

Stereoisomerism

How can two molecules with the same atoms, joined in the same order, still be different?

●● Intermediate

Organic Chemistry

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Before you start: it helps to understand [Hydrocarbons and Naming Alkanes](#) and [Functional Groups](#).

What is it?

Isomers are compounds with the same molecular formula but different structures. There are two main kinds:

- **Structural isomers** have their atoms **joined in a different order** (different chains, positions of a group, or functional groups), for example butane and methylpropane.
- **Stereoisomers** have the atoms joined in the **same order**, but arranged **differently in space**.

There are two types of stereoisomerism:

1. **Cis-trans (geometric, E/Z) isomerism**, caused by restricted rotation around a C=C double bond (or a ring).
2. **Optical isomerism**, caused by a **chiral centre**: a carbon atom bonded to four **different** groups.

KEY IDEA

Stereoisomers can only be told apart in **three dimensions**. Cis-trans isomers exist because a C=C double bond cannot rotate; optical isomers exist because a carbon with four different groups has two mirror-image arrangements that cannot be superimposed, like a left and a right hand.

Why does it matter?

- **Medicines.** Many drugs work like a key in a lock: only one mirror-image form fits the target in the body. The active form of ibuprofen is one enantiomer; the tragedy of thalidomide (1950s–60s) involved two enantiomers with different effects.
- **Smell and taste.** One form of limonene smells of oranges, its mirror image of lemons; one form of carvone smells of spearmint, the other of caraway.
- **Properties.** Cis and trans isomers have different boiling points, melting points and shapes, which matters in fats (cis and trans fats).

How does it work?

1. Cis-trans isomerism

A C=C double bond contains a π bond, so the carbons **cannot rotate** relative to each other. If **each** carbon of the double bond carries **two different** groups, two isomers exist:

- **cis**: the two similar groups on the **same side** of the double bond;
- **trans**: on **opposite sides**.

But-2-ene ($\text{CH}_3\text{CH}=\text{CHCH}_3$) has cis and trans isomers. But-1-ene ($\text{CH}_2=\text{CHCH}_2\text{CH}_3$) does not, because one carbon carries two identical H atoms.

2. The E/Z system

When the groups are all different, “cis” and “trans” are ambiguous. The **E/Z** system ranks the two groups on **each** carbon separately, using the **Cahn-Ingold-Prelog (CIP) priority rules** (section 4). The first rule is simply: higher atomic number = higher priority.

- **Z** (*zusammen*, together): the two higher-priority groups are on the **same side**.
- **E** (*entgegen*, opposite): they are on **opposite sides**.

3. Optical isomerism

A carbon bonded to four **different** atoms or groups is a **chiral centre** (often marked with an asterisk, C*). The molecule and its mirror image are **non-superimposable**: they are **enantiomers**. Enantiomers have identical boiling points, melting points and most chemical reactions, but they:

- rotate the plane of **plane-polarized light** in opposite directions (they are **optically active**);
- can behave differently with other chiral molecules, such as enzymes and receptors in the body.

A 50 : 50 mixture of two enantiomers is a **racemic mixture**; it does not rotate polarized light, because the two effects cancel.

4. The Cahn-Ingold-Prelog (CIP) priority rules

Both E/Z and R/S labels depend on ranking groups. Apply these rules **in order**, stopping as soon as the groups are ranked:

1. **Look at the atom directly attached.** Higher atomic number = higher priority: $\text{I} > \text{Br} > \text{Cl} > \text{S} > \text{F} > \text{O} > \text{N} > \text{C} > \text{H}$. (For isotopes, the heavier wins: $\text{D} > \text{H}$.)
2. **If there is a tie, move outwards.** For each tied group, list the **three** atoms attached to that first atom, highest first, and compare the lists item by item. The **first point of difference** decides.
 - $-\text{CH}_2\text{CH}_3$ is (C, H, H) and beats $-\text{CH}_3$, which is (H, H, H).

- $-\text{CH}_2\text{OH}$ is (O, H, H) and beats $-\text{CH}(\text{CH}_3)_2$, which is (C, C, H), because O beats C at the first comparison; you never add up the atoms.
3. **Count multiple bonds as duplicated atoms.** A double bond counts as two single bonds to the same element: $\text{C}=\text{O}$ is treated as C attached to (O, O); $\text{C}\equiv\text{N}$ as (N, N, N).
- $-\text{COOH}$ is (O, O, O); $-\text{CHO}$ is (O, O, H); so $-\text{COOH}$ beats $-\text{CHO}$.

5. Assigning R or S: step by step

Each chiral centre is labelled **R** or **S**, and the label becomes part of the name, for example (R)-butan-2-ol.

