CHAPTER 14

ISOMERISM

Isomerism is a very common phenomenon in organic chemistry and is one of the factors responsible for the existence of a very large number of organic compounds. The term **isomerism** (Greek, *isos* meaning equal and *meros* meaning parts) was first used by **Berzelius** to describe compounds with the same molecular formula but having different physical or chemical properties.

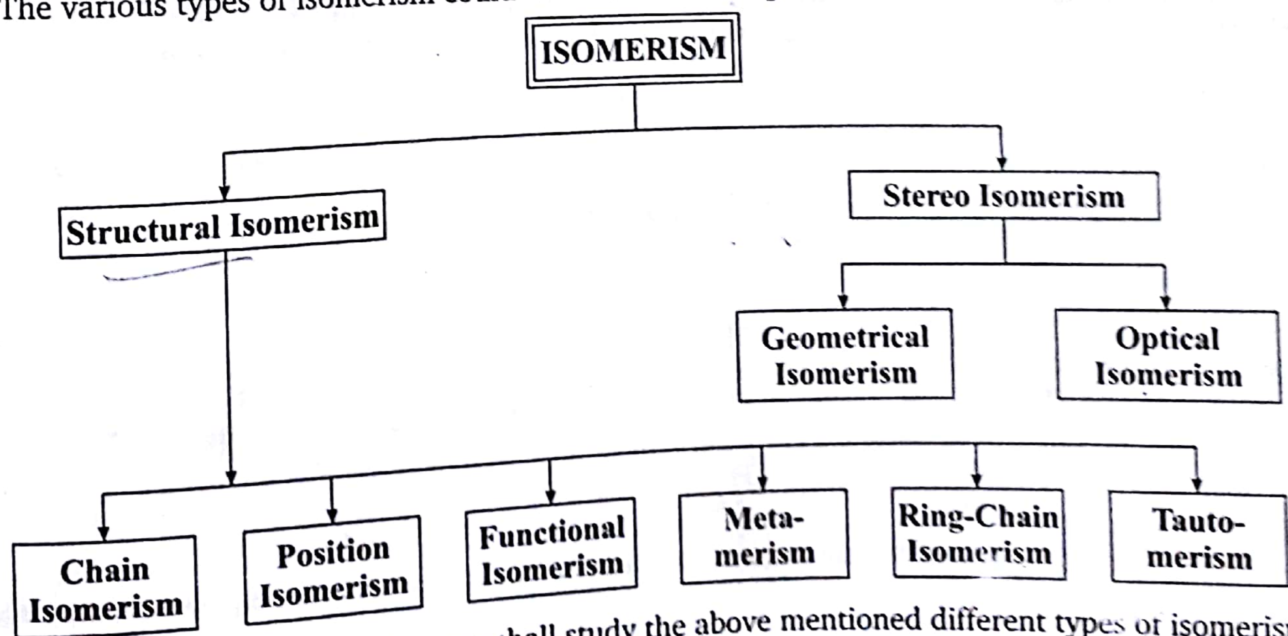
The isomerism may be defined as follows.

When two or more compounds having the same molecular formula differ in physical or chemical properties, the phenomenon is known as isomerism and such compounds are called isomers.

Classification

The two isomers differ either in their chemical structures or in the spatial arrangement of atoms or groups present in their molecules. The difference in chemical structures gives rise to **Structural isomerism**, whereas different spatial arrangements of atoms or groups give birth to **Stereo isomerism.** The chemical structures of two isomers may differ in several ways. Depending upon the variety of structural differences, we have several types of structural isomerism, e.g., *chain isomerism, position isomerism, functional isomerism, metamerism, ring-chain isomerism* and *tautomerism*.

The various types of isomerism could be summarised as given below.



In the forthcoming discussion, we shall study the above mentioned different types of isomerism.

14.1 STRUCTURAL ISOMERISM

When two or more compounds having the same molecular formula possess different chemical structures on account of different arrangement of atoms in their molecules, the phenomenon is known as structural isomerism and such compounds are called structural isomers.

