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CH 06

Isomerism & Stereochemistry — E/Z, R/S and Conformations

06

Structural isomerism, geometrical isomerism with E/Z, chirality, R/S by the CIP rules, Fischer projections, meso compounds, counting stereoisomers, optical rotation and conformations — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Classify isomers as chain, position, functional, metamers, tautomers or stereoisomers
- Decide when geometrical isomerism is possible and assign E/Z using CIP priorities
- Identify stereocentres and assign R/S, including from Fischer projections
- Count stereoisomers, recognise meso compounds, and calculate enantiomeric excess
- Compare conformations of ethane, butane and cyclohexane, and spot chirality without a stereocentre

INSIDE

A The big picture
B Structural isomerism
C Geometrical isomerism
D CIP rules and E/Z

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

One question sorts every kind of isomer.

IN ONE LINE

Same formula, different connections → structural isomers. Same connections, different arrangement in space → stereoisomers: geometrical (around a double bond or ring) or optical (non-superimposable mirror images).

Type	What differs	Example
Chain	Carbon skeleton	Butane and 2-methylpropane
Position	Position of a group or multiple bond	Propan-1-ol and propan-2-ol
Functional	Functional group	Ethanol and methoxymethane
Metamerism	Alkyl groups either side of a functional group	Diethyl ether and methyl propyl ether
Tautomerism	Position of an H and a double bond, in rapid equilibrium	Keto and enol forms of acetone
Geometrical	Arrangement around C=C or a ring	cis- and trans-but-2-ene
Optical	Mirror-image arrangement at a stereocentre	(R)- and (S)-butan-2-ol

THINK OF IT LIKE THIS

Your left and right hands have the same parts joined in the same order — same "formula", same "connections". Yet you cannot lay one exactly over the other. That is chirality. A left glove and a right glove are enantiomers; a glove and a sock are structural isomers.

SECTION B

Structural isomerism

B

Count carefully and draw each skeleton once.

- **Chain:** C_4H_{10} has 2 isomers; C_5H_{12} has 3 (pentane, 2-methylbutane, 2,2-dimethylpropane); C_6H_{14} has 5.
- **Functional pairs worth memorising:** alcohols ↔ ethers ($C_nH_{2n+2}O$); aldehydes ↔ ketones ($C_nH_{2n}O$); carboxylic acids ↔ esters ($C_nH_{2n}O_2$); alkynes ↔ dienes (C_nH_{2n-2}); cyanides ↔ isocyanides.
- **Metamerism** occurs only within one functional class (ethers, ketones, secondary amines, esters).
- **Tautomerism** needs an α-hydrogen next to C=O. Simple ketones exist almost entirely as the keto form; the enol is favoured when it is stabilised (phenol; 1,3-diketones such as acetylacetone by conjugation and an internal hydrogen bond).

SOLVED EXAMPLE 01 — COUNTING STRUCTURAL ISOMERS

How many structural isomers have the formula $C_4H_{10}O$?

SOLUTION

1. Alcohols: butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol — 4.
2. Ethers: 1-methoxypropane, 2-methoxypropane, ethoxyethane — 3.

ANSWER 7 structural isomers (8 if the two enantiomers of butan-2-ol are counted).

SECTION C

Geometrical isomerism

When rotation is blocked, two arrangements become two compounds.

Rotation about a C=C (or within a ring) is restricted. If **each** carbon of the double bond carries **two different groups**, two arrangements exist.

- But-2-ene ($CH_3CH{=}CHCH_3$): cis and trans exist. But-1-ene ($CH_2{=}CHCH_2CH_3$): no — C1 carries two H atoms.
- **cis** isomers usually have a higher dipole moment and boiling point; **trans** isomers pack better, so they usually have a higher melting point and are more stable.
- cis-But-2-enedioic acid (maleic acid) forms an anhydride on heating; the trans isomer (fumaric acid) cannot — its COOH groups are too far apart.
- Ring compounds show it too: cis- and trans-1,2-dimethylcyclopropane.
- Oximes (C=N–OH) and azo compounds (N=N) show geometrical isomerism as well.

