

Isomerism

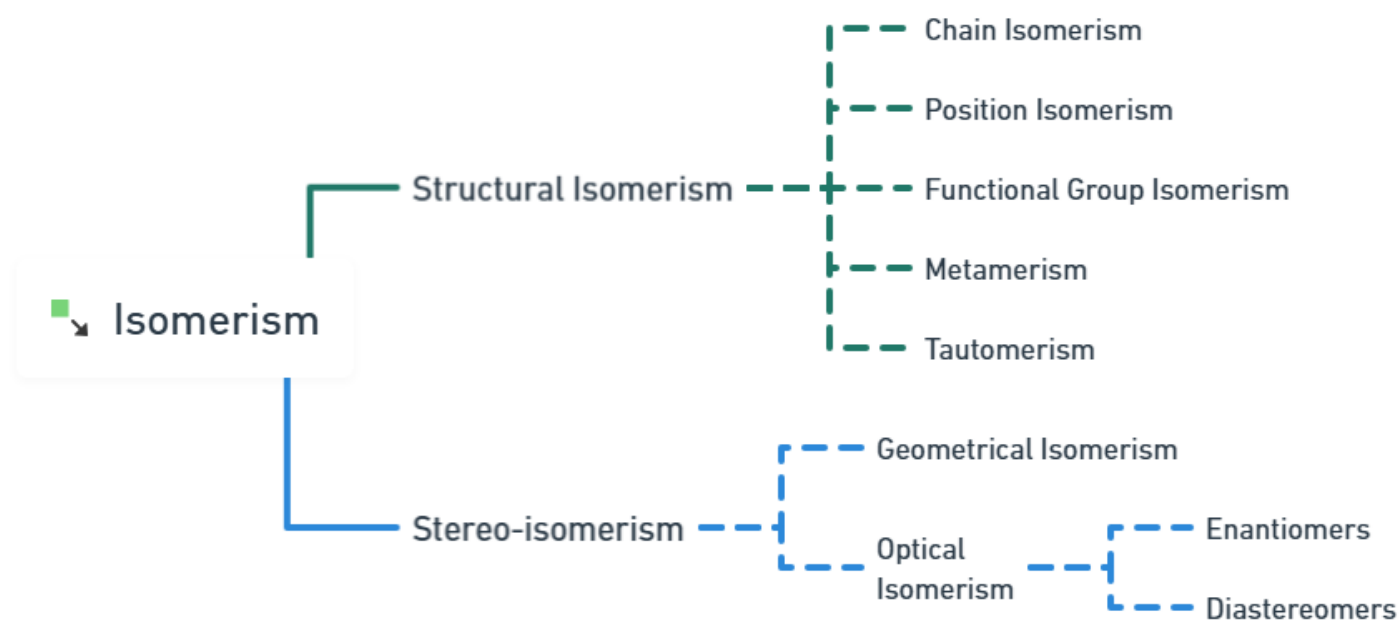
Isomerism

- Isomerism is a phenomenon where two or more compounds have the same molecular formula (i.e., same number and types of atoms), but different structures or arrangements of atoms, leading to different physical, chemical, and biological properties.

Classification of Isomerism:

- Isomerism is broadly classified into two main types:

1. **Structural (or Constitutional) Isomerism**
2. **Stereoisomerism**



Structural isomerism

- Structural isomerism**, also known as **constitutional isomerism**, is a type of isomerism where compounds have the same **molecular formula** but differ in the **connectivity or arrangement** of their atoms.
- Though the isomers contain the same number and types of atoms, the way these atoms are connected is different, leading to variations in chemical and physical properties.
- Structural isomerism is classified into several types based on how the atomic arrangements differ.

1. Chain Isomerism

Description:

- Involves compounds with different arrangements of the carbon skeleton, which can manifest as straight chains, branched chains, or a mix of both.

Example:

- C_5H_{12} represents:
 - **n-Pentane** (straight-chain)
 - **2-Methylbutane** (branched-chain)

2. Position Isomerism**Description:**

- Occurs when compounds have identical molecular formulas and functional groups, but the functional groups are located at different positions on the carbon chain.

Example:

- C_3H_8O represents:
 - **1-Propanol** (hydroxyl group on carbon-1)
 - **2-Propanol** (hydroxyl group on carbon-2)

3. Functional Group Isomerism**Description:**

- Features compounds that share the same molecular formula but have different functional groups, leading to distinct chemical properties.

