10 Stereochemistry

"An extension of the theory of asymmetry without being a direct consequence of if: for the conviction that the geometrical structure of the molecule even for optical isomers exercise such a great influence on the chemical affinities, and could be gained by new actual observations."

—Emil Fischer

CHAPTER OUTLINE

10.1 INTRODUCTION

The Stereochemistry is the study of three dimensional configuration of the atoms that make up molecules and the ways in which the arrangement affects the physical and chemical properties of a molecule.

One of the major problems in organic chemistry is to find out how the atoms are arranged in molecules, *i.e.,* to determine the structure of organic compounds. Each different arrangement of atoms corresponds to a different compound and each compound has its own characteristic set of chemical and physical properties. There is definitely a relationship between the molecular structure, *i.e.*, arrangement of atoms or groups of atoms in a molecule and its properties.

Compounds which have the same molecular formula, but different structural formula are called *isomers* and the compounds having different configuration, *i.e.,* different relative position of atoms or groups in space arc called *stereoisomers*. In other words, the molecules that have same atomic connectivity,

but different arrangements of their aroms in space, *i.e.*, different configuration, are known as *stereoisomers* and the study of stereoisomers and their properties is known as *stereochemistry*. The prefix 'stereo' means 'three-dimensional', so stereochemistry is also known as 3D Chemistry.

In this chapter, we shall deal with different types of structural as well as stereoisomers of organic compounds.

10.2 ISOMERISM

In organic chemistry we find numerous organic compounds having same molecular formula but differing in their physical and chemical properties. Such compounds are called ***isomers*** and the phenomenon is known as ***isomerism***.

As different compounds possess the same molecular formula, the difference in their physical and chemical properties is attributed to different spatial arrangement of the molecules.

There are two main types of isomerism, as given below:

(*i*) Structural isomerism, and (*ii*) Stereoisomerism

(*i*) **Structural Isomerism:** It is due to different arrangements of atoms within the molecule. Structural isomerism is further divided into:

(*a*) Chain isomerism (*b*) Position isomerism

(*c*) Functional isomerism (*d*) Metamerism and

(*e*) Tautomerism

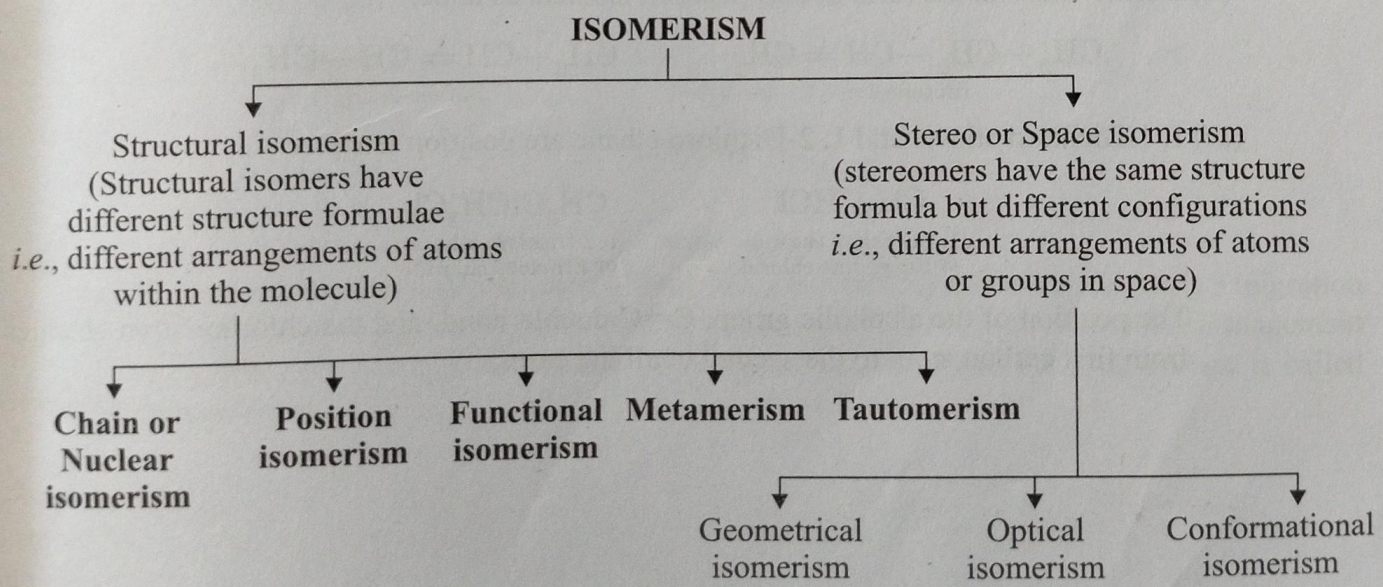
(*ii*) **Stereoisomerism:** It is due to difference in the arrangement of atoms around the carbon atom in space. Stereoisomers have the same molecular as well as structural formulae but possess different spatial arrangements of atoms in space (3D geometry), *i.e.*, configuration. It is also known as space-isomerism. It is classified as:

(*a*) Geometrical or Cis-trans isomerism,

(*b*) Optical isomerism and

(*c*) Conformational isomerism

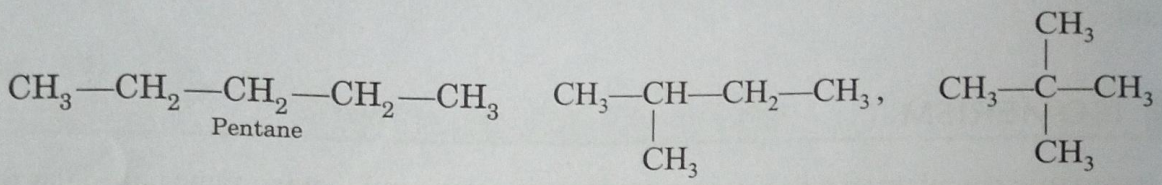
Various types of isomerism have been summarised below:



10.3 STRUCTURAL ISOMERISM

(*a*) **Chain Isomerism:** This is due to the difference in the nature of carbon chain. For example,

(*i*) Pentane (C_5H_{12}) exists in three isomeric forms, viz., *n*-pentane, iso-pentane and neo-pentane.

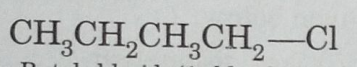


Pentane

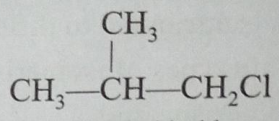
Iso-pentane (2-methyl butane)
pentane

neo-pentane

(*ii*) Butyl chloride (C_4H_9Cl) exists in chain isomers as *n*-butyl chloride and isobutyl chloride:

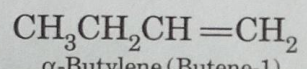


n-Butyl chloride (1-chlorobutane)

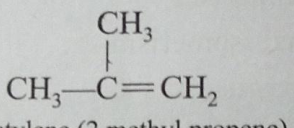


Isobutyl chloride
(1-chloro, 2-methyl propane)

(*iii*) Butylene (C_4H_8) has the following two chain isomers:



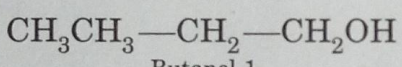
α-Butylene (Butene-1)



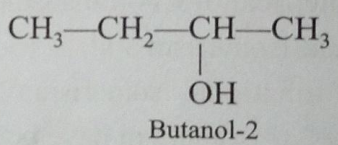
Iso butylene (2 methyl propene)

(*b*) **Position Isomerism:** This is due to the difference in the position occupied by an atom or a functional group in a carbon chain, *e.g.*,

(*i*) Butanol (C_4H_9OH) exists as two-position isomers as under:

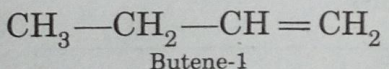


Butanol-1

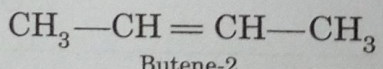


Butanol-2

(*ii*) Butene exists in the form of two-position isomers as under:

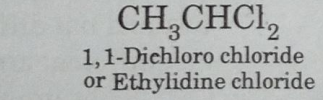


Butene-1

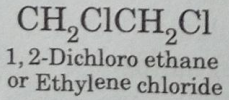


Butene-2

(*iii*) 1, 1-Dichloro ethane and 1, 2-Dichloro ethane are position isomers:



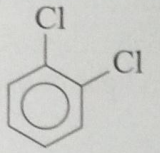
1,1-Dichloro chloride
or Ethylidine chloride



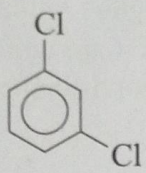
1, 2-Dichloro ethane
or Ethylene chloride

The position of the alcoholic group, C=C double bond, and the chlorine atom changes from first carbon atom to the second in all the cases.

