

# Isomerism

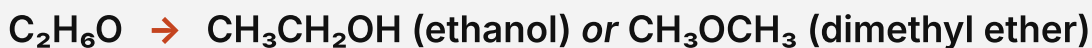
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- |                                   |                                    |
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## 1 At a glance

### Isomers: same molecular formula, different arrangement

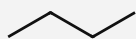
- **Isomers** are different compounds with the **same molecular formula**.
- **Structural (constitutional) isomers** differ in which atoms are joined to which.
- **Stereoisomers** have the same connections but a different arrangement in 3D.
- Because isomers are different compounds, their properties differ. Only enantiomers share almost all physical properties.



An early famous pair: in 1828 Wöhler heated ammonium cyanate and obtained urea. Both have the formula  $CH_4N_2O$ , yet they are completely different compounds.

## 2 Structural isomers

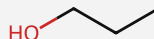
Structural isomers have the same atoms joined in a different order. There are four main types, plus two special cases.



**Butane**  
straight chain,  
 $C_4H_{10}$



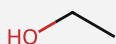
**2-Methylpropane**  
branched chain,  
 $C_4H_{10}$



**Propan-1-ol**  
OH on C1,  $C_3H_8O$



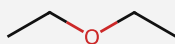
**Propan-2-ol**  
OH on C2,  $C_3H_8O$



**Ethanol**  
an alcohol,  $C_2H_6O$



**Methoxymethane**  
an ether,  $C_2H_6O$



**Ethoxyethane**  
 $C_2H_5 \mid C_2H_5$ ,  
 $C_4H_{10}O$



**1-Methoxypropane**  
 $CH_3 \mid C_3H_7$ ,  $C_4H_{10}O$

Pairs, left to right: chain isomers, position isomers, functional group isomers, metamers.

| Type                | What changes                                                           | Example pair (same formula)                                                           |
|---------------------|------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| Chain               | the carbon skeleton:<br>straight or branched                           | butane and 2-methylpropane ( $C_4H_{10}$ )                                            |
| Position            | the position of a group or<br>multiple bond on the same<br>chain       | propan-1-ol and propan-2-ol<br>( $C_3H_8O$ ); but-1-ene and but-2-ene<br>( $C_4H_8$ ) |
| Functional<br>group | the functional group itself                                            | ethanol and methoxymethane<br>( $C_2H_6O$ ); propanal and propanone<br>( $C_3H_6O$ )  |
| Metamerism          | the alkyl groups on either<br>side of $-O-$ , $-S-$ , $-NH-$ or $-CO-$ | ethoxyethane and 1-methoxypropane<br>( $C_4H_{10}O$ )                                 |
| Ring-chain          | an open chain or a ring                                                | propene and cyclopropane ( $C_3H_6$ )                                                 |
| Tautomerism         | an H atom and a double<br>bond move, in rapid<br>equilibrium           | propanone and prop-1-en-2-ol (keto<br>and enol forms)                                 |

**Careful: tautomers are real isomers, not resonance structures.**

Tautomers differ in where an atom (usually H) sits, so they are separate compounds in equilibrium. Resonance structures differ only in where electrons are drawn; they are not separate compounds.

### 3 How many isomers?

The number of structural isomers grows explosively as the carbon chain gets longer. For the alkanes:

| Alkane formula | Structural isomers |                                                                                      |
|----------------|--------------------|--------------------------------------------------------------------------------------|
| $C_4H_{10}$    | 2                  |     |
| $C_5H_{12}$    | 3                  |    |
| $C_6H_{14}$    | 5                  |    |
| $C_7H_{16}$    | 9                  |    |
| $C_8H_{18}$    | 18                 |    |
| $C_9H_{20}$    | 35                 |    |
| $C_{10}H_{22}$ | 75                 |    |
| $C_{20}H_{42}$ | 366,319            |  |

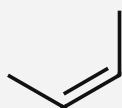
Data: OpenStax *Organic Chemistry*, section 3.2 (Table 3.2). The bar is on a log scale.

#### Why so many?

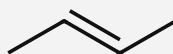
Every extra carbon can be attached at several different positions on each smaller skeleton, so the number of distinct branching patterns multiplies at every step.

### 4 Geometrical (cis-trans) isomers

When rotation about a bond is blocked (a C=C double bond, or a ring), two groups can sit on the **same side** (cis) or on **opposite sides** (trans).