Example:

- C_2H_6O represents:
 - **Ethanol** (alcohol, $-OH$ functional group)
 - **Dimethyl Ether** (ether, $-O-$ functional group)

4. Metamerism**Description:**

- Characterized by compounds with the same molecular formula and functional group but differing in the distribution of alkyl groups on either side of the functional group.
- This type of isomerism is typical in ethers and esters.

Example:

- $C_4H_{10}O$ represents:
 - **Diethyl Ether** ($CH_3CH_2-O-CH_2CH_3$)
 - **Methyl Propyl Ether** ($CH_3-O-CH_2CH_2CH_3$)
- These compounds exhibit metamerism due to the different alkyl group distributions around the oxygen atom.

5. Tautomerism**Description:**

- A unique form of structural isomerism where isomers can rapidly interconvert, typically through proton migration.
- Tautomers coexist in equilibrium, influenced by environmental conditions like temperature and pH.

Example:

- **Acetone** (C_3H_6O) predominantly exists in the keto form, but a minor fraction can be found in the enol form (an adjacent alcohol and carbon-carbon double bond), exemplifying keto-enol tautomerism.

Stereoisomerism

- **Stereoisomerism** is a form of **isomerism** in which molecules have:
 - The **same molecular formula**
 - The **same sequence of bonded atoms** (i.e., the same structural formula)
 - But a **different spatial arrangement** of atoms or groups in 3D space
- So, unlike structural (constitutional) isomers, stereoisomers differ only in how atoms are oriented in space, not in how they're connected.

Classification of Stereoisomerism

A. Geometrical Isomerism (cis-trans or E/Z)

- Occurs due to restricted rotation (e.g., around double bonds or in cyclic systems)
- Groups are arranged differently in space relative to a reference plane
- **Examples:**
 - **Cis-but-2-ene** (same groups on the same side)
 - **Trans-but-2-ene** (same groups on opposite sides)
 - **E/Z isomerism** in alkenes with different substituents

B. Optical Isomerism

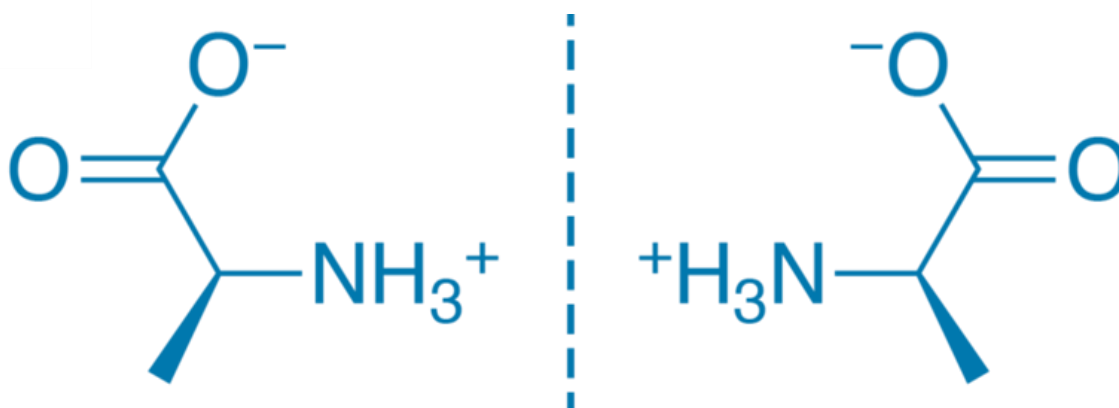
- Arises due to the presence of chiral centers or asymmetry
- Molecules that can rotate plane-polarized light
- Based on the concept of chirality

Optical Isomerism

Definition:

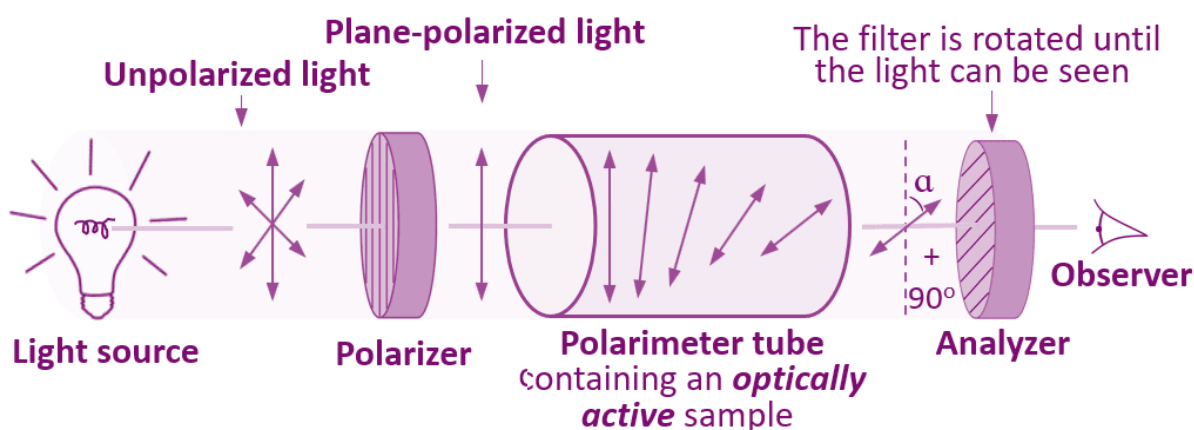
- Optical isomerism occurs when molecules can exist in two (or more) non-superimposable forms (stereoisomers) that differ in the way they interact with plane-polarized light.

- If a molecule can rotate the plane of polarized light, it is said to be "optically active."



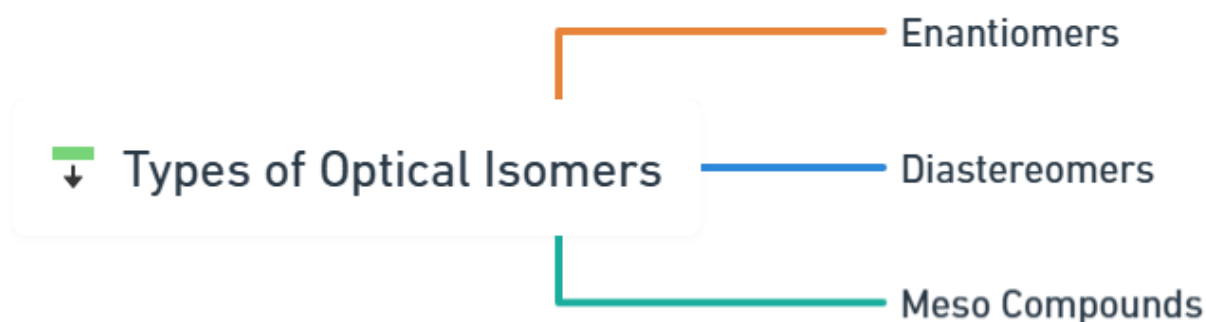
How Optical Activity is Measured

- Plane-Polarized Light:** Ordinary light consists of waves vibrating in all planes. A polarizer (like a Nicol prism) filters out all but one plane of vibration, creating plane-polarized light.
- Polarimeter:** An instrument used to measure how much a substance rotates plane-polarized light.
 - If the substance rotates the plane to the right (clockwise), it is called "dextrorotatory" (labeled as "+" or "d-").
 - If it rotates the plane to the left (counterclockwise), it is called "levorotatory" (labeled as "-" or "l-").



The polarizer passes the light in *only one plane*

Types of Optical Isomers



A. Enantiomers

- Non-superimposable mirror images

- Identical physical properties (except for optical rotation)
- Rotate plane-polarized light equally but in opposite directions
- **Represented as:**
 - **(+)-enantiomer** (dextrorotatory)
 - **(-)-enantiomer** (levorotatory)

B. Diastereomers

- Stereoisomers that are not mirror images
- Occur when there are two or more chiral centers
- Physical and chemical properties are different
- **Example:** In a molecule with 2 chiral centers, (R,R) and (R,S) are diastereomers

C. Meso Compounds

- Contain chiral centers
- But are achiral overall due to an internal plane of symmetry
- Are optically inactive
- Superimposable on their mirror images
- **Example:** Meso-tartaric acid

Racemic Mixtures

- A **1:1 mixture of two enantiomers**
- Optical activities **cancel each other out**
- The mixture is **optically inactive**
- Symbolized as: (±)-compound

Number of Optical Isomers

- If a compound has n chiral centers, the maximum number of stereoisomers is:
- 2^n , where:
 - Half are enantiomers
 - The rest may be diastereomers
 - Subtract meso forms (if any) to find optically active forms

Example:

- A molecule with 2 chiral centers → up to **4 isomers**
 - (R,R), (S,S), (R,S), (S,R)
 - If (R,S) and (S,R) are **meso**, then only 3 unique stereoisomers exist



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