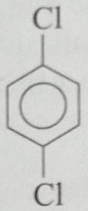
(*iv*) *o*-, *m*- and *p*- Dichlorobenzenes also show position isomerism:



o-Dichloro
1, 2-Dichloro benzene



m-Dichloro benzene
1, 3-Dichloro benzene



p-Dichloro benzene
1, 4-Dichloro benzene

(*c*) **Functional Isomerism:** This is shown by compounds having same molecular formula but different functional groups, *e.g.*,

			Molecular Formula
(*i*)	$CH_3—CH_2—OH$ Ethanol	$CH_3—O—CH_3$ Dimethyl ether	C_2H_6O
(*ii*)	$CH_3—CH_2CHO$ Propionaldehyde	$CH_3—CO—CH_3$ Acetone	C_3H_6O
(*iii*)	CH_3CH_2COOH Propionic acid	CH_3COOCH_3 Methyl acetate	$C_3H_6O_2$
(*iv*)	$CH_3C \equiv N$ Methyl cyanide	$CH_3—N \rightleftharpoons C$ Methyl isocyanide	H_3CCN
(*v*)	$CH_3CH_2NH_2$ Ethylamine	$CH_3—\underset{\displaystyle H}{\underset{\vert}{N}}—CH_3$ Dimethylamine	C_2H_7N

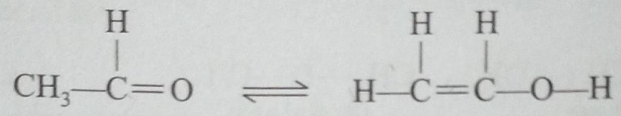
(*d*) **Metamerism:** This isomerism is shown by the compounds having the same molecular formula and even the same functional group, but the two alkyl groups attached to the same functional group are different. These isomers belong to same homologous series, *e.g.*,

(*i*)	$C_2H_5—O—C_2H_5$ Dimethyl ether	$CH_3—O—C_3H_7$ Methyl propyl ether
(*ii*)	$C_2H_5—CO—C_2H_5$ Diethyl ketone	$CH_3—CO—C_3H_7$ Methyl propyl ketone
(*iii*)	$(C_2H_5)_2N—H$ Diethylamine	$CH_3CH_2CH_2(CH_3)N—H$ Methyl propylamine

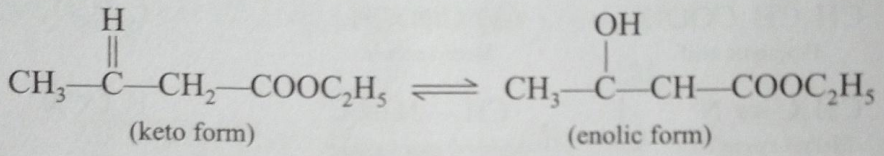
(*e*) **Tautomerism:** It is a special case of functional isomerisms and arises due to 1, 3 migration of a proton from a carbon atom to another atom (oxygen or nitrogen) with the rearrangement of carbon-carbon single and double bond called *tautomers* and the phenomenon is called *tautomerism.*

Further, tautomeric forms also exist in equilibrium with each other, the stable isomer being in large amount and less stable isomer being in small amount. For example

(*i*) Acetaldehyde and vinyl alcohol are tautomers of each other. Acetaldehyde being more, stable isomer is in large amount as compared to vinyl alcohol. Since one of the isomers *i.e.*, acetaldehyde contains a keto group (—C(=O)—) and the other, *i.e.*, vinyl alcohol contains an enolic group (=C(—OH)—), this type of tautomerism is also called **keto-enol tautomerism.**

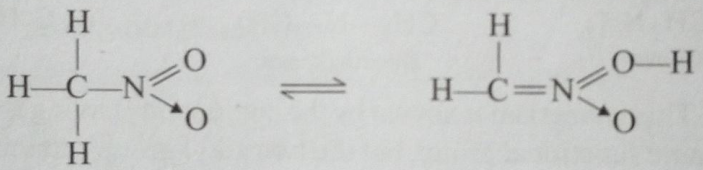


(*ii*) Similarly, acetoacetic ester also shows keto enol tautomerism; keto form being major product and enolic form being minor product



(keto form) (enolic form)

(*iii*) Normal and Aci-forms of nitro methane are tautomers



(Normal Form) (Aci Form)

The compounds showing tautomerism give reactions of the functional groups present in each tautomer, *i.e.*, reactions of both the functional groups. The two tautomers can be separated by special methods and can be kept in separate forms only under special conditions. Under ordinary conditions tautomers exist in equilibrium with each other.

10.4 STEREOISOMERISM

The isomerism which arises due to difference in the arrangement of atoms in space is called stereoisomerism. The isomers which have the same molecular structure but different relative arrangements of atoms or groups in space, *i.e., different configuration* are called stereoisomers and the phenomenon is called **stereoisomerism**. There are three types of stereoisomerism:

(*a*) Optical isomerism
(*b*) Geometrical isomerism
(*c*) Conformational isomerism.

10.4.1 Optical Isomerism

It has been observed that certain compounds resemble one another in their chemical properties as well as in most of their physical properties but they differ in their behaviour towards the action of *plane polarised light*. Such compounds are called *optically active* and this phenomenon is called *optical activity*. Compounds, which rotate the plane polarised light towards the right are said to be *dextro-rotatory* and are represented as *d* or (+) form, where as those which rotate it to the left are called *laevo-rotatory* represented as *l* or (–) form. These isomers are said to show optical isomerism. Before proceeding further, it is important to understand the terms **polarised light** and **optical activity**.

Polarised Light: An ordinary ray of light consists of electromagnetic waves and its vibrations taking place in all planes perpendicular to the direction in which it travels. *Monochromatic light,* on the other hand, consists of waves of one wave length. Even such a ray has its vibrations in all the planes.

When if a ray of monochromatic light is passed through a Nicol prism, the wave motion of emergent light is restricted to only one plane. Such a beam of light which has vibration only in one plane is called plane polarized light or unidirectional light. The Nicol prism used to obtain plane polarized light is called a *polarizer* (Fig. 10.1).

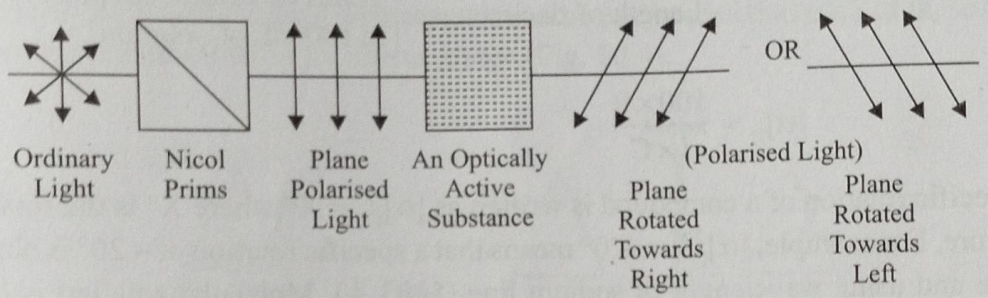


Fig. 10.1 Polarization of light

Optical Activity: When the plane polarized light is allowed to fall on another Nicol prism with its axis parallel to the first Nicol prism, the plane polarized light passes thought it without undergoing any deviation. The first Nicol prism is known as *polarizer* and the second Nicol prism is known as *analyzer.* If the axis of analyzer is kept at right angle to polarizer complete darkness appears due to total internal reflection (Fig. 10.2).

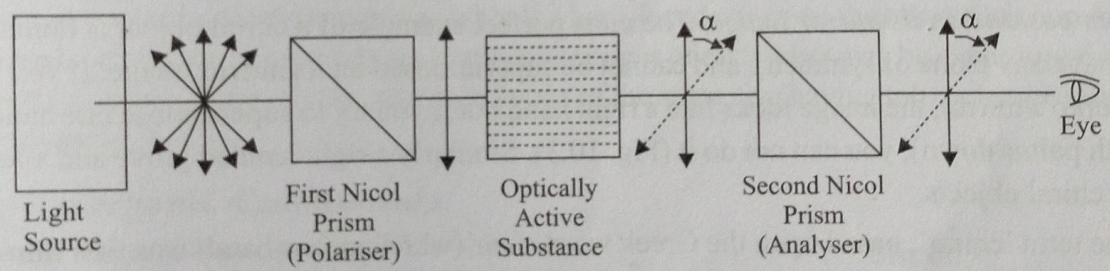


Fig. 10.2 Representation of polarimeter (the dotted lines indicate the angle of rotation)

The arrangement of polarizer and analyzer with their axis perpendicular to each other is used to study the behaviour of solutions of organic compound towards plane polarized light. For this purpose a polarimeter tube containing solution of organic compound is placed between the two Nicol prisms. If some light appears, it indicates that organic compound has rotated plane polarized light through a certain angle. *Such compounds which can rotate the plane polarized light through a certain angle are known as optically active compounds. The property by virtue of which the organic compounds can rotate the plane polarized light is known as optical activity.*

The angle through which plane polarized light is rotated by an optically active compound is known as *angle of rotation.* It can be represented by alpha (α) and it can be determined with the help of an instrument called *Polarimeter.*

The angle of rotation depends upon the following factors:

(*i*) Nature of the compound (*ii*) Nature of Solvent

(*iii*) Concentration of solution (*iv*) Wavelength of light used

(*v*) Length of the solution column through which the light passes

(*vi*) Temperature

The rotatory power of a given solution is usually expressed as *specific rotation,* which can be defined as the angle of rotation (α) produced by *one decimetre length* of solution having one gram of the substance per millilitre. The measurement of rotation is carried out at temperature T using sodium light (the D lines).

$$\text{Specific rotation} = \frac{100 \times \text{observed angle of rotation } \theta}{\text{Length of decimeters} \times \left[\begin{matrix}\text{grams of substances present} \\ \text{in 100 mL of solution}\end{matrix}\right]}$$

or $$[\alpha]_D = \frac{100 \times \theta}{l \times C}$$

The specific rotation of a compound is written as $[\alpha]_C^{T^\circ} = X^\circ$ where X° is the rotation in degree at T° temperature. For example, $[\alpha]_D^{20^\circ} = -20^\circ$ means that a specific rotation of -20° is obtained at 20°C of temperature and using wavelength of sodium line (5893 Å). Molecular rotation is the product of specific rotation and molecular mass.

