

Geometrical Isomerism

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Definition:

- Geometrical isomerism is a type of stereoisomerism (same molecular formula and bonding order, but different spatial arrangements of atoms or groups).
- It occurs due to the restricted rotation around double bonds or within cyclic compounds, especially when two different groups are attached to the atoms involved in the restriction.

Why rotation is restricted?

- In a **C=C double bond**, one bond is sigma (σ), and the other is pi (π).
- The π -bond is formed by the sideways overlap of unhybridized p orbitals.
- Rotating around the double bond would break the π -bond, which requires energy.
- Therefore, rotation is restricted, and different spatial arrangements are possible.

Conditions for geometrical isomerism:

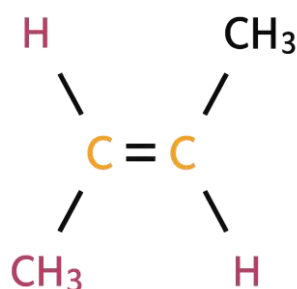
- There must be a rigid structure like:
 - C=C double bond**
 - C=N double bond** (in oximes)
 - Ring systems** (cyclic compounds)
- Each of the doubly bonded carbon atoms (or the atoms with restricted rotation) must be attached to two different groups.

Examples:

- Alkenes:** 2-butene ($\text{CH}_3\text{CH}=\text{CHCH}_3$) – exists in **cis** and **trans** forms.
- Cyclic compounds:** 1,2-dichlorocyclohexane – can show **cis** and **trans** forms based on the position of Cl atoms.
- Oximes:** $\text{CH}_3\text{CH}=\text{NOH}$ (aldoximes and ketoximes)

For example:

trans-2-butene



- Swapping the positions of H and CH_3 on one carbon leads to a different isomer.

Nomenclature of Geometrical Isomers

There are **three main systems** used to name geometrical isomers:

1. Cis-Trans Nomenclature

- **When it is used:** Simple alkenes or cycloalkanes with identical groups
- **Basis of naming:** Relative positioning of identical groups

2. E-Z Nomenclature

- **When it is used:** Alkenes with different groups on each double-bonded carbon
- **Basis of naming:** Priority based on atomic number (Cahn-Ingold-Prelog rules)

3. Syn-Anti Nomenclature

- **When it is used:** Oximes, imines, enols, etc.
- **Basis of naming:** Position of specific groups (e.g., OH, H) relative to each other

Cis-Trans Nomenclature

When to Use:

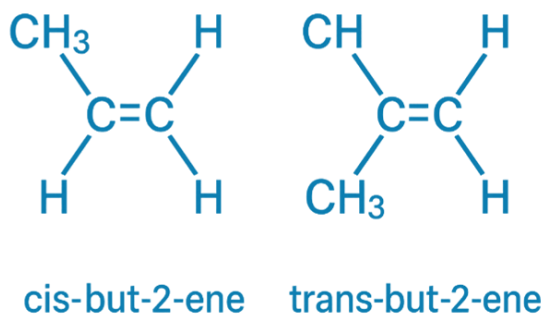
- Use the Cis-Trans system when each carbon in the double bond has one identical group.
- It is suitable for:
 - Simple **alkenes** with symmetrical groups,
 - **Cycloalkanes**, where two substituents are on the ring.

Definitions:

- **Cis:** Similar or identical groups are on the **same side** of the double bond or ring.
- **Trans:** Similar or identical groups are on **opposite sides**.

Example:

But-2-ene



- In the **cis isomer**, the two CH₃ groups are on the same side.
- In the **trans isomer**, they are on opposite sides.

E-Z Nomenclature System (Cahn-Ingold-Prelog Priority Rules)

Why Use E-Z?

- When each carbon in the double bond has two different substituents, the cis-trans system is not sufficient.
- In such cases, the E-Z system provides a consistent method to assign configuration.

Step-by-Step Rules:

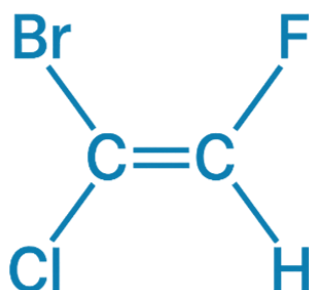
1. **Identify** the double bond and the two carbon atoms involved.
2. **Assign priorities** to the substituents on each carbon using **Cahn-Ingold-Prelog rules**:
 - Higher atomic number = higher priority.
 - If the first atoms are identical, move outward along the chain until a difference is found.
 - Double/triple bonds are treated as multiple single-bonded atoms for priority purposes.
3. **Determine configuration**:
 - If the two highest-priority groups are on the **same side**, the isomer is **Z** (from the German *Zusammen*, meaning together).
 - If they are on **opposite sides**, the isomer is **E** (from the German *Entgegen*, meaning opposite).

Advantages:

- Applicable to **any alkene**, including complex cases.
- Avoids ambiguity present in the cis-trans system.

Example:

1-bromo-1-chloro-2-fluoroethene



- **Left carbon (C1):**
 - Br (Z = 35) > Cl (Z = 17) → Br is higher priority.
- **Right carbon (C2):**
 - F (Z = 9) > H (Z = 1) → F is higher priority.
- Since **Br and F are on opposite sides** of the double bond → **E-isomer**.
- If Br and F were on the **same side**, it would be the **Z-isomer**.



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