1. **Find the chiral centre:** the carbon with four different groups.
2. **Rank the four groups** 1 (highest) to 4 (lowest) with the CIP rules.
3. **Point group 4 away from you.** In a wedge-and-dash drawing it should be on the **hashed** bond. (Group 4 is very often H.)
4. **Trace a path from 1 to 2 to 3**, ignoring group 4.
5. **Read the direction:** clockwise = **R** (*rectus*, right); anticlockwise = **S** (*sinister*, left).
6. **If group 4 points towards you** (on a solid wedge), work out the direction as drawn and then **reverse** it: clockwise means S, anticlockwise means R.

A helpful check: swapping **any two** groups on a chiral centre turns R into S (and S into R).

∞ THINK OF IT LIKE THIS

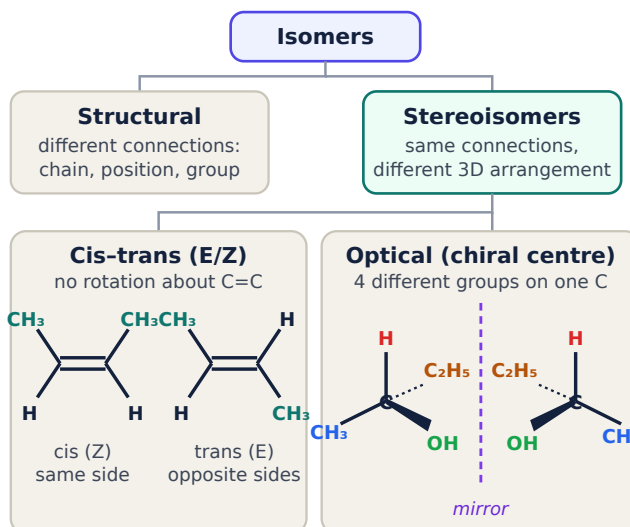
Your hands are the classic chiral objects: they are mirror images, but no matter how you turn them, a left hand never fits exactly over a right one. A left-hand glove won't fit a right hand, just as one enantiomer of a drug may not fit its target in the body.

🔍 MORE PRECISELY

R and S describe the **arrangement in space**; the sign of optical rotation, + or –, is **measured** with a polarimeter. The two are not linked: some R compounds rotate light to the right (+) and others to the left (–). Older books label amino acids and sugars D or L instead, a system based on comparison with glyceraldehyde. Molecules can have more than one chiral centre; a molecule with n chiral centres can have up to 2^n stereoisomers.

Types of isomerism

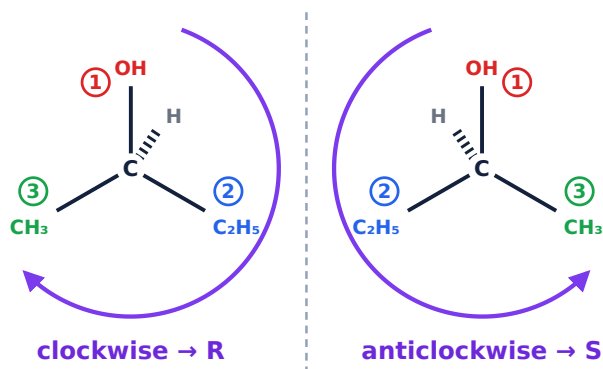
Same molecular formula, different structure



Types of isomerism, with cis/trans-but-2-ene and a pair of mirror-image (chiral) molecules.

Assigning R and S: butan-2-ol

Priorities: OH (1) · CH₂CH₃ (2) · CH₃ (3) · H (4)



- 1 Rank the four groups with the CIP rules (1 = highest).
- 2 Point group 4 away from you (hashed bond).
- 3 Trace 1 → 2 → 3: clockwise = R, anticlockwise = S.
(If group 4 points towards you, reverse the answer.)

R/S in three steps: rank the groups, put group 4 at the back, then trace 1 → 2 → 3 (clockwise = R, anticlockwise = S).

Worked example

WORKED EXAMPLE: Which alkenes show cis-trans isomerism?

Question: Which of these show cis-trans isomerism: (a) propene, $\text{CH}_2=\text{CHCH}_3$ (b) 1,2-dichloroethene, $\text{ClCH}=\text{CHCl}$ (c) 2-methylbut-2-ene, $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$?

Step 1 (a) The first carbon has two H atoms: **no**.

Step 2 (b) Each carbon has H and Cl (two different groups): **yes**, cis and trans forms. Their boiling points differ: cis 60 °C, trans 48 °C, because the cis isomer is polar.

Step 3 (c) One carbon has two CH_3 groups: **no**.

WORKED EXAMPLE: Assigning E or Z

Question: In $\text{CHCl}=\text{CHBr}$, the Cl and Br atoms are on the same side of the double bond. Is this the E or the Z isomer?

Step 1 On one carbon, Cl (atomic number 17) outranks H (1).

Step 2 On the other carbon, Br (35) outranks H (1).

Step 3 The two higher-priority atoms, Cl and Br, are on the **same side**: **Z**.

WORKED EXAMPLE: Finding a chiral centre

Question: Which carbon in butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, is a chiral centre?