10.5 CONCEPT OF CHIRALITY

Chiral Structures

A structure or object is said to be chiral (or disymmetric) if it has no plane of symmetry and is not superimposable on its mirror image. The most perfect example of a chiral object is human hand. It does not have any plane of symmetry and cannot be superimposed on its mirror image. If you hold your left hand upto a mirror, the image looks like a right hand but if you try to superimpose one hand over the other (both palms down), you can not do it (Fig. 10.3). Similarly a right handed glove and a left handed glove are chiral objects.

The term 'chiral', based upon the Greek word *cheir* (which means hand) was first introduced by Calm, Ingold and Prelog in 1964. Thus chirality means 'handedness", *i.e.*, the relationship which exists between the left and right hands. In recent years, the terms *chiral* and *chirality* have almost completely replaced the old terms *disymmetric* and *dissymmetry* respectively.

Many organic molecules such as lactic acid [$CH_3CH(OH)COOH$] and 2-chlorobutane [$CH_3CHClCH_2CH_3$] represent chiral structures. *The substances having chiral structures are said to possess the property of chirality and these substances are optically active.*

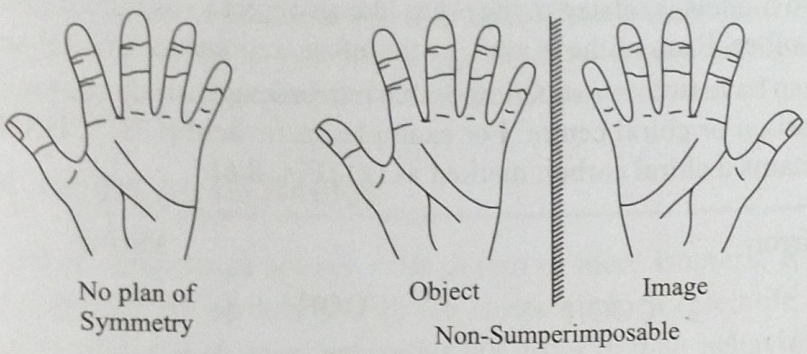


Fig. 10.3 Chiral structure

Achiral Structures

A structure or object which has a ***plane of symmetry*** *and is superimposable on its mirror image is known as achiral (or* ***symmetrical****).* A line of symmetry is a plane, real or imaginary, which divides a structure or an object into two equal halves so that one half is the mirror image of the other half. For example, the letter A represents achiral structures. It can be easily seen that each of these has a plane of symmetry and is superimposable on its mirror image (Fig. 10.4).

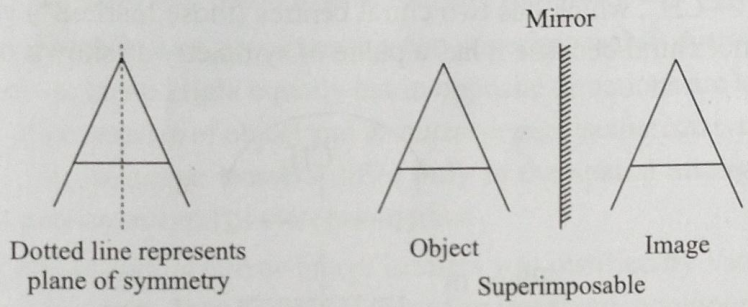


Fig. 10.4 Achiral structure

Similarly, many molecules such as those of methane and carbon tetrachloride are symmetrical in nature.

Two objects are said to be superimposable if when placed one upon the other, their corresponding parts lie on each other. Two objects that are like mirror images of each other may be either superimposable or non-superimposable. For example, two note books of the same size having mirror image relationship are superimposable.

Chirality in Organic Compounds

Most of the organic compounds are chiral in nature due to the presence of at least one *chiral carbon or chiral centre* in the molecule. Previously a chiral carbon atom was referred to **asymmetric carbon.** A **chiral carbon or chiral centre** *is a carbon atom which is bonded to four different monovalent atoms or groups such as* C_{abcd}. There can be two different tetrahedral models for C_{abcd} which differ in the spatial arrangements of various groups attached to carbon as shown in Fig. 10.5.

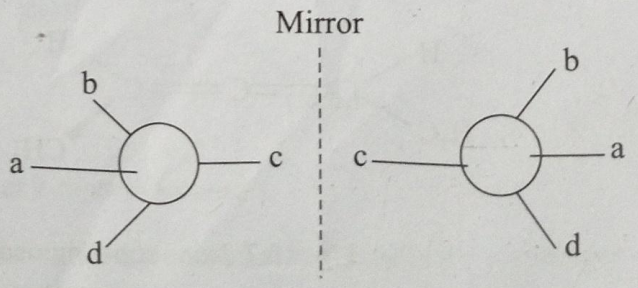


Fig. 10.5 Non-superimposable mirror image models of chiral C atom.

Each of the two models is related to the other like an object to its mirror image and one cannot be superimposed on the other. Each of these models, therefore, represents a chiral structure.

Similarly we can have two non-superimposable mirror image structures for any known compound containing a chiral carbon or chiral centre. For example, lactic acid [CH_3*CH(OH)COOH] is a chiral molecule since it contains a chiral carbon marked as (*) **[Fig. 8.6].**

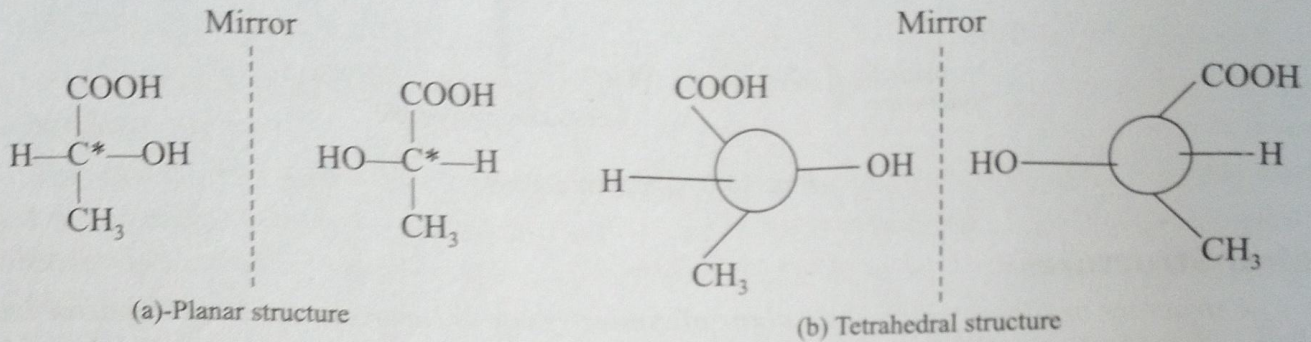
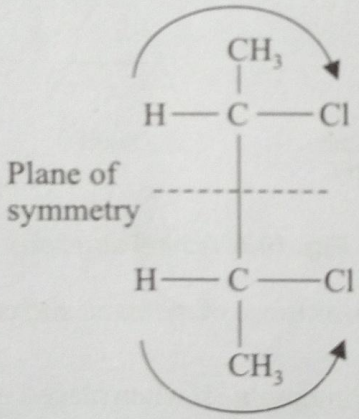


Fig. 10.6 Non-superimposable mirror images: Lactic acid

It must be emphasized, however, that certain molecules may contain more than one chiral centre and still they may be achiral or non-dissymmetric. For instance, 2, 3-dichlorobutane, CH_3—*CHCl—*CHCl—CH_3, which has two chiral centres (those marked*) exists in many isomeric forms one of which is not chiral because it has a plane of symmetry as shown below:



On the other hand, we have certain molecules that are chiral even though they do not contain any chiral carbon. Allenes (RCH = C = CHR) represent a well known class of such compounds as illustrated below:

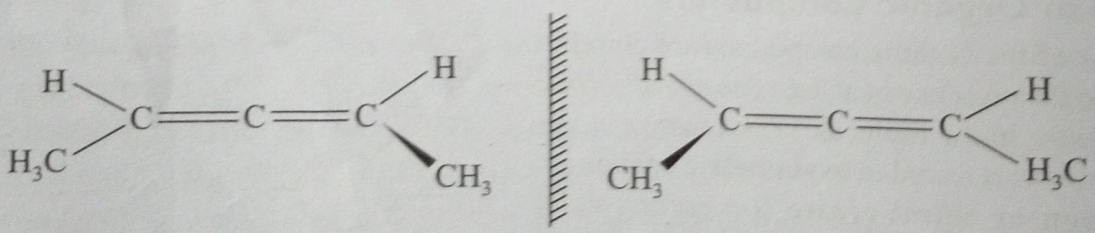


Fig. 10.7 Non- superimposable mirror image of 2, 3-pentadiene

It may be seen by molecular models that chirality in 2, 3-pentadiene arises due to the fact that the two groups singly bound to one of the end carbon atoms of allene system are in a different plane than the two groups singly bound to the other end carbon of the allene system

10.6 TYPES OF OPTICAL ISOMERS

The optically active compounds always exist in two or more isomeric forms, and differ with respect to their optical activity. As already stated, the isomers which resemble one another in their chemical reactions and most of the physical properties but differ in their behaviour towards polarised light are called ***optical isomers*** and the phenomenon is known as ***optical isomerism.***

There are two main types of optical isomerism. These are:

(*i*) Enantiomerism (*ii*) Diastereomerism.