Structural isomerism is of following types :

(i) Chain isomerism (ii) Position isomerism (iii) Functional isomerism (iv) Metamerism (v) Ring-chain isomerism (vi) Tautomerism

A brief discussion of the above types of structural isomerism is given in the following subsections.

14.1.1 Chain Isomerism

It is also known as *nuclear isomerism* or *skeletal isomerism*. It arises due to difference in the structure of carbon chain which forms the skeleton or nucleus of the molecule. It may be defined as follows.

When two or more compounds having the same molecular formula possess different arrangement of carbon atoms in the main chain, the phenomenon is known as chain isomerism and such compounds are referred to as chain isomers.

Some examples are given below.

(i) 1-bromobutane and 1-bromo-2-methylpropane possess the same molecular formula, *i.e.*, C_4H_9Br but 1-bromobutane contains a straight chain of four carbon atoms, whereas 1-bromo-2-methylpropane has a chain of only three carbon atoms. Thus, the two differ in their carbon skeletons.

$$\mathbf{C_4H_9Br:}\ \underset{\text{1-bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br} \qquad \underset{\text{1-bromo-2-methylpropane}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2Br}$$

(ii) Similarly, butan-1-ol and 2-methylpropan-1-ol differ in their carbon skeletons although they possess the same molecular formula, $C_4H_{10}O$.

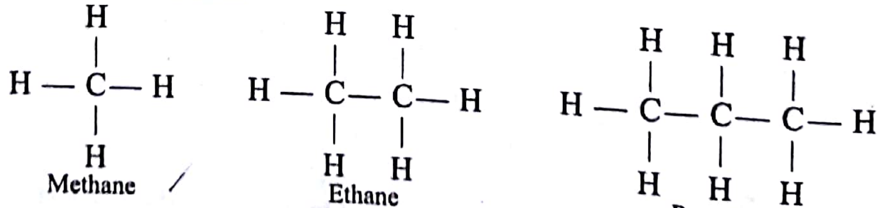
$$\mathbf{C_4H_{10}O:}\ \underset{\substack{\text{Butan-1-ol}\\ (n\text{-butyl alcohol})}}{CH_3-CH_2-CH_2-CH_2OH} \qquad \underset{\substack{\text{2-methylpropan-1-ol}\\ (iso\text{-butyl alcohol})}}{CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2OH}$$

The two alcohols mentioned above differ in the structure of the main chain. Butan-1-ol contains a chain of four carbon atoms, whereas 2-methylpropan-2-ol contains a chain of only three carbon atoms.

Structural Isomerism in Alkanes

Alkanes do not possess multiple bonds or functional groups. Therefore, they are able to exhibit only *chain isomerism*.

The first three members, *i.e.*, methane, ethane and propane do not show chain isomerism because they are unable to exhibit different arrangement of carbon atoms in the main chain. Hence, they have only one type of structural formula.



Methane Ethane Propane

Structural

Butane (C_4H_{10}) : The next member, *i.e.*, butane can have two chain isomers, *n*-butane and *iso*-butane.

$$CH_3 - CH_2 - CH_2 - CH_3$$
Butane
(*n-butane*)

$$\begin{array}{c} CH_3 - CH - CH_3 \\ | \\ CH_3 \end{array}$$
2-methylpropane
(*iso-butane*)

The two isomers differ in their carbon skeleton. *n*-butane possesses a straight chain, whereas iso-butane has a branched chain. The carbon skeletons of these isomers are as shown below.

$$C - C - C - C \qquad \begin{array}{c} C - C - C \\ | \\ C \end{array}$$

Pentane (C_5H_{12}) : Pentane has three chain isomers. They are as follows.

