Chapter 1
Introduction

1.1 Introduction

Stereochemistry is the chemistry of organic compounds in three dimensions. The term stereochemistry has been derived from the Greek word '*steros*' meaning solid. In fact, stereochemistry is an important branch of chemistry. It is not only concerned with the geometry of the molecules but is also of immense use in understanding the pathway of chemical transformations.

The origin of stereochemistry stems from the discovery of plane-polarised light by French physicist Malus (1809). Subsequently, another French physicist Biot (1815) discovered the existence of two types of quartz crystals, which rotated the plane-polarised light in opposite directions. It was found that this property was not only associated with the crystalline structure but some compounds in solution also exhibited this property. It was Pasteur who studied various salts of tartaric acid and observed that optically inactive sodium ammonium tartarate is actually a mixture of two different kinds of crystals which were mirror images of each other and rotated the plane-polarised light in opposite directions. He was able to separate them by using a hand lens and a pair of tweezers. It was concluded that the optical activity in solution is due to some molecular property which is retained in solution. It is now well known that this property is due to the presence of asymmetric carbon in the compound. A detailed discussion on this forms the subject matter of a sub-section chapter (see Chap. 2).

It is now well known that a very large number of compounds can be represented in more than one form. The phenomenon of the existence of two or more compounds having the same molecular formula is known as isomerism. Such compounds are referred to as isomers. Thus, it can be said that the isomers have the same molecular formula. However, they differ from each other in their physical and chemical properties.

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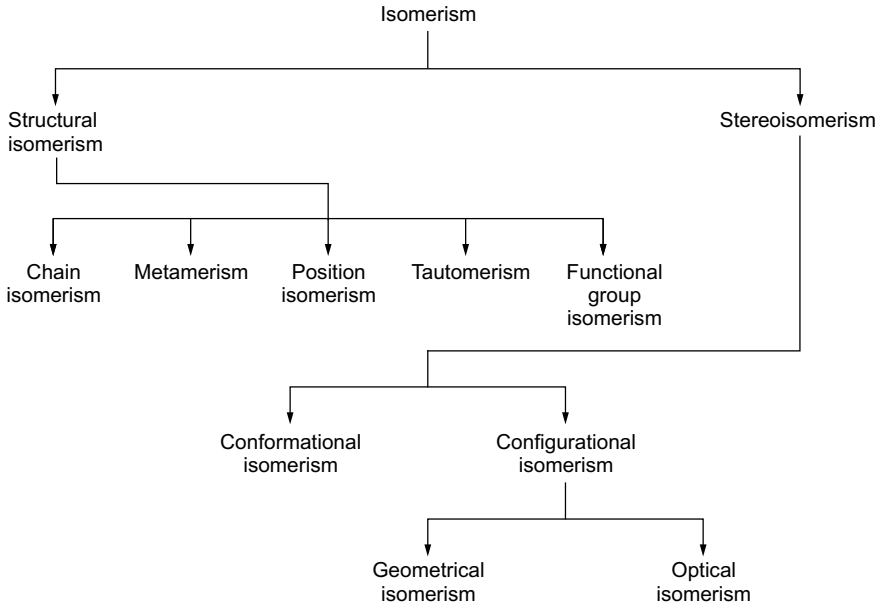
Isomerism is basically of two types. These are structural isomerism and stereoisomerism. The structural isomerism, as we know, is due to the difference in the structures of the molecules. These structural differences can be further classified into, *i.e.*, chain isomerism, position isomerism and functional group isomerism. Besides these, we also come across metamerism and tautomerism. On the other hand, stereoisomerism is not structural isomerism; it is due to constituent atoms or groups differing in their arrangement in space. The different types of isomerisms are represented below:



The stereoisomers can be either conformational isomers (leading to conformational isomerism); they arises due to rotation about a carbon–carbon sigma bond (single bond) or configurational isomers, which are of two types, viz., geometrical isomers (leading to geometrical isomerism) and optical isomers (leading to optical isomerism).