10.6.1 Enantiomerism

In 1948, Pasteur observed that an aqueous solution of sodium ammonium tartarate was found to be optically active. He separated two distinct types of crystals from the solution of this compound and found that each of crystal possessed optical activity equal in magnitude but opposite in its sign. The shape of the two types of crystals was found to different and they were non-superimposable.

Such isomers whose molecular structures are non-superimposable mirror images of each other and which rotate the plane-polarised light equally but in opposite directions are known as **enantiomers or enantiomorphs.** The phenomenon of object and its mirror-image isomerism is called **enantiomerism.** Since the object and its mirror-image isomers differ only in the spatial arrangement of atoms these enantiomerism is only a particular type of stereoisomerism.

The existence of object and its mirror-image isomers was justified by Van't Hoff on the basis of tetrahedral concept of carbon atom. Tetrahedral models of an imaginary compound of the type C_{abcd} has already been shown and that of tartaric acid will be shown in next article. These models represent two enantiomers of the compound.

Similarly, we can construct models of enantiomeric forms of [$CH_3CH(OH)COOH$] and 2-methyl-1-butanol [$C_2H_5CH(CH_3)CH_2OH$], (Fig. 10.8), which is also known to *exhibit enantiomerism.*

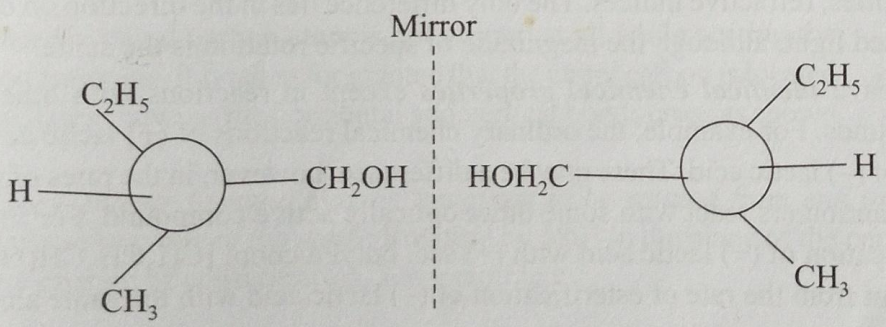
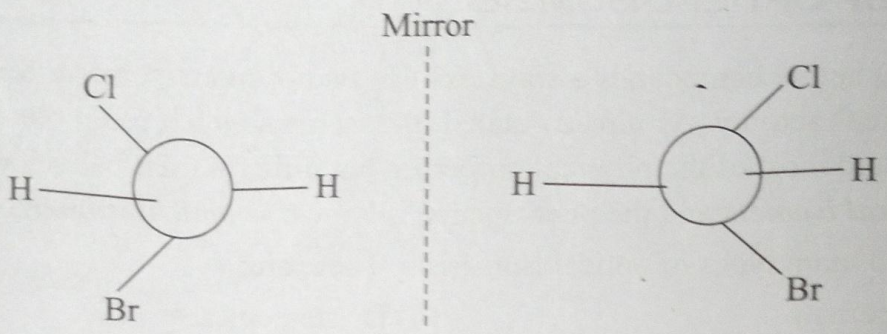


Fig. 10.8 Enantiomeric forms of 2-methyl-1-butanol.

We find that it is possible to construct two models which are non-superimposable mirror images of each other and as such they represent the different enantiomers.

It may be pointed out, however, that the molecules of most of the compounds containing a tetrahedral carbon atom are superimposable on their mirror images as illustrated below with the help of models of bromochloromethane CFF, ClBr. Such compounds do not exhibit enantiomerism because all their molecules are of the same type.



Essential Condition for Enantiomerism

Enantiomeric molecules are always non-superimposable mirror images of each other. The non-superimposability of mirror images invariably arises due to chiral nature of the molecules. *A molecule is termed as chiral if it has no plane of symmetry and is, therefore, non-superimposable on its mirror image.*

Chirality in **most** of the enantiomeric molecules is itself due to the presence of at least one chiral carbon in the molecule. For example, lactic acid [CH_3*CH(OH)COOHl and 2-methyl-1-butanol [C_2H_5*CH(CH_3)CH_2OH] contain one chiral carbon each (the one marked*) and therefore exist as enantiomeric forms as shown already. On the other hand, there can be molecules such as 2, 3-pentadiene which do not contain any chiral carbon but they still possess the property of chirality and thus exhibit enantiomerism.

It may be concluded, therefore, the chirality (*i.e.*, the property of existing as non-superimposable mirror images) *is the fundamental and only condition of enantiomerism.*

Characteristics of Enantiomers

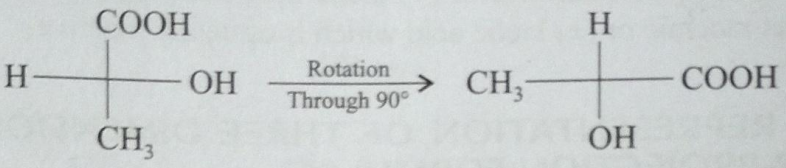
The important characteristics of the enantiomers of a given substance are described below:

(*i*) They have ***identical physical properties*** such as melting points, boiling points, densities, solubilities, refractive indices. The only difference lies in the direction on of rotation of plane polarised light, although the magnitude of specific rotation is the same.

(*ii*) They have ***identical chemical properties*** except in reactions with other optically active compounds. For example, the ordinary chemical reactions of (+) lactic acid are exactly like those of (–) lactic acid. There may be a difference, however, in the rates of reactions at which two enantiomers react with some other optically active compound. For instance, the rate of esterification of (+) lactic acid with (+) sec. butyl alcohol [$CH_3CH_2CH(OH)CH_3$] would be different from the rate of esterification of (–) lactic acid with the same alcohol.

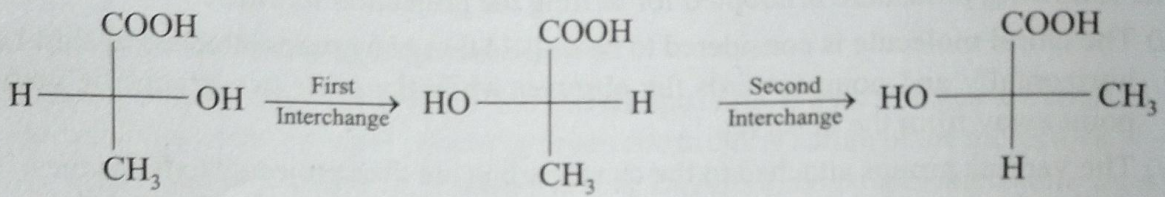
(*iii*) They have ***different biological properties.*** In contrast to physical and usual chemical properties, enantiomers arc quite different in their biological properties. For example, (+) sugar plays an important role in animal metabolism whereas (–) sugar is not metabolized at all. Similarly, (+) tartaric acid is readily consumed by the mould penicillium *glaucum* while (–) tartaric acid is not.

But rotation by 90° or 270° leads to inversion of configuration (*i.e.*, changes one configuration into its mirror image) so that the new configuration represents the enantiomer of the original compound.



III (–) Lactic acid IV(–) Lactic acid

(*vi*) If positions of two groups or atoms about the chiral carbon are interchanged it also leads to inversion of configuration. But if we carry out two such interchanges, the configuration remains unaltered.



V (–) Lactic acid

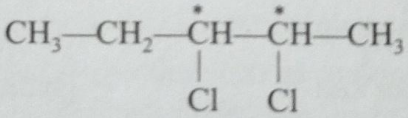
VI(+) Lactic acid
Inversion of configuration

VII(–) Lactic acid
Configuration same as that of I

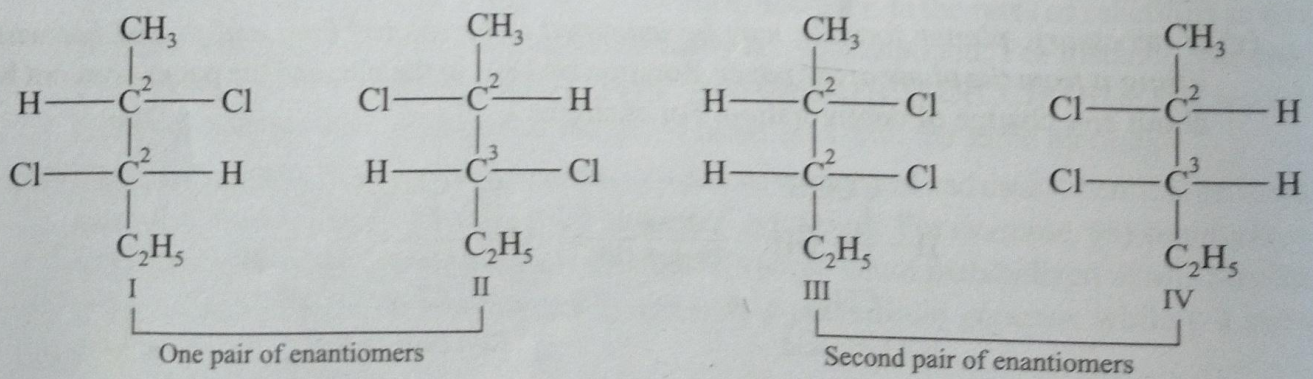
It is quite evident from above that one interchange is equivalent to rotation by 90° or 270° while two interchanges are equivalent to rotation by 180°.