KEY IDEA

Counting geometrical isomers in a polyene: an unsymmetrical chain with n stereogenic double bonds has 2^n geometrical isomers. If the two ends of the chain are identical, some arrangements turn out to be the same molecule and the count is lower — draw them out for small n.

SECTION D

CIP rules and E/Z

D

cis/trans fails when four different groups are attached — E/Z never does.

1. **Higher atomic number = higher priority** at the first point of difference: Br > Cl > O > N > C > H.
2. **Tie? Move outward:** compare the sets of atoms attached next. $-CH_2OH$ (O, H, H) beats $-CH(CH_3)_2$ (C, C, H).
3. **Multiple bonds count as duplicates:** C=O is treated as C bonded to (O, O); –CHO beats $-CH_2OH$.
4. **Isotopes:** higher mass wins (D > H).

KEY IDEA

Z (zusammen, together): the two higher-priority groups are on the **same side**. **E** (entgegen, opposite): on **opposite sides**. Decide priority separately on each carbon of the double bond.

SOLVED EXAMPLE 02 — CIS IS NOT ALWAYS Z

In one isomer of 2-chlorobut-2-ene, $CH_3C(Cl)=CHCH_3$, the Cl and the CH_3 on C3 are on the same side. Is it E or Z, and is it cis or trans with respect to the two methyl groups?

SOLUTION

1. On C2: Cl (17) > CH_3 (6) → Cl is higher priority.
2. On C3: CH_3 > H → CH_3 is higher priority.
3. Higher-priority groups (Cl and C3–CH_3) on the same side → Z.
4. The two methyl groups are then on opposite sides → trans by the methyls.

ANSWER **(Z)-2-chlorobut-2-ene — even though the methyls are trans.**

CHECK YOURSELF

C1 Can but-1-ene show geometrical isomerism?

C2 Which has the higher priority: $-CH=CH_2$ or $-CH(CH_3)_2$?

Answers at the end of the chapter.

SECTION E

Chirality and enantiomers

E

Mirror images that cannot be superimposed.

- A **stereocentre** (chiral centre) is commonly an sp^3 carbon with four different groups.
- A molecule is **chiral** if it has no plane of symmetry or centre of symmetry (more strictly, no improper axis). A chiral molecule is not superimposable on its mirror image.

- **Enantiomers:** non-superimposable mirror images. Identical physical properties (m.p., b.p., solubility) except the direction in which they rotate plane-polarised light; they react differently only with other chiral substances (e.g. enzymes).
- **Diastereomers:** stereoisomers that are not mirror images — different physical properties. Geometrical isomers are diastereomers.
- **Racemic mixture:** 50:50 enantiomers, optically inactive by external compensation. **Meso compound:** has stereocentres but an internal plane of symmetry, optically inactive by internal compensation.

	Enantiomers	Diastereomers
Mirror images?	Yes	No
Physical properties	Identical (except sign of rotation)	Different
Separated by	Resolution (chiral reagent)	Ordinary methods (crystallisation, chromatography)

SECTION F

F

Assigning R and S

Four steps, every time.

1. Rank the four groups on the stereocentre by CIP priority (1 highest, 4 lowest).
2. View the molecule with group 4 pointing **away** from you.
3. Trace 1 → 2 → 3. **Clockwise = R** (rectus); **anticlockwise = S** (sinister).
4. If group 4 is pointing **toward** you, read the direction and then **reverse** it.

SOLVED EXAMPLE 03 — LACTIC ACID

Rank the groups on the stereocentre of lactic acid, $CH_3CH(OH)COOH$.

SOLUTION

1. Atoms attached: O (from OH), C (COOH), C (CH_3), H.
2. OH is first (O). COOH beats CH_3: its carbon carries (O, O, O) against (H, H, H).
3. H is last.

ANSWER Priority: –OH > –COOH > –CH_3 > –H. The direction 1 → 2 → 3 with H at the back then gives R or S.