Chain isomerism arises due to the different carbon skeletons of the isomers (called chain isomers). Some examples are

	Chain isomers	
C_4H_{10}	$CH_3CH_2CH_2CH_3$ Butane	$CH_3-CH(CH_3)-CH_3$ Isobutane
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$ *n*-Pentane	$CH_3CH(CH_3)CH_2CH_3$ Isobutane (2-methylbutane)

Position isomerism as the name implies is due to the difference in the position of the substitutions of the isomers (called position isomers). As an example, C_3H_8O can be 1-propanol or 2-propanol.

$CH_3CH_2CH_2OH$ 1-Propanol (*n*-Propyl alcohol)	$CH_3CH(OH)CH_3$ 2-Propanol (isopropyl alcohol)

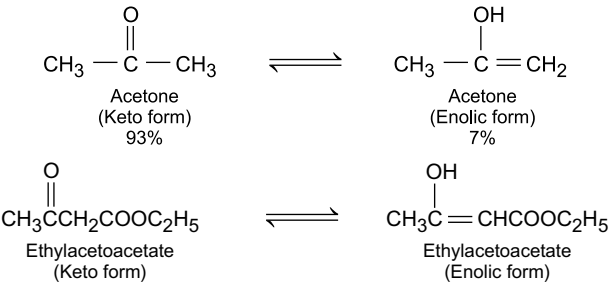
Functional group isomerism arises due to different functional groups. The isomers are called functional isomers. As an example, C_3H_6O can be either acetone or propanal and C_3H_8O can be either an ether or an alcohol.

C_3H_6O	$CH_3C(=O)CH_3$ Acetone	CH_3CH_2CHO Propanal
C_3H_8O	$CH_3CH_2OCH_3$ Methoxyethanel (Ethyl methyl ether)	$CH_3CH_2CH_2OH$ Propanal (*n*-Proyl alcohol)

In case of metamerism, the isomers (known as metamers) have the same functional group. Some examples include

$C_4H_{10}O$	$CH_3OCH_2CH_2CH_3$ Methoxy propane (Methylpropyl ether)	$CH_3CH_2OCH_2CH_3$ Ethoxyethane (Diethyl ether)
$C_5H_{10}O$	$CH_3CH_2C(=O)CH_2CH_3$ 3-Pentanone (Diethyl ketone)	$CH_3C(=O)CH_2CH_2CH_3$ 2-Pentanone (Methylpropylketone)

In **tautomerism** a compound can exist in two interconvertible forms known as tautomers. It is also called dynamic isomerism or Keto-enol tautomerism. Some examples are



Stereoisomerism, as has already been stated, is due to differences in the arrangement of atoms or groups in space. Stereoisomerism is of two types, viz., conformational isomerism and configurational isomerism. A discussion on these forms is the subject matter of subsequent chapters (*see* Chap. 2, Sect. 2; Chaps. 3 and 4).

Stereochemistry plays a special role in drugs. It is now known that only one enantiomer of a drug is useful for the effective treatment of a disease. As an example, the well-known drug ibuprofen (which contains a stereogenic centre) exists as a pair of enantiomers. However, only (S)-ibuprofen is effective as an anti-inflammatory agent. The (R)-ibuprofen shows no anti-inflammatory activity but is slowly converted into the (S)-enantiomer in vivo. Another drug, fluoxetine, is used as an antidepressant; in this case, only the (R)-enantiomer is the active component. The most interesting example is the case of the drug thalidomide, which was taken during pregnancy to avoid morning sickness. This drug (which was a mixture of (R) and (S) enantiomers) caused catastrophic birth defects to children born to women who took thalidomide. It was subsequently formed that only the (R) enantiomer has the desired effect and the (S)-enantiomer was responsible for birth abnormalities. This has been discussed in detail in Sect. 18.2 of Chap. 18.

Stereochemistry plays a vital role in the outcome of products obtained in various reactions like addition reactions, elimination reactions, substitution reactions, rearrangement reactions, free radical reactions and pericyclic reactions. All these form the subject matter of Part-III of this book.