10.7.1 Diastereomerism: Compounds having More than One Chiral Carbon

We have learnt that a compound containing one chiral centre exists in two stereoisomeric forms which are known as enantiomers of each other. But compounds containing more than one chiral centre can exist in more than two stereoisomeric forms. To illustrate this statement, let us consider the case of 2, 3-dichloropentane:



which contains two chiral centres. Since the four different groups attached to one chiral centre are not the same as those attached to the other, the two chiral carbon atoms are dissimilar from one another. There are as many as four stereoisomers (I, II, III and IV) possible for this compound.

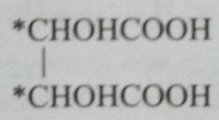


Comparison of Enantiomers and Diastereomers

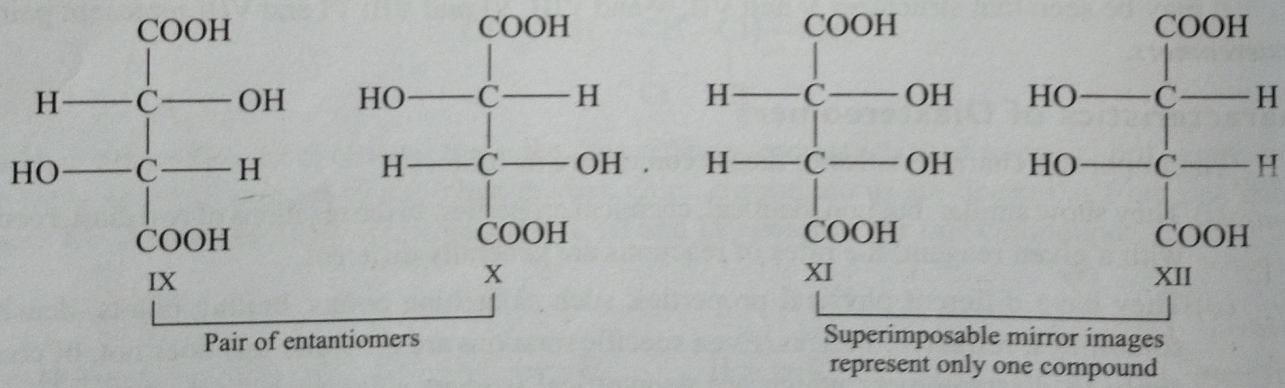
Enantiomers	Diastereomers
1. These stereoisomers have a mirror image relationship.	1. These stereoisomers do not have a mirror image relationship.
2. These have similar physical properties, such as melting point, boiling point, solubility in a given solvent, density, etc.	2. These have different physical properties such as melting point, boiling point, solubility in a given solvent, density, etc.
3. These cannot be separated by such methods.	3. These can be separated by fractional distillation, fractional crystallization and adsorption chromatography.
4. They have optical rotation in opposite direction but to the same extent.	4. They may have optical rotation in the same or opposite directions but to a different extent.
5. They have identical chemical properties except with other optically active compounds.	5. They have identical chemical properties but differ in the rate of reactions with optically active compounds.

10.8 MESO COMPOUNDS

Consider **a compound containing two similar chiral centres,** *i.e.*, having the same set of four different groups attached to each of the chiral carbon atoms. A typical example is tartaric acid:



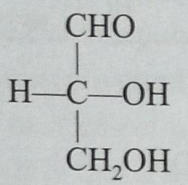
In view of the fact that it has two chiral centres, one may expect the existence of four stereoisomers of this acid having the configurations IX. X, XI and XII.



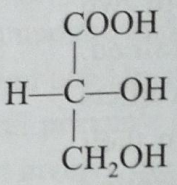
Formulae IX and X are non-superimposable mirror images of each other and, therefore, represent a pair of optically active enantiomers.

Formulae XI and XII again have a mirror image relationship. Close examination of these formulae, shows that one of these structures may be superimposed on the other just by rotating it through 180° within the plane of the paper. These two formulae, therefore, represent two superimposable mirror image molecules of the same compound. *Further examination of formula XI (or XII) reveals that in*

It must be emphasized that there is no direct relationship between absolute configuration and direction of rotation of polarised light. Two substances may have similar relative configurations and yet may rotate the plane of light in different directions. For example, D-(+)-glyceraldehyde and D-(–) glyceric acid have similar configuration even though the former is dextrorotatory-while the latter is levorotatory.

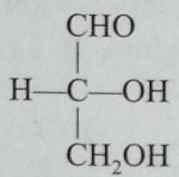


D-(+)-Glyceraldehyde

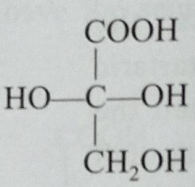


D-(–)-Glyceric acid

Similarly two compounds may have different configurations and even then they may rotate the plane of light in the same direction. For example, D-(+)-glyceraldehyde and L-(+)-lactic acid have opposite configurations but the same sign of rotation.



D-(+)-Glyceraldehyde

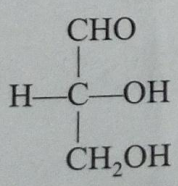


L-(–)-Lactic acid

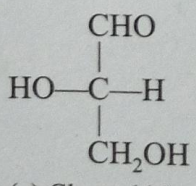
(B) Absolute Configuration

Bijvoet (1951) was able to determine the absolute configuration of a compound by using X-ray diffraction studies. 'The actual arrangement in space of the atoms or groups constituting a particular stereoisomer is called absolute configuration. The first compound whose absolute configuration was determined was sodium rubidium salt of (+)-tartaric acid. Bijvoet confirmed that (+)-tartaric acid actually has the same configuration, which was previously assumed to have on the basis of configurational relationship between glyceraldehyde and tartaric acid (as described earlier). If the assumed configuration of (+)-tartaric acid was correct, the assumed configuration of the two enantiomers of glyceraldehyde must also be correct. As such the configuration of all other compounds derived by correlation with glyceraldehydes must be correct ones. Thus the relative configuration assigned to D-(–)-glyceric acid, L-(–)-lactic acid (discussed earlier), carbohydrates and a large number of other compounds actually represent their absolute configuration.

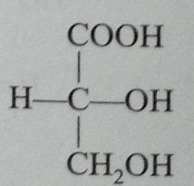
The absolute configurations of some simple but stereochemically important compounds are given below in the planar form:



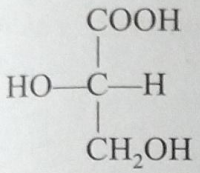
D-(+)-Glyceraldehyde

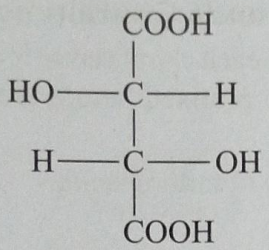


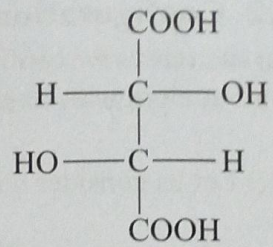
L-(–)-Glyceraldehyde



D-(–)-Lactic acid

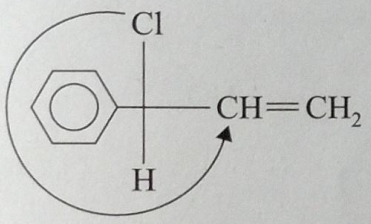

L-(+)-Lactic acid


D-(-)-Tartaric acid

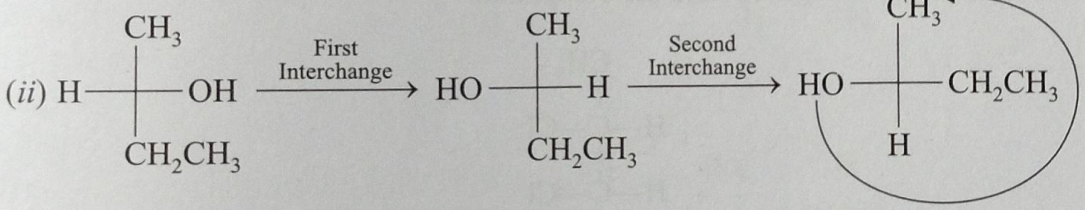

L-(+)-Tartaric acid

10.10.1 Configuration on the Basis of Projection Formulae

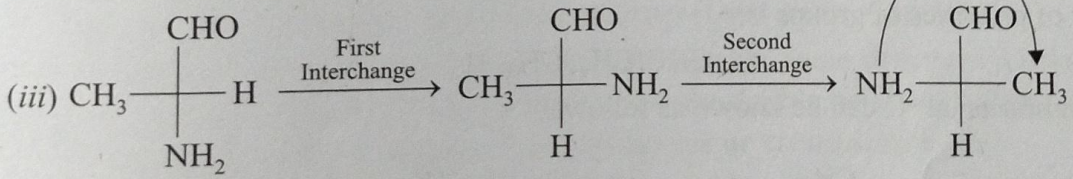
While assigning configuration to a stereoisomer on the basis of projection formula, the procedure is essentially the same as in case of three dimensional formulae. However, if the group of lowest priority is pointing towards us (*i.e.*, bonded horizontally) an additional step is required. In such cases the given formula is converted into another projection formula by making two **interchanges** so that the group or atom of lowest priority is placed vertically downwards or upwards. Then the configuration is assigned following the usual procedure:

(*i*) 

The sequence of priorities is Cl,  . $CH{=}CH_2$, H. Therefore, configuration is S.

