

13.3 ISOMERISM IN ORGANIC COMPOUNDS

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Learning outcomes

By the end of this chapter, students should be able to:

- Define and classify isomerism in organic compounds (structure isomerism, types of structure isomerism: chain isomerism, position isomerism, functional isomerism, metamerism and tautomerism).
- State and explain the concept of geometrical isomerism (cis & trans) & optical isomerism (d & l form).

13.3 Isomerism in Organic Compounds

Isomers are different compounds possessing the same molecular formula. The phenomenon by which **different compounds are represented by the same molecular formula** is called isomerism.



Think

Same formula, different arrangement → Isomers



Remember

Same molecular formula ≠ necessarily the same compound.

13.4 Classification of Isomerism



Types of isomerism:

Isomerism is of two different types:

1. Structural isomerism
2. Stereoisomerism

13.5 Structural isomerism and its types: chain isomerism, position isomerism, functional isomerism, metamerism and tautomerism

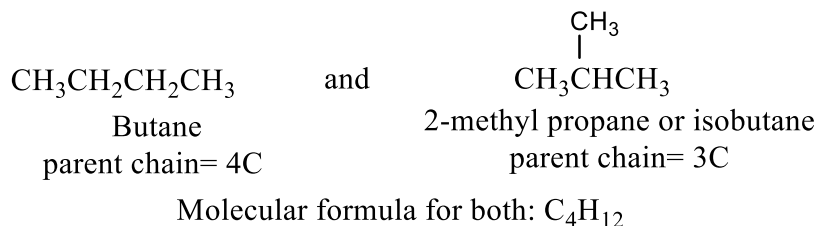
Structural isomerism

Compounds with the **same molecular formula but different structures** are termed structural isomers, and the phenomenon is called structural isomerism. There are 5 types of structural isomers:

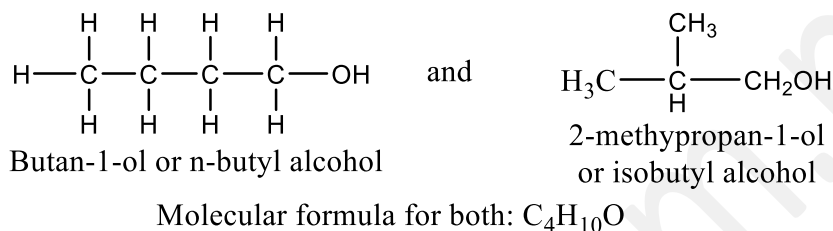
1. Chain or nuclear, or skeletal isomerism
2. Position isomerism
3. Functional isomerism
4. Tautomerism
5. Metamerism

1. Chain (or skeletal) isomerism

If two or more compounds have the **same molecular formula but have different carbon chains** or skeletons, then they are called chain isomers. This phenomenon is called chain isomerism. For example: C_4H_{10} . The two isomers of C_4H_{10} differ only in the length of the carbon chain.



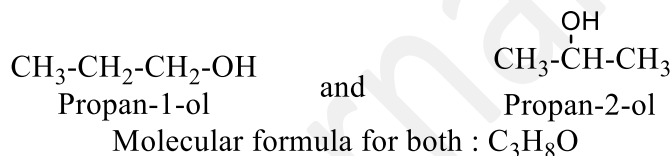
Similarly, butyl alcohol and isobutyl alcohol are two chain isomers



2. Position isomerism

The compounds having the same molecular formula but **different positions of functional groups** (or multiple bonds or substituents) are termed as position isomers. Such phenomenon is known as positional isomerism.

For example, the two isomers of the compound having molecular formula C_3H_8O are as follows:

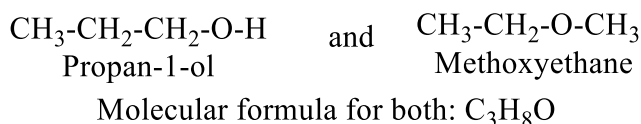


3. Functional isomerism

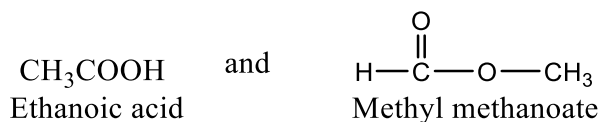
The compounds with the same molecular formula but **different functional groups** are termed as functional isomers, and the phenomenon is known as functional isomerism.