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$
Pentane
(*n-pentane*)

$$\begin{array}{l} CH_3 - CH - CH_2 - CH_3 \\ \qquad\;\; | \\ \qquad CH_3 \end{array}$$
2-methylbutane
(*iso-pentane*)

$$\begin{array}{c} CH_3 \\ | \\ CH_3 - C - CH_3 \\ | \\ CH_3 \end{array}$$
2, 2-dimethylpropane
(*neo-pentane*)

Hexane (C_6H_{14}) : Hexane has five chain isomers. Their structures and names are as follows.

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$
Hexane

$$\begin{array}{l} CH_3 - CH - CH_2 - CH_2 - CH_3 \\ \qquad\;\; | \\ \qquad CH_3 \end{array}$$
2-methylpentane

$$\begin{array}{l} CH_3 - CH_2 - CH - CH_2 - CH_3 \\ \qquad\qquad\quad\;\; | \\ \qquad\qquad\quad CH_3 \end{array}$$
3-methylpentane

$$\begin{array}{l} CH_3 - CH - CH - CH_3 \\ \qquad\;\; | \qquad\; | \\ \qquad CH_3 \;\; CH_3 \end{array}$$
2, 3-dimethylbutane

$$\begin{array}{l} \qquad\;\; CH_3 \\ \qquad\quad\; | \\ CH_3 - C - CH_2 - CH_3 \\ \qquad\quad\; | \\ \qquad\;\; CH_3 \end{array}$$
2, 2-dimethylbutane

From the above discussion it is clear that for alkanes, the number of structural isomers (chain isomers) increases with increase in the number of carbon atoms. We have already seen that whereas pentane has three isomers, hexane has five isomers. The number of isomers for heptane (C_7H_{16}) is nine, which is still higher. Octane (C_8H_{18}) possesses 18 isomers and for decane ($C_{10}H_{22}$) the number is as high as 75.

14.1.2 Position Isomerism

When two or more compounds having the same molecular formula possess different positions of double bond, triple bond or functional group, the phenomenon is known as position isomerism and the compounds are known as position isomers.

Some examples are as follows.

(i) But-1-ene and But-2-ene have the same molecular formula, C_4H_8 and are position isomers because they have different positions of double bonds as shown below.

$$C_4H_8 : CH_2 = CH - CH_2 - CH_3$$
But-1-ene

$$CH_3 - CH = CH - CH_3$$
But-2-ene

(ii) The molecular formula C_4H_6 represents two butynes, But-1-yne and But-2-yne. The former contains triple bond at position 1, whereas the latter has a triple bond at position 2.

$$C_4H_6 : CH \equiv C - CH_2 - CH_3$$
But-1-yne

$$CH_3 - C \equiv C - CH_3$$
But-2-yne

(iii) Similarly, propan-1-ol and propan-2-ol have the same molecular formula but possess —OH groups at different positions. Therefore, they are also position isomers.

$$C_3H_8O: \underset{\text{Propan-1-ol}}{CH_3-CH_2-CH_2-OH} \qquad \underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}$$

14.1.3 Functional Isomerism

When two or more compounds having the same molecular formula contain different functional groups (i.e., belong to different families), the phenomenon is known as functional isomerism and such compounds are termed as functional isomers. Some examples are as follows.

(i) Ethanol (ethyl alcohol) and methoxymethane (dimethyl ether) both have the same molecular formula, C_2H_6O but contain different functional groups. Ethanol contains —OH group and belongs to alcohol family, whereas methoxymethane contains —O— group and belongs to ether family.

$$C_2H_6O: \underset{\substack{\text{Ethanol}\\ (\textit{ethyl alcohol})}}{CH_3-CH_2-OH} \qquad \underset{\substack{\text{Methoxymethane}\\ (\textit{dimethyl ether})}}{CH_3-O-CH_3}$$

(ii) Propanal and propan-2-one possess the same molecular formula, C_3H_6O and are functional isomers because the functional groups present in them are different. The former contains an aldehydic ($-\overset{\overset{H}{|}}{C}=O$) group while the latter possesses a ketonic group ($>C=O$).