(*ii*) 

The sequence of priorities is OH, CH_2CH_3, CH_3, H. Therefore, configuration is S.

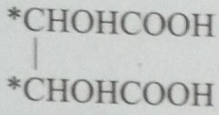
(*iii*) 

The sequence of priorities is NH_2, CHO, CH_3, H. Therefore, configuration is R.

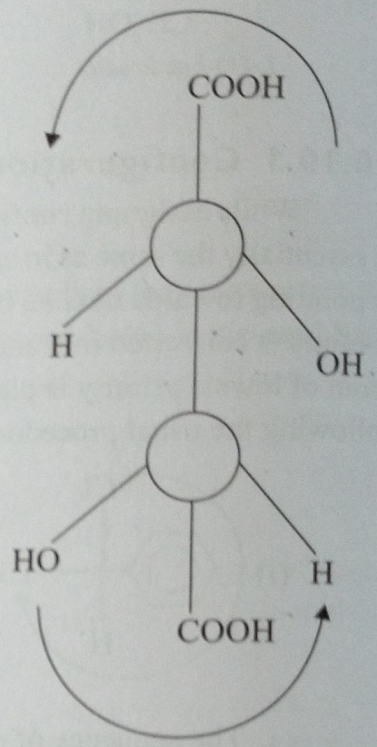
10.10.2 Configuration of Compounds Containing More Than One Chiral Centre

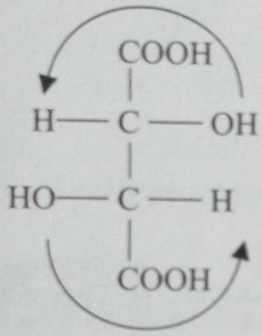
In such cases the configuration about each chiral centre is ascertained separately. The specification of each atom alongwith its number is then prefixed before the name of the compounds as illustrated below:

(*i*) Let us consider one of the forms of tartaric acid,

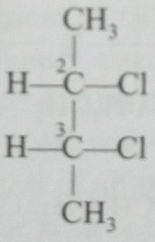


Each chiral centre in this molecule has the same set of four groups attached to it. The sequence of priorities of these groups is OH, COOH, CHOH-COOH, H. Following this sequence of priorities, the configurations around each of the chiral centres is S so that the compound may be designated are (2S, 3S)-tartaric acid.





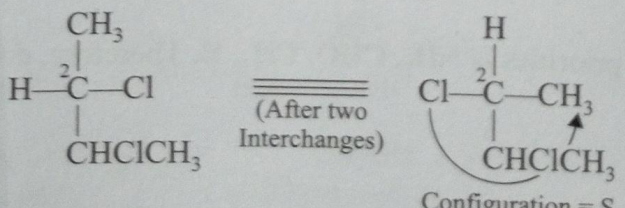
(*ii*) Let us now assign configuration to the compound



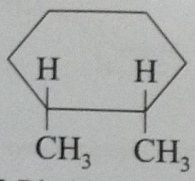
Each of carbon atoms 2 and 3 has the groups CH_3, H, Cl and $CHClCH_3$ attached to it. The order of priorities of groups is:

Cl, $CHClCH_3$, CH_3, H

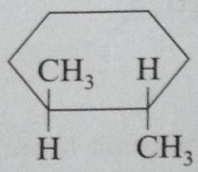
Configuration at ^2C can be known as follows:



For example, 1,2-dimethyl cyclohexane exists in two geometrical isomeric forms. If two methyl groups are on opposite sides of the ring, they are *trans* and when they are on the same side they are *cis*. These compounds are geometrical isomers of each other.

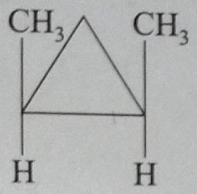


cis-1,2-Dimethylcyclohexane

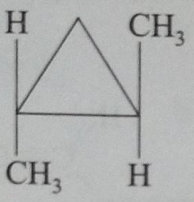


trans-1,2-Dimethylcyclohexane

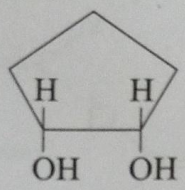
The following are other examples of geometrical isomers of cyclic compounds.



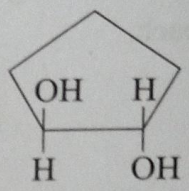
cis-1,2-Dimethyl cyclopropane



trans-1,2-Dimethyl cyclopropane



cis-1,2-Cyclopentanediol



trans-1,2-Cyclopentanediol

10.12 CONFORMATION OF ALKANES

Rotation around carbon-carbon single bond. Single covalent bond (σ bond) present between two carbon atoms is formed by the overlap of their sp^3 hybrid orbitals along the inter-nuclear axis. The electron distribution of the molecular orbital, thus formed, is cylindrically symmetrical around the axis of the bond. *Due to the axial symmetry of the molecular orbital, rotation around the C—C bond is almost free.* As a result of this rotation, alkanes can have different spatial arrangements, *i.e.* different relative arrangement of their atoms in space.

Such different spatial arrangements of atoms or groups of atoms in a molecule that can be readily inter-converted by rotation around C-C single bond are called conformers. They are rotational isomers and the phenomenon is called, conformational isomerism. The molecular geometry corresponding to a conformer is known as conformation.

10.12.1 Conformation of Ethane

In ethane molecule, if it is supposed that the position of one of the carbon atoms is kept fixed and the other is rotated about it, a large number of arrangements of the hydrogen of the carbon with respect to the hydrogen of the other can be obtained. Out of the infinite number of possible conformations of ethane, two conformations represent the extremes, as shown in Fig. 10.9. These are:

1. Eclipsed conformation
2. Staggered conformation.

1. **Eclipsed conformation:** In this conformation, the tetrahedrally attached three hydrogen atoms to front carbon are exactly in front of those attached to the back carbon, *i.e.*, hydrogen atoms of both the carbon atoms are crowded together.
2. **Staggered conformation:** In this conformation, the tetrahedrally attached hydrogen atoms to two carbon atoms are as far apart as possible. It is important to note the basic structure of the molecule and the various bond lengths and bond angles remain the same in both the conformations. These are called **Sawhorse method** of representing the conformations. (Fig. 10.9).

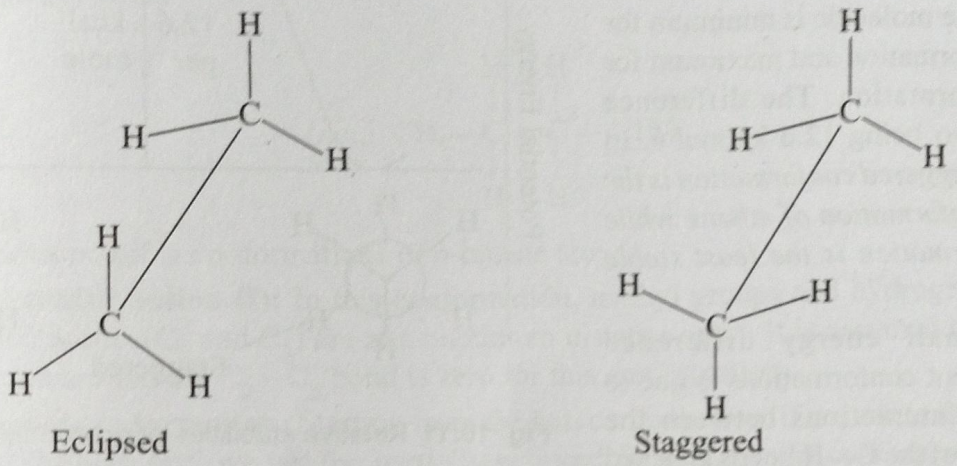


Fig. 10.9 Eclipsed and staggered conformations of Ethane

Newman's style of representing the conformations of molecules is more popular Thus the two conformations of ethane may be represented by **Newman's projections** as **shown** in Fig. 10.10.

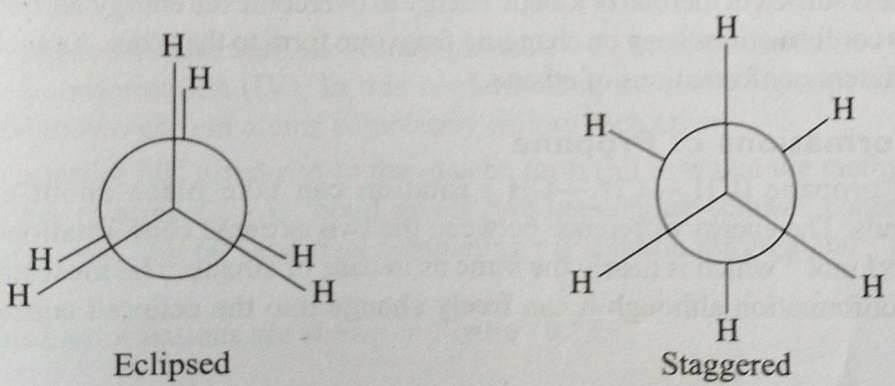


Fig. 10.10 Newmen's projection for the conformations of Ethane.

