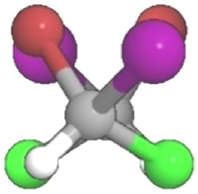

UNIT 1

MOLECULAR SYMMETRY AND CHIRALITY

Structure

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1.1 INTRODUCTION

You have studied in your undergraduate classes that stereochemistry involves the study of arrangement of atoms of a molecule in three dimensions. The two important aspects of stereochemistry are stereoisomerism and the stereochemical changes which occur during a chemical reaction. Broadly speaking the isomerism is of two types viz., constitutional and stereoisomerism and the compounds showing these types of isomerism are called the constitutional isomers and stereoisomers, respectively. The constitutional isomers differ in their bonding sequence and the connectivity of atoms. Just to recall the type of constitutional isomers which are chain isomers, position isomers and functional isomers and three special cases viz., metamers, tautomers and ring chain isomers. We would not discuss these types because it is expected that you have a fair knowledge of the same.

In contrast to the constitutional isomers, stereoisomers have the same bonding sequence, but they differ in the orientation of their atoms in space. Although you have studied these isomers also in your previous classes yet we will study more about these isomers in this course. We would start with describing the representation of molecules in 2 dimensions as it is not always possible to visualise and explain the stereochemical structures in 3 dimensions. Then we will study about the classification of stereoisomers. The focus would lie on the reasons of existence of optical isomers i.e., absence of symmetry elements, would be described in detail. The unit deals with another important aspect of optical isomerism and the optical isomers which is chirality. How does chirality relate to asymmetry would also be elaborated. The concept of chirality will be extended further to compounds with more than one chiral carbon atom in the next unit.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ draw the organic molecules by different projections and explain the stereochemistry of the molecule;
- ❖ classify stereoisomers and explain the different types;
- ❖ describe different types of symmetry elements;
- ❖ explain the relationship between symmetry and the molecular properties;
- ❖ define chirality and explain the existence of chirality in molecules with one chiral centre; and
- ❖ explain the relationship between chirality and symmetry.

1.2 REPRESENTATION OF ORGANIC MOLECULES IN TWO DIMENSIONS

The