For example,

1. Aldehydes and ketones, e.g. $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3
2. Alcohol and ether, e.g. $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3

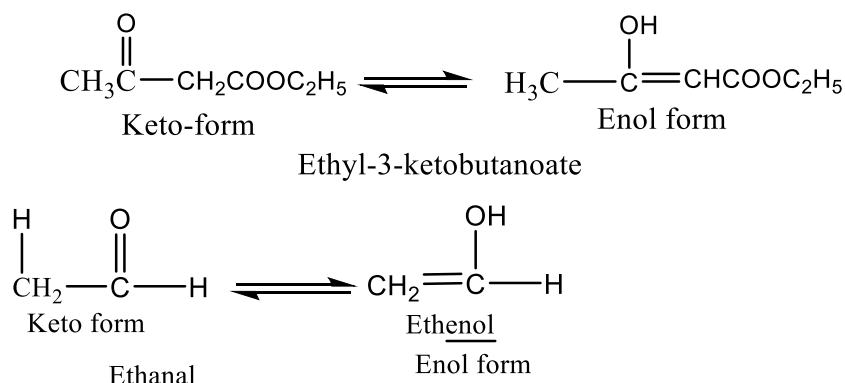


3. Carboxylic acid and esters, e.g.



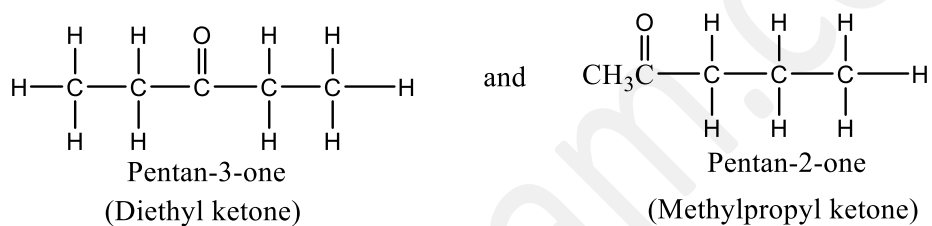
4. Tautomerism

It is a **special** type in which the isomers are interconvertible due to the **change in the position of the hydrogen** atom within the molecule. For example:



5. Metamerism

The compounds of the same family having the same molecular formula, which **differ in the arrangement of carbon atoms on either side of the functional group**, are termed metamers, and the phenomenon is called metamerism. *Ketones, Ethers, Esters*, etc., can exhibit metamerism.



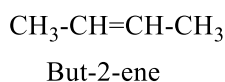
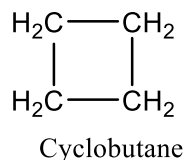
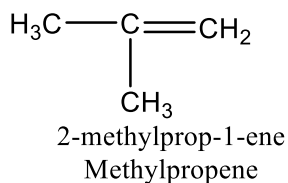
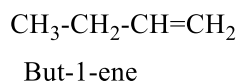
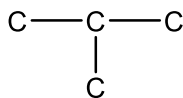
Molecular formula for both: $\text{C}_5\text{H}_{10}\text{O}$



Both have $\text{C}_4\text{H}_{10}\text{O}$, but the carbon groups on the two sides of $-\text{O}-$ are distributed differently.

Worked Example

Write down two structural isomers and their IUPAC names of C_4H_8 .



13.6 Concept of geometrical isomerism and optical isomerism

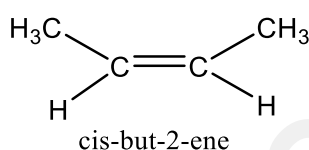
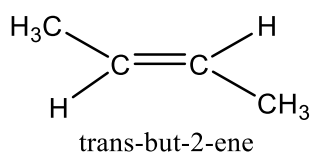
Compounds having the same molecular formula and structural formula but different spatial arrangements of the atoms or groups of atoms in a molecule are called stereoisomers. The phenomenon of existence of such compounds is called **stereoisomerism**.