Carbon 2 is bonded to **four different groups**: $-\text{H}$, $-\text{OH}$, $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$. It is a chiral centre, so butan-2-ol exists as **two enantiomers**. No other carbon qualifies: each of the others carries at least two H atoms.

WORKED EXAMPLE: Ranking groups with the CIP rules

Question: Rank the four groups on the chiral carbon of alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$.

Step 1 Attached atoms: N (in $-\text{NH}_2$), C (in $-\text{COOH}$), C (in $-\text{CH}_3$) and H.

Step 2 N has the highest atomic number: $-\text{NH}_2$ is **1**. H is lowest: **4**.

Step 3 Tie between the two carbons: $-\text{COOH}$ is (O, O, O), counting C=O twice; $-\text{CH}_3$ is (H, H, H). So $-\text{COOH}$ is **2** and $-\text{CH}_3$ is **3**.

 WORKED EXAMPLE: Assigning R or S

Question: A drawing of butan-2-ol shows the chiral carbon with H on a hashed bond (pointing away), OH at the top, CH_2CH_3 at the lower right and CH_3 at the lower left. Is it R or S?

- Step 1** Priorities: $-\text{OH}$ 1 (O); $-\text{CH}_2\text{CH}_3$ 2 (C, H, H); $-\text{CH}_3$ 3 (H, H, H); $-\text{H}$ 4.
- Step 2** Group 4 (H) already points away from you.
- Step 3** Trace 1 $\rightarrow$ 2 $\rightarrow$ 3: top $\rightarrow$ lower right $\rightarrow$ lower left. That is **clockwise**, so the molecule is **(R)-butan-2-ol** (the left-hand molecule in the figure).
- Step 4** If the same drawing had H on a solid wedge (towards you), the clockwise path would have to be reversed: it would be **S**.

 WORKED EXAMPLE: E or Z with a tie-break

Question: In 3-methylpent-2-ene, $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_3$, the CH_3 on carbon 2 and the CH_2CH_3 on carbon 3 are on the same side. Is it E or Z?

- Step 1** Carbon 2 carries $-\text{CH}_3$ and $-\text{H}$: $-\text{CH}_3$ has the higher priority.
- Step 2** Carbon 3 carries $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_3$: both start with C, so move outwards: (C, H, H) beats (H, H, H), so $-\text{CH}_2\text{CH}_3$ has the higher priority.
- Step 3** The two higher-priority groups are on the **same side**: **Z**.

 WORKED EXAMPLE: Amino acids

Question: Explain why alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, is chiral but glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}$, is not.

The central carbon in alanine carries $-\text{H}$, $-\text{CH}_3$, $-\text{NH}_2$ and $-\text{COOH}$: four different groups, so it is chiral. In glycine, the central carbon carries **two** H atoms, so it is not.

Common mistake

 **COMMON MISTAKE:** Forgetting that both carbons need two different groups

Cis-trans isomerism needs **two different groups on each** carbon of the double bond. If either carbon has two identical groups (such as two H atoms), there is only one form.

 **COMMON MISTAKE:** Calling any carbon with four bonds chiral

A chiral centre needs four **different** groups. A CH_2 or CH_3 carbon is never chiral, because it has at least two identical H atoms.

 COMMON MISTAKE: Thinking E always means trans

E/Z depends on **priority**, not on which groups look alike. In some molecules the E isomer has the similar groups on the same side, so “E = trans” is only true when the two pairs of groups are the same.

 COMMON MISTAKE: Forgetting to reverse when group 4 points towards you

The clockwise = R rule only works when the lowest-priority group points **away** from you. If it is on a solid wedge, the answer you read off must be **reversed**.

 COMMON MISTAKE: Adding up atoms in a tie-break

CIP ranking compares atoms **one at a time**, highest first, and stops at the first difference. (O, H, H) beats (C, C, C), because O beats C straight away.

 COMMON MISTAKE: Thinking R means (+)

R and S come from the 3D arrangement; + and – come from an experiment with polarized light. There is no simple link between them.

 NOTATION NOTE

- Wedges (▲) point towards you; hashed wedges point away; plain lines lie in the page.
- A chiral centre is often marked with an asterisk: C*.

Remember this

REMEMBER THIS

- **Structural isomers:** different connections. **Stereoisomers:** same connections, different 3D arrangement.
- **Cis-trans** needs a C=C (no rotation) with two different groups on each carbon.
- **CIP rules:** higher atomic number first; if tied, move outwards and compare at the first difference; multiple bonds count as duplicated atoms.
- **E/Z:** rank the two groups on each carbon; Z = higher priorities together; E = opposite.
- **R/S:** rank 1–4, point 4 away, trace 1 → 2 → 3: clockwise R, anticlockwise S (reverse if 4 points towards you).
- A **chiral centre** has four different groups; it gives a pair of non-superimposable mirror images (enantiomers).
- **Enantiomers** rotate plane-polarized light in opposite directions; a racemic mixture does not rotate it.

References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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