$$C_3H_6O: \underset{\text{Propanal}}{CH_3-CH_2-\overset{\overset{H}{|}}{C}=O} \qquad \underset{\text{Propan-2-one}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

(iii) Similarly the molecular formula $C_3H_6O_2$ represents two functional isomers, one containing a carboxyl group ($-\overset{\overset{O}{\|}}{C}-OH$) while the other an ester ($-\overset{\overset{O}{\|}}{C}-O-$) group.

$$C_3H_6O_2: \underset{\text{Propanoic acid}}{CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH} \qquad \underset{\text{Methylethanoate}}{CH_3-\overset{\overset{O}{\|}}{C}-OCH_3}$$ ester

14.1.4 Metamerism

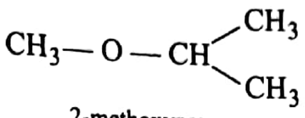
This type of isomerism is exhibited by the members belonging to the same family and arises due to the unequal distribution of carbon atoms on the two sides of the functional group.

When two or more compounds having the same molecular formula and the same functional group possess different types of alkyl groups attached on both sides of the functional group, the phenomenon is known as metamerism and such compounds are termed as metamers.

Some examples are given below.

(i) The molecular formula $C_4H_{10}O$ represents following three ethers.

$CH_3-O-CH_2CH_2CH_3$
1-methoxypropane
(*methyl propyl ether*)

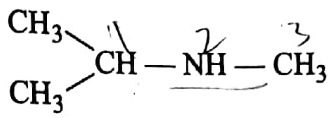

2-methoxypropane
(*methyl isopropyl ether*)

$CH_3CH_2-O-CH_2CH_3$
Ethoxyethane
(*diethyl ether*)

All the three compounds possess the same functional group, —O— and belong to the same family. The alkyl groups present on both sides of group —O— are different in all the three compounds. Hence, they are metamers.

(ii) Similarly, the molecular formula $C_4H_{11}N$ represents three secondary amines which are metamers.

$CH_3CH_2CH_2-NH-CH_3$
N-methyl-1-aminopropane
(*methylpropylamine*)


N-methyl-2-aminopropane
(*methylisopropylamine*)

$CH_3CH_2-NH-CH_2CH_3$
N-ethyl-1-aminoethane
(*diethylamine*)

14.1.5 Ring-Chain Isomerism

RING - CHAIN ISOMERISM

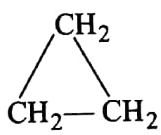
This type of isomerism is due to the difference in the mode of linking of carbon atoms and may be defined as follows.

When two or more compounds having the same molecular formula differ in the mode of linking of carbon atoms and have open chain and closed chain structures, the phenomenon is called ring-chain isomerism and such compounds are referred to as ring-chain isomers.

Some examples of ring-chain isomerism are as follows.

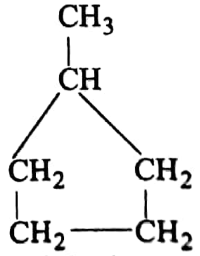
(i) Propene and cyclopropane have the same molecular formula C_3H_6 but have different modes of linking of carbon atoms. Propene has an open chain structure, whereas cyclopropane has a cyclic structure.

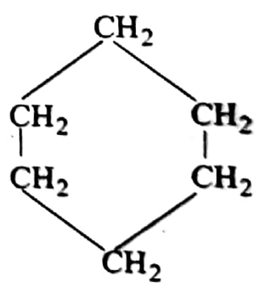
C_3H_6 : $CH_3-CH=CH_2$
Propene


Cyclopropane

(ii) Molecular formula C_6H_{12} represents the following three compounds which differ in the mode of linking of carbon atoms. Hex-1-ene is an open chain compound, whereas 1-methylcyclopentane and hexane are cyclic compounds.