Stereoisomerism can be further subdivided into geometrical and optical isomerism.

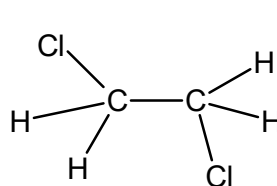
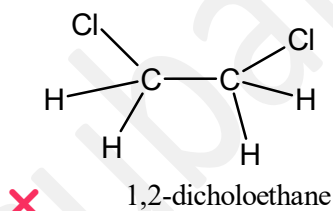
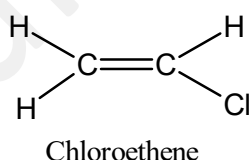
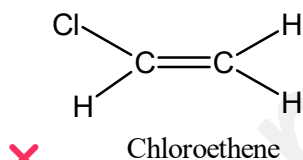
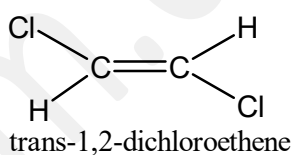
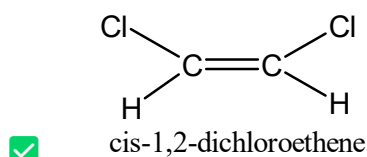
Geometrical Isomerism (cis, trans isomerism)

When the same molecular formula represents two compounds which differ in the spatial arrangement of atoms or groups around a carbon-carbon double bond, these are geometrical isomers. Such isomerism arises due to the inability to rotate around a double bond.

e.g, But-2-ene has two geometrical isomers, i.e, cis-but-2-ene and trans-but-2-ene



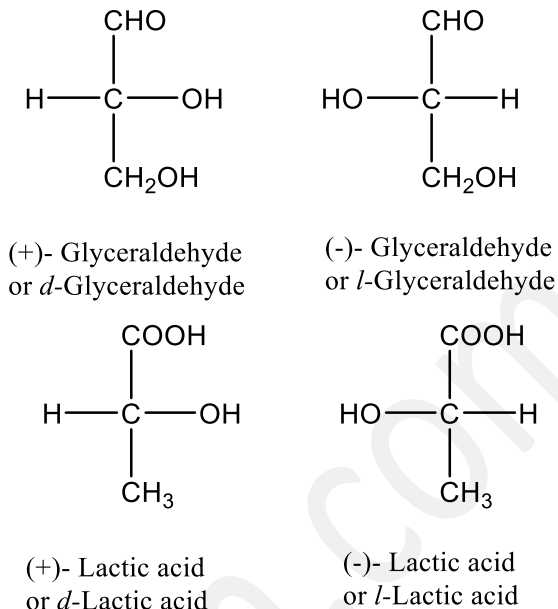
1,2-dichloroethene can be taken as another example of such isomerism.



Optical isomerism

- Optical isomerism can be defined as the phenomenon by which isomers are obtained due to different arrangements of atoms or groups in three-dimensional space.
- Optical isomerism is a type of stereoisomerism shown by compounds whose non-superimposable mirror-image forms differ in their interaction with plane-polarised light**
- Such compounds resemble each other in their chemical and most physical properties but differ in **optical rotation**.

- Optical rotation is a phenomenon where the plane of the **plane-polarised light** is rotated either in a clockwise or anticlockwise direction.
- The optical rotation is measured by an instrument called a polarimeter.
- The optical isomers which are mirror images of each other are called **enantiomers**.
- The enantiomer which rotates the plane of polarised light in the clockwise direction (right) and the anti-clockwise direction are called dextrorotatory and laevorotatory, respectively and designated as + or *d*- and - or *l*-, respectively.



For a compound to exhibit enantiomerism, there should be the presence of a chiral carbon atom. A carbon atom that is bonded to 4 different groups is called a chiral carbon. In the above four examples, it can be seen that the central atom is chiral.

★ Quick revision

Structural → different connectivity

Stereoisomerism → same connectivity, different 3-D arrangement

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