KEY IDEA

R/S and + / − are unrelated. R/S is a naming rule from the 3D structure; (+)/(−) is measured with a polarimeter. (R)-glyceraldehyde happens to be (+), but (R)-lactic acid is (−). D/L is a third, older system based on glyceraldehyde.

SECTION G

Fischer projections

G

A flat drawing of a 3D stereocentre.

- **Horizontal lines** come **toward** you; **vertical lines** go **away**. The stereocentre sits where they cross.
- **If the lowest-priority group is on a vertical line:** read 1 → 2 → 3 directly.
- **If it is on a horizontal line** (the usual case with H): read 1 → 2 → 3 and **reverse** the answer.
- **Swapping any two groups once** inverts the configuration; swapping twice restores it.
- **Rotating the drawing by 180° in the plane** keeps the configuration; rotating by 90° inverts it.

SOLVED EXAMPLE 04 — READING A FISCHER PROJECTION

In a Fischer projection of glyceraldehyde, CHO is at the top, CH_2OH at the bottom, OH on the right and H on the left. Assign R or S.

SOLUTION

1. Priorities: OH (1) > CHO (2) > CH_2OH (3) > H (4).
2. OH (right) → CHO (top) → CH_2OH (bottom): going right → up → down around the centre is anticlockwise.
3. H is on a horizontal line (toward the viewer), so reverse: anticlockwise → clockwise.

ANSWER R — this is D-(+)-glyceraldehyde.

SECTION H

Counting stereoisomers

H

Start with 2^n, then look for symmetry.

$$\text{Maximum stereoisomers} = 2^n$$

n = number of stereogenic units (stereocentres + stereogenic double bonds)

- If the molecule can be divided into two identical halves, **meso** forms appear and the total drops.
- **Tartaric acid** (2 identical stereocentres): (R,R), (S,S) and meso — **3** stereoisomers, 2 optically active.

- **2,3-Dibromobutane:** 3 (a pair of enantiomers + meso). **2,3-Dibromopentane** (different ends): $2^2 = 4$, no meso.
- **Pent-3-en-2-ol** $CH_3CH{=}CHCH(OH)CH_3$: one stereocentre + one stereogenic C=C → 4.

SOLVED EXAMPLE 05 — SPOTTING MESO

How many stereoisomers does HOOC–CH(OH)–CH(OH)–COOH have, and how many are optically active?

SOLUTION

1. Two stereocentres → at most 4.
2. The molecule has two identical halves, so (R,S) and (S,R) are the same compound, with a mirror plane — meso.
3. (R,R) and (S,S) are a pair of enantiomers.

ANSWER 3 stereoisomers; 2 optically active, 1 meso.

CHECK YOURSELF

C3 How many stereoisomers does 2,3-dichlorobutane have?

C4 Is a meso compound chiral?

Answers at the end of the chapter.

SECTION I

Optical rotation

I

Measuring chirality with a polarimeter.

$$[\alpha] = \alpha / (l \times c)$$

α = observed rotation (degrees); l = tube length in dm; c = concentration in g mL^{-1}

- **Dextrorotatory (+ or d):** rotates to the right; **laevorotatory (− or l):** to the left.
- Enantiomers rotate by equal amounts in opposite directions; a racemate shows zero.

$$\text{Enantiomeric excess (ee)} = \text{observed } [\alpha] / [\alpha] \text{ of pure enantiomer} \times 100\%$$

% major = (100 + ee)/2; % minor = (100 − ee)/2

SOLVED EXAMPLE 06 — ENANTIOMERIC EXCESS

Pure (S)-X has [α] = +12.0°. A sample shows +6.0°. Find ee and the composition.

SOLUTION

1. ee = 6.0 / 12.0 × 100 = 50%.
2. Major (S) = (100 + 50)/2 = 75%; minor (R) = 25%.

ANSWER ee = 50%; 75% (S), 25% (R).

SECTION J

Conformations

J

Rotation about single bonds — not separate compounds.