In Newman projection, the two carbons forming a bond are represented by two circles, one behind the other, so that only the front carbon is seen. The hydrogen atoms attached to the front carbon are depicted by C—H bonds from the centre of the circle. The C—H bonds of the back carbon are drawn from the circumference of the circle.

One conformation of ethane gets converted into the other when rotated through an angle of 60°.

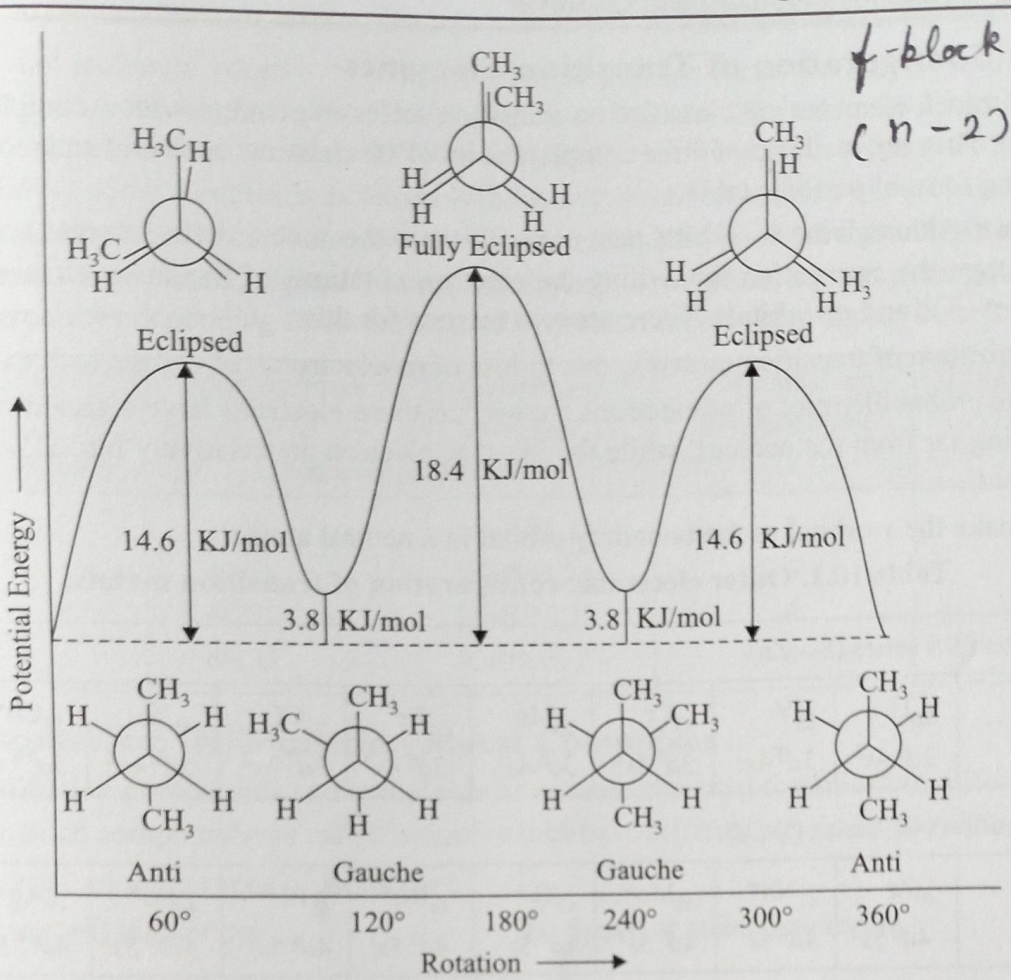


Fig. 10.14 Energy Changes during rotation around the carbon-carbon bond in n-Butane

10.13 ISOMERISM IN TRANSITIONAL METAL COMPOUNDS

Transition Elements

The transition elements are those which either in their elemental state or in their commonly occurring oxidation states have partly filled *d*- and *f*-sub-shell. *d*-block elements usually are called transition elements and *f*-block elements are called inner transition elements.

The transition elements are the elements which show a slow and gradual change in characteristic similarity between highly reactive *s*-block elements on one side and *p*-block elements on the other side of the periodic table. It is also from their position in the periodic table where they lie between the most electropositive *s*- and the most electronegative *p*- block elements and thus represent a transition (change) from them and are called **transition elements**. They are also called *d*- block elements because the successive electrons are added in the *d*-orbital of the $(n-1)$ or penultimate shell. **Their last two shells are incomplete.** They lie in the groups 3 to 12 in the periodic table.

Thus, the d-block elements are defined as the elements in which last electron enters in d-sub shell of their penultimate shell (n – 1) i.e., next to the outermost shell.

Electronic Configuration of Transition Elements

The *d*- block elements are classified as transition series of element with incomplete $3d$, $4d$, $5d$ and $6d$ orbital. They are made up of three complete rows of 10 elements each and an incomplete fourth row in the long form of periodic table.

Caution. Although the $4s$- orbital penetrates closer to the nucleus than $3d$ orbitals and therefore, has lower energy, the convention for writing the electron notations of transition elements is to write electrons in $(n-1)d$ and ns-orbitals. There are two reasons for this:

(*a*) Ionization of transition metals is due to loss of ns-electrons (of course with exception).

(*b*) The probability plot of ns electrons shows that these electrons have a greater probability of being far from the nucleus, while the $(n-1)d$ electron are relatively buried deep inside the atom.

This make the *s*-orbital as the boundary orbital in a neutral atom.

Table 10.1. Outer electronic configuration of transition metals.

First Transition ($3d$) series (Sc–Zn)									
$_{21}Sc$ [Ar] $3d^1\,4s^2$	$_{22}Ti$ $3d^2\,4s^2$	$_{23}V$ $3d^3\,4s^2$	$_{24}Cr$ $3d^5\,4s^2$	$_{25}Mn$ $3d^5\,4s^1$	$_{26}Fe$ $3d^6\,4s^2$	$_{27}CO$ $3d^7\,4s^2$	$_{28}Ni$ $3d^8\,4s^2$	$_{29}Cu^*$ $3d^{10}\,4s^2$	$_{30}Zn$ $3d^{10}\,4s^1$
Second Transition ($4d$) series (Y-Cd)									
$_{39}Y$ [Ar]$4d^1 5s^2$	$_{40}Zr$ $4d^2\,5s^2$	$_{41}Nb^*$ $4d^4\,5s^1$	$_{42}Mo^*$ $4d^5\,5s^1$	$_{43}Tc^*$ $4d^6\,5s^2$	$_{44}Ru^*$ $4d^7\,5s^1$	$_{45}Rh^*$ $4d^8\,5s^1$	$_{46}Pd^*$ $4d^{10}\,5s^0$	$_{47}Ag^*$ $4d^{10}\,5s^1$	$_{48}Cd$ $4d^{10}\,5s^2$
Third Transition ($5d$) series (La- Hg)									
$_{57}La$ [Xe]$5d^1\,6s^2$	$_{72}Hf$ $5d^2\,6s^2$	$_{73}Ta$ $5d^3\,6s^2$	$_{74}W$ $5d^4\,6s^2$	$_{75}Re$ $5d^5\,6s^2$	$_{76}Os$ $5d^6\,6s^2$	$_{77}Ir$ $5d^7\,6s^2$	$_{78}Pt$ $5d^9\,6s^1$	$_{79}Au$ $5d^{10}\,6s^1$	$_{80}Hg$ $5d^{10}\,6s^2$
Fourth Transition ($6d$) series (Ac-Mt.)									
$_{89}Ac$ [Rn]$6d^1\,7s^2$	$_{104}Rf$ $6d^2\,7s^2$	$_{105}Db$ $6d^3\,7s^2$	$_{106}Sq$ $6d^4\,7s^2$	$_{107}Bh$ $6d^5\,7s^2$	$_{108}Hs$ $6d^6\,7s^2$	$_{109}Mt$ $6d^7\,7s^2$	$_{110}Ds$ $6d^8\,7s^2$	$_{111}Rg$ $6d^{10}\,7s^1$	$_{112}Cn$ $6d^{10}\,7s^2$

10.13.1 Complex Formation by Transition Elements

Transition metals form a large number of complex compounds. Here the metal ions bind a number of anions or neutral molecules (called ligands) giving compounds showing characteristic properties. Some example of such complex compounds are:

$[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ $[Cu(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$

Their tendency to form complexes is due to the following reasons:

(*i*) The presence of vacent $(n-1)d$ orbitals which can accept one or more electron pairs from ligands.

(*ii*) High charge density due to small size and high charge of the transition metal ion,

(*iii*) Availability of several oxidation states.

A complex molecule consists of a highly charged positive metal ion (Lewis acid) with vacant *d*-orbital capable of receiving lone pairs of electrons from ligands attached to the central metal ion or atom to form a complex ion is called **co-ordination number** of the central metal atom or ion.

