

CHAPTERWISE NOTES

Organic Chemistry

Structural Isomerism

ISOMERISM

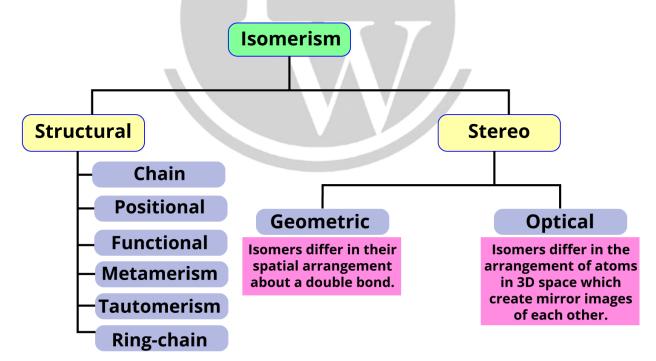
- Such organic compounds having the same molecular formula but differing from each other at least in some physical properties or chemical properties or both are known as isomers, and the phenomenon is known as isomerism.
- ❖ The term isomer was first introduced by Berzelius
- The difference in properties of isomers is due to the difference in the relative arrangements of various atoms or groups present in their molecules.
- ❖ There are two main types of isomerism:

1. Structural isomerism or constitutional isomerism

2. Space or stereoisomerism

STRUCTURAL ISOMERISM

- ➤ It is due to the difference in the manner in which the constituent atoms or groups are linked to one another within the molecule, without any reference to space.
- > Structural isomers are compounds having the same molecular formula but different structural formulas.
- > Structural isomerism is further classified into different types:



1. CHAIN ISOMERISM:

- ★ This type of isomerism is *due to differences in the arrangement of carbon 'atoms constituting the chain, i.e., a straight or branched chain of carbon atoms.*
- ★ It is also known as *nuclear or skeletal isomerism*.
- ★ Pentane (C5H12) exists in 3 isomeric forms:

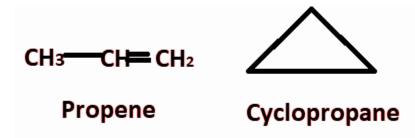
2. POSITION ISOMERISM

It is due to the difference in the positions occupied by the particular atom or group (substituents) in the same carbon chain or due to different positions of double or triple bonds in alkenes and alkynes.

Example:

3. RING-CHAIN ISOMERISM

This type of isomerism is due to different modes of linking of carbon atoms, i.e., the isomers possess either open-chain or closed-chain structures.



4. **FUNCTIONAL ISOMERISM**

- → Compounds having the same molecular formula but different functional groups in their molecules show functional isomerism and are called functional isomers.
- → As the functional group largely determines the properties of a compound, such isomers differ in their physical and chemical properties.

5. METAMERISM

- ❖ It is the isomerism in the same homologous series.
- ❖ It is due to the presence of different alkyl groups attached to the same polyvalent functional group or atom (i.e., -S ---, -NH- and -CO-).
- So, the compounds having the same molecular formula but different structural formulae due to different-sized or different-natured alkyl groups on either side of the functional group are called metamers and the phenomenon is known as metamerism.

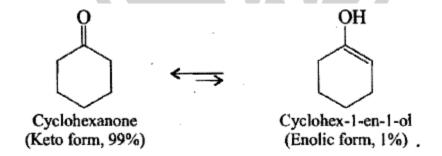
$$C_5H_{13}N$$
 C_3H_7 — N
 CH_3 ; C_2H_5 — N
 CH_3

Dimethyl propyl amine N -Ethyl- N -methyl ethanamine

❖ If the same polyvalent functional group is there in two or more organic compounds, then never write "chain" or "position isomerism"; it will be "metamerism," e.g.,

6. TAUTOMERISM

- → The type of isomerism in which a substance exists in two readily interconvertible different structures leading to dynamic equilibrium is known as tautomerism, and the different forms are called tautomers (or tautomerides).
- → It is caused by the wandering nature (1, 2, or mainly 1, 3 migration) of mobile hydrogen atoms between two polyvalent atoms within the same molecule.
- → The keto form is more stable (by about 18 kcal/mol) than the enolic form



ESSENTIAL CONDITIONS OF TAUTOMERISM

Aldehydes and ketones having at least one α-hydrogen atom show keto-enol tautomerism., Following compounds do not show tautomerism.