- **Conformations** interconvert by rotation about σ bonds at room temperature, so they cannot be isolated (they are not isomers in the usual sense).
- **Ethane:** staggered (most stable) and eclipsed (least stable); the energy difference (torsional strain) is about 12.5 kJ mol^{-1}. Drawn as Newman or sawhorse projections.
- **Butane (C2–C3):** anti (CH_3 groups 180° apart, most stable) < gauche (60°, about 3.8 kJ mol^{-1} higher) < partly eclipsed < fully eclipsed (CH_3 on CH_3, least stable).
- **Cyclohexane:** the **chair** is the most stable (no angle strain, all bonds staggered); the boat is less stable (flagpole clash and eclipsing). Twist-boat lies between.
- In the chair, substituents prefer **equatorial** positions; an axial group suffers 1,3-diaxial interactions. A tert-butyl group locks the ring with itself equatorial.

Chirality without a stereocentre

- **Allenes** R(H)C=C=C(H)R with different groups on each end are chiral: the two end groups lie in perpendicular planes (e.g. penta-2,3-diene).
- **Biphenyls** with bulky ortho substituents cannot rotate freely about the central bond; if each ring is unsymmetrically substituted, the molecule is chiral (atropisomerism).

SECTION K

Exam trap gallery

K

Where marks are lost in stereochemistry.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
But-1-ene shows geometrical isomerism.	No — C1 carries two identical H atoms.

WHY Each double-bond carbon needs two different groups.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
cis always means Z.	Not always: Z/E uses CIP priority, cis/trans compares similar groups.

WHY 2-Chlorobut-2-ene: Z can be trans by the methyls.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
A molecule with stereocentres is always chiral.	Meso compounds have stereocentres but are achiral.

WHY An internal mirror plane cancels the rotation.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
(R) means dextrorotatory.	R/S is a naming rule; (+)/(−) is measured.

WHY (R)-lactic acid is (−).

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Lowest priority toward you: read the direction as it is.	Reverse the direction you read.

WHY The rule assumes group 4 points away.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Tartaric acid has 4 stereoisomers.	3: (R,R), (S,S) and meso.

WHY Two identical halves make (R,S) = (S,R).

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Conformers are isomers that can be separated.	They interconvert rapidly at room temperature.

WHY The rotation barrier is small (e.g. 12.5 kJ mol^{-1} for ethane).

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Swapping two groups in a Fischer projection keeps the configuration.	One swap inverts it; two swaps restore it.

WHY Each swap changes R ↔ S.

MEMORY HOOK

"Z = Zame Zide" — higher-priority groups together.

"Away and clockwise = R"; toward you, flip it.

"Two in a mirror = meso" — identical halves cut the count.

"Chair, equatorial, anti" — the comfortable choices.

SECTION L

Practice MCQs

L

Levels: Easy, Moderate, Tough.

Q01 Butan-1-ol and diethyl ether are: [EASY]

(a) chain isomers
(b) position isomers
(c) functional isomers
(d) metamers

Q02 Which shows geometrical isomerism? [EASY]

(a) But-1-ene
(b) But-2-ene
(c) 2-Methylpropene
(d) Propene

Q03 A carbon with four different groups is called: [EASY]

(a) achiral
(b) a stereocentre
(c) meso
(d) prochiral only

Q04 A racemic mixture is optically inactive because of: [EASY]

(a) internal compensation
(b) external compensation
(c) no stereocentre
(d) a plane of symmetry

Q05 The most stable conformation of butane is: [EASY]

(a) eclipsed
(b) gauche
(c) anti
(d) fully eclipsed

Q06 Highest CIP priority among these is: [MODERATE]

(a) $-CH_2OH$
(b) $-CHO$
(c) $-COOH$
(d) $-CH_3$

Q07 Number of stereoisomers of tartaric acid: [MODERATE]

(a) 2
(b) 3
(c) 4
(d) 5

Q08 Number of stereoisomers of 2,3-dibromopentane: [MODERATE]

(a) 2
(b) 3
(c) 4
(d) 8

Q09 Diastereomers have: [MODERATE]