The stability of the complexes increases with increase in atomic number of the element. Moreover, the complexes of atoms with higher oxidation states and thus smaller size are relatively more stable.

Complexes have linear, square planar, tetrahedral, octahedral, square pyramidal or trigonal bipyramidal structures depending upon the type of hydridization involved during their formation.

Lewis acids (acceptors) (Central metal ions)	Lewis bases Ligands (donors)	Complexes Number	Co-ordination hybridization	Type of Structure
Ag^{+} +	$2NH_3$ →	$[Ag(NH_3)_2]^{+}$	2	sp
Cu^{+2} +	$4\ NH_3$ →	$[Cu(NH_3)_4]^{2+}$	4	dsp^2
Zn^{2+} +	$4CN$ →	$[Zn(CN)_4]^{-2}$	4	sp^3
Cr^{3+} +	$6H_2O$ →	$[Cr(H_2O_6]^{3+}$	6	d^2sp^3

10.13.2 Isomerism in Transition Metal Complexes

Co-ordination compounds and complexes have same chemical formulae but different structural arrangements. Such compounds are called isomers which have different physical and chemical properties.

There are two main types of isomerism

(A) Structural isomerism (B) Space or stereo isomerism

(A) Structural Isomerism

These isomers have same molecular formulae but different structural arrangements of atom around central metal ion.

It is mainly of the following types:

1. **Ionisation isomerism:** Ionisation isomers yield different ions in solution although they have same composition. This type of isomerism is due to the exchange of anions between the complex ion and the ions outside it, *i.e.*, in coordination sphere. For example, $[Co(NH_3)_5Br]SO_4$ is red-violet and in solution gives a precipitate with $BaCl_2$ confirming the presence of SO_4^{2-} ion.

   On the other hand, $[Co(NH_3)_5SO_4]Br$ is red, and does not give test for sulphate ion in the solution, but instead gives a precipitate of AgBr will $AgNO_3$.

   Other examples of ionization isomerism are:

   (*i*) $[Pt(NH_3)_4(OH)_2]SO_4$ and $[Pt(NH_3)_4SO_4](OH)_2$

   (*ii*) $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$

   (*iii*) $[Co(NH_3)_5\ NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

2. **Hydrate isomerism:** Since water is one of the most effective co-ordinating agents, therefore, the number of water molecules which may enter into the co-ordination sphere may vary resulting in the formation of hydrate isomers. For example, there are three different hexa-hydrates of chromic chloride with an empirical formula of $CrCl_3 \cdot 6\ H_2O$. One of these hydrate is violet and

the other two are green in colour. All the three differ in the number of molecules of water in the co-ordination sphere. The formulae which have been assigned to these hydrate isomers are:

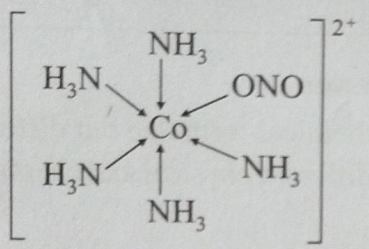
$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$	$[Cr(H_2O)_4Cl_2]Cl \cdot 2\,H_2O$
Violet	Bluish green	Dark green
(three ionic chlorines)	(two ionic chlorines)	(one ionic chlorine)

Similarly other compounds in which hydrate isomerism is observed are:

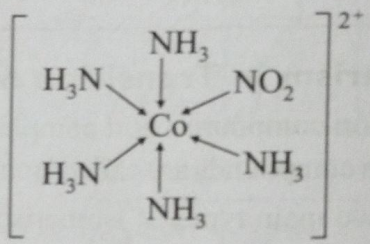
(*i*) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2)Cl \cdot H_2O$

(*ii*) $[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl \cdot H_2O$

3. **Linkage Isomerism:** Isomerism of this type occurs *when more than a single atom in a ligand may function as a donor. Such ligands are called ambidentate ligands.* For example, in the case of NO_2 either a nitrogen or an oxygen atom may act as donor giving two different isomers. Thus two different isomers with molecular formula $[Co(NO_2)(NH_3)_5]^{2+}$ have been prepared. One isomer has N-atom of NO, group linked to cobalt atom and the other has O-atom linked to cobalt



Nitrito-pentamminecobalt (III) ion (Red)



Nitro-pentamminecobalt (III) ion (Yellow)

Other Examples are:

(*i*) $[Cr(H_2O)_5SCN]^{2+}$ and $[Cr(H_2O)_5NCS]^{2+}$

(*ii*) $[(NH_3)_2(py)_2Co(NO_2)_2]NO_3$ and $[(NH_3)_2(py)_2\ Co(ONO)_2]\ NO_3$ etc.

4. **Co-ordination Isomerism:** This type of isomerism is possible when both positive and negative ions of a salt are complex ions. The two isomers differ in the distribution of ligands in the cation (positive ion) and the anion.

Two important examples are:

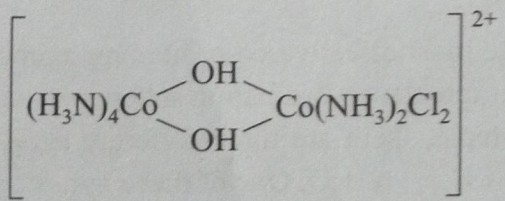
(*i*) $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$

(*ii*) $[Cr(NH_3)_6]\ [Co(C_2O_4)_3]$ and $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$

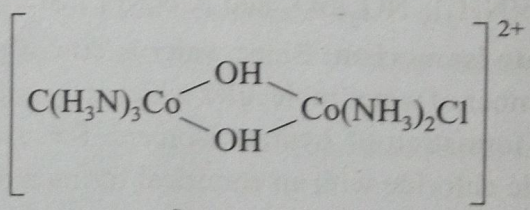
(*iii*) $[Pt(NH_3)_4]\ [PtCl_6]$ and $[PtCl_2(NH_3)_4]\ [PtCl_4]$

This type of isomerism may be caused by interchange of ligand between the two complex ions.

5. **Co-ordination position isomerism:** This type of isomerism is due to *the difference in the distribution of ligands in two coordination centres. Generally the bridged complexes involving different ligands show this isomerism e.g..*

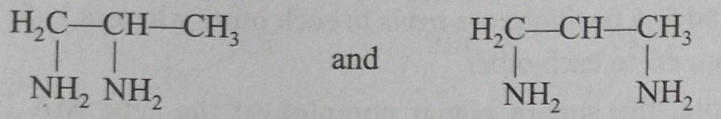


Unsymmetrical



Symmetrical

6. **Ligand Isomerism:** This isomerism arises in those complexes in which the two ligands are isomers themselves, *e.g.*,



1, 2-diamino propane 1, 3-diamino propane

When these form the complexes, we get ligand isomers. This type of isomerism is quite rare.

7. **Polymerisation isomerism:** This is not true isomerism because it occurs between compounds having the same empirical formula, but different molecular weights. Thus $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_4][PtCl_4J$ have the same empirical formula.

(B) Stereoisomerism or Space Isomerism

This is due to the different relative positions of the ligands. It is of two types:

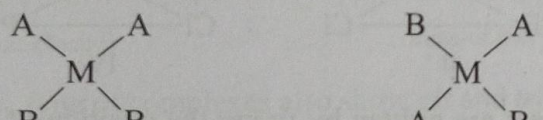
1. Geometrical isomerism 2. Optical isomerism

1. **Geometrical isomerism:** Geometrical isomers differ in the spatial distribution of atoms or groups around central atom or atoms in polynuclear compounds. Those complexes in which the two same ligands occupy adjacent positions to each other are called *cis*-isomer while ligands occupying position opposite to each other are called *trans* isomer.

This isomerism cannot be exhibited by co-ordination compounds having 2 or 3 co-ordination number as it is not possible to have more than a single arrangement of ligands in space around the Central-ion in these cases. Geometrical isomerism with respect to the metal has also not been found among tetrahedral complexes of type MA_4 or MA_2B_2 (where A and B represents ligands) which do not show this isomerism because all the four ligands are equidistant from each other. This type of isomerism is shown by ***square planar and octahedral complexes.***

(*a*) **Cis-trans isomerism in square planar complexes is of various types:**

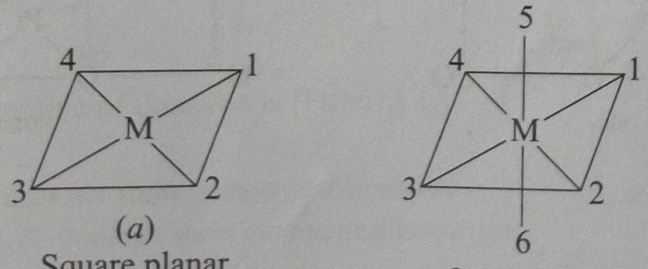
(*i*) Any complex of the type MA_2B_2 can exist in *cis-trans* form.



cis- trans-

It is because the ligands may be equidistant from the central atom, but they are not equidistant from each other. Consequently it is possible to distinguish between ligands that lie next to each other on the edge of the square and those which lie opposite to each other on the square diagonally.

Thus geometrical isomerism is an important key in co-ordination compound with co-ordination number 4 and 6. The *cis-trans* positions in square planes and octahedral complexes are reviewed as follows:



(*a*) Square planar Octahedral