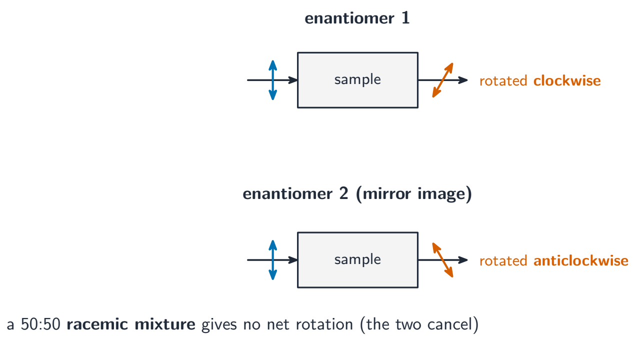
Build the skills to answer exam questions on **optical isomerism 旋光异构** — **chiral centres 手性中心**, **enantiomers 对映体**, **plane-polarised light 平面偏振光** and **racemic mixtures 外消旋混合物**.

**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

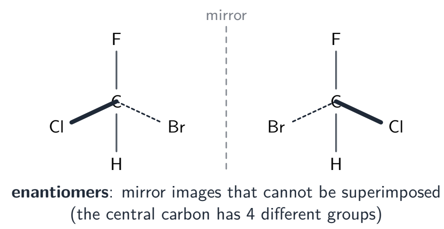
## 1 Worked examples

### Chirality and optical activity




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






*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:

- $S_N2$: 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** 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** 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]



## Solutions

**2.1** a chiral centre — a carbon atom bonded to four different groups.

**2.2** the two enantiomers are present in equal amounts, so their equal and opposite rotations cancel.

**2.3** A carbon atom with four different groups attached; the molecule is not superimposable on its mirror image.

**2.4** It contains equal amounts of the two enantiomers, which rotate the plane of polarised light by equal amounts in opposite directions, so the rotations cancel.

**2.5** They differ in the direction in which they rotate plane-polarised light; they are identical in all ordinary physical properties such as boiling point, and in reactions with non-chiral reagents.

**3.1 C**. A chiral carbon has four different groups attached.

**3.2 B**. Enantiomers share all physical properties such as boiling point; only the direction of optical rotation and biological activity differ.

**3.3** (a) the central carbon (bonded to –OH, –COOH, $-CH_3$ and –H) is the chiral centre; it has 2 enantiomers.
(b) they rotate plane-polarised light in opposite directions; they may have different biological effects.

**3.4** the two enantiomers can behave very differently in the body — one may be effective or safe while the other is inactive or harmful; so the maker wants only the beneficial single enantiomer.

**3.5** (a) Carbon 2; it carries $-$H, $-$Br, $-CH_3$ and $-CH_2CH_3$, which are four different groups.
(b) Two tetrahedral structures drawn as mirror images, using wedges and dashes, which cannot be superimposed on each other.
(c) The product is optically active; in $S_N2$ the hydroxide attacks from the side opposite the bromine, so the configuration is inverted and a single enantiomer of the alcohol is formed rather than a mixture.
(d) The mechanism goes through a carbocation intermediate which is planar, with the positive carbon having three groups in a plane; the nucleophile attacks either face with equal probability, giving equal amounts of the two enantiomers, so the product is racemic and optically inactive.
(e) The carbonyl carbon in butanone is planar; the cyanide ion attacks from either face with equal probability, giving equal amounts of the two enantiomers of the hydroxynitrile, whose rotations cancel.