**cis-But-2-ene (Z)**  
bp 3.7 °C · mp -138.9 °C



**trans-But-2-ene (E)**  
bp 0.8 °C · mp -105.5 °C

Melting and boiling points: Wikipedia, '2-Butene'. The more symmetrical trans isomer packs better in the solid, so it melts higher.

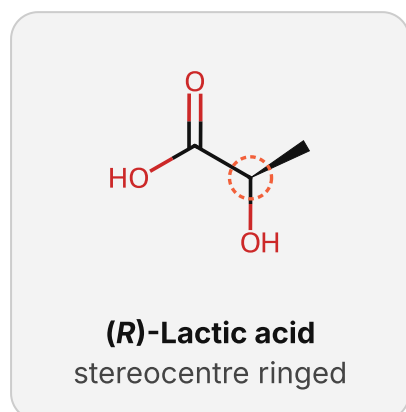
- Two conditions: **restricted rotation**, and **two different groups on each carbon** of the double bond.
- But-1-ene,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_3$ , has no cis/trans isomers: C1 carries two identical H atoms.
- Rings work too: cis- and trans-1,2-dimethylcyclohexane cannot interconvert without breaking a bond.

### E/Z works for every alkene.

Cis/trans is fine when each carbon has one H. For crowded alkenes, rank the two groups on each carbon by CIP priority: higher-priority groups on the same side = **Z** (*zusammen*, together); opposite sides = **E** (*entgegen*, opposite).

## 5 Optical isomers: enantiomers and diastereomers

A carbon carrying four different groups is a **stereocentre** (chiral carbon,  $\text{C}^*$ ). The molecule and its mirror image cannot be laid on top of each other: they are **enantiomers**.



- **Enantiomers** are non-superimposable mirror images. They have identical melting points, boiling points and solubilities, and rotate plane-polarised light by equal amounts in opposite directions.
- **Diastereomers** are stereoisomers that are not mirror images: for example cis- and trans-but-2-ene, or two forms of a molecule with two stereocentres that differ at only one of them. Their physical properties differ.
- A 50:50 mixture of two enantiomers is a **racemic mixture**. It is optically inactive, because the two rotations cancel.

## 6 How to classify any pair

Ask three questions, in this order:

| Question                           | If yes                          | If no                                           |
|------------------------------------|---------------------------------|-------------------------------------------------|
| 1. Same molecular formula?         | go to question 2                | not isomers                                     |
| 2. Atoms joined in the same order? | stereoisomers: go to question 3 | structural isomers                              |
| 3. Mirror images of each other?    | enantiomers                     | diastereomers (this includes cis/trans isomers) |

### First check: are they identical?

Before calling two drawings isomers, turn one of them in your mind. If it can be laid exactly on the other, they are the same compound drawn two ways.

## 7 Do isomers behave differently?

| Pair               | Physical properties                                         | Chemical properties                                                                            |
|--------------------|-------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Structural isomers | different: ethanol boils at 78 °C, dimethyl ether at -24 °C | usually different: ethanol reacts with sodium to give H <sub>2</sub> ; dimethyl ether does not |
| Diastereomers      | different melting points, boiling points and solubilities   | similar reactions, but at different rates                                                      |
| Enantiomers        | identical, except the direction of optical rotation         | identical with non-chiral reagents; different with chiral ones such as enzymes                 |

### Why do enantiomers smell different?

The receptors in your nose are chiral. (*R*)-(-)-Carvone smells of spearmint and (*S*)-(+)-carvone of caraway seeds (Wikipedia, 'Carvone').

## 8 One-minute revision

1. Isomers: same molecular formula, different compounds.
2. Structural: chain, position, functional group, metamerism (plus ring–chain and tautomerism).
3. Stereoisomers: same connections, different 3D arrangement.
4. Cis/trans needs restricted rotation and two different groups on each carbon; E/Z is the general system.
5. Enantiomers are mirror images with identical physical properties; diastereomers are not mirror images and differ.

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Organic Pulse · free notes by Dr. Sandeep G. Sontakke. Main sources: NCERT Chemistry Class 11, Unit 8 (section 8.6); OpenStax *Organic Chemistry*, sections 3.2 and 5.9; Clayden *et al.*, *Organic Chemistry* (2nd ed.), ch. 14.

Watch the shorts: [youtube.com/@OrganicPulse-y9q](https://youtube.com/@OrganicPulse-y9q)