(a) identical physical properties
(b) different physical properties
(c) equal and opposite rotations
(d) the same melting point always

Q10 In a Fischer projection the horizontal bonds point: [MODERATE]

(a) away from the viewer
(b) toward the viewer
(c) in the plane
(d) randomly

Q11 Which pair are metamers? [MODERATE]

(a) Ethanol and methoxymethane
(b) Diethyl ether and methyl propyl ether
(c) Propanal and propanone
(d) Butane and isobutane

Q12 A sample has ee = 80%. Its composition is: [MODERATE]

(a) 80:20
(b) 90:10
(c) 60:40
(d) 100:0

Q13 Which is chiral? [TOUGH]

(a) meso-tartaric acid
(b) Penta-2,3-diene
(c) Propa-1,2-diene
(d) 2,2-Dimethylpropane

Q14 Number of stereoisomers of $CH_3CH{=}CHCH(OH)CH_3$: [TOUGH]

(a) 2
(b) 3
(c) 4
(d) 8

Q15 Pure (R)-Y has [α] = -20°. A sample shows -5°. The percentage of (S)-Y is: [TOUGH]

(a) 25%
(b) 37.5%
(c) 62.5%
(d) 75%

Answer key with explanations

Q01 **(c) functional isomers** — Alcohol vs ether.

Q02 **(b) But-2-ene** — Each C=C carbon has two different groups.

Q03 **(b) a stereocentre** — Chiral centre.

Q04 **(b) external compensation** — Equal and opposite rotations.

Q05 **(c) anti** — CH_3 groups 180° apart.

Q06 **(c) –COOH** — C with (O, O, O).

Q07 **(b) 3** — Includes one meso.

Q08 **(c) 4** — Different ends; no meso.

Q09 **(b) different physical properties** — Not mirror images.

Q10 **(b) toward the viewer** — Horizontal = toward.

Q11 **(b) Diethyl ether and methyl propyl ether** — Same class, different alkyl groups.

Q12 **(b) 90:10** — (100 + 80)/2 = 90.

Q13 **(b) Penta-2,3-diene** — Allene with different end groups.

Q14 **(c) 4** — One C=C + one stereocentre.

Q15 **(b) 37.5%** — ee = 25%; minor = (100 - 25)/2.

Check-yourself answers

C1 No — C1 carries two hydrogen atoms.

C2 $-CH{=}CH_2$. At the first atom both give (C, C, H) — the double bond is counted twice. One atom further, the vinyl branch $=CH_2$ carries (C, H, H) while each methyl of isopropyl carries only (H, H, H), so

vinyl wins.

C3 Three: a pair of enantiomers and a meso form.

C4 No — it has stereocentres but is achiral (superimposable on its mirror image).

QUICK REVISION

One-page revision

Read this page the night before the exam.

Structural

- Chain, position, functional, metamers, tautomers
- C_4H_{10} 2; C_5H_{12} 3; C_6H_{14} 5
- $C_4H_{10}O$: 7 structural
- Keto ⇌ enol needs an α-H

Geometrical

- Each C=C carbon: two different groups
- cis: higher μ and b.p.; trans: higher m.p.
- Maleic (cis) → anhydride; fumaric cannot
- Also oximes, rings, N=N

CIP and E/Z

- Higher Z first; tie → go outward
- Double bonds duplicated
- Z = same side; E = opposite
- cis is not always Z

R/S and Fischer

- Lowest away: clockwise = R
- Lowest toward you: reverse
- Fischer: horizontal = toward
- One swap inverts; 180° rotation keeps

Counting and rotation

- Max 2^n; identical halves → meso
- Tartaric acid 3; 2,3-dibromopentane 4
- $[\alpha] = \alpha/(l \times c)$
- ee = obs/pure × 100; major = (100 + ee)/2

Conformations

- Ethane staggered; barrier ≈ 12.5 kJ
- Butane anti < gauche < eclipsed
- Cyclohexane chair; bulky equatorial
- Allenes, biphenyls: chiral, no stereocentre

END OF NOTES · RAMGOVINDYADAV.COM