C_6H_{12} : $CH_3-CH_2-CH_2-CH_2-CH=CH_2$
Hex-1-ene


1-methylcyclopenatane


Cyclohexane

14.1.6 Tautomerism

It is a special type of functional isomerism in which the isomers exist simultaneously in dynamic equilibrium with each other.

interconvertible

Tautomerism may be defined as the phenomenon in which a single compound exists in two readily interconvertible forms which differ markedly in the relative position of at least one atomic nucleus, generally hydrogen.

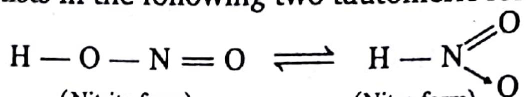
Some examples of tautomerism are as follows.

(i) Hydrocyanic acid (HCN) exists in the following tautomeric forms :

$$H-C\equiv N \rightleftharpoons H-N \overrightarrow{=} C$$

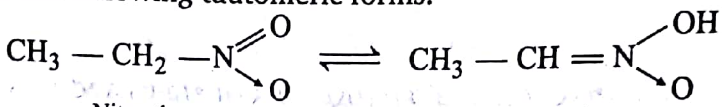
Hydrocyanic acid — Isohydrocyanic acid

(ii) Nitrous acid (HNO_2) exists in the following two tautomeric forms :



(Nitrite form) — (Nitro form)

(iii) Nitroethane has the following tautomeric forms.

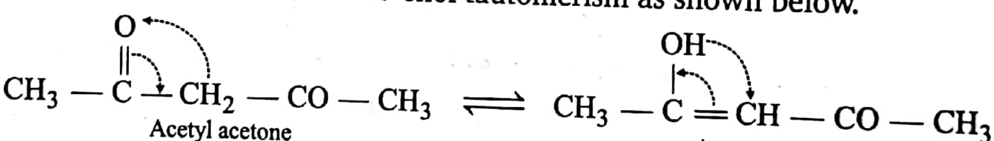


Nitroethane (nitro-form) — Isonitroethane (aci-form)

Keto-Enol Tautomerism

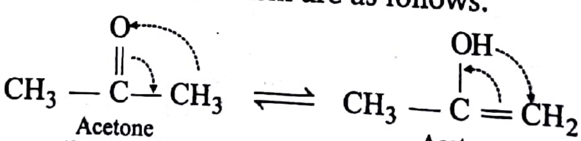
Tautomerism is of various types. Among these, the **keto-enol tautomerism** is the most important one. *In keto-enol tautomerism, a compound exists in two interconvertible forms, one containing a keto group (known as* **keto-form)** *and the other containing an alcoholic group* **(known as enolic-form).** *The two forms continuously change into each other through the oscillation of a proton and π-electrons.*

For example, acetyl acetone shows keto-enol tautomerism as shown below.

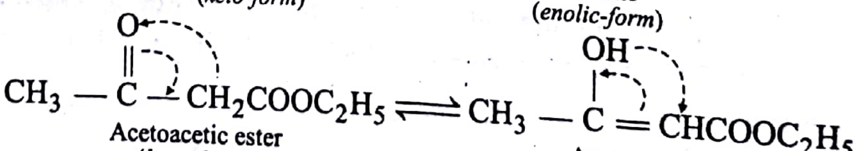


Acetyl acetone (*keto-form*) — Acetyl acetone (*enolic-form*)

Some more examples of keto-enol tautomerism are as follows.



Acetone (*keto-form*) — Acetone (*enolic-form*)



Acetoacetic ester (*keto-form*) — Acetoacetic ester (*enolic-form*)

Characteristics of Tautomeric Changes

(i) Tautomerism (only *cationotropy*) is caused by the wandering of a hydrogen atom between two polyvalent atoms present in the molecule. The change is accompanied by a rearrangement of single and double bonds.

(ii) It is a reversible intramolecular change.

(iii) The two tautomeric forms are not equally stable. The less stable form is called *labile form*.

(iv) Since the two tautomeric forms remain in dynamic equilibrium, their separation is difficult by the ordinary methods. However, the two tautomeric forms of a substance may be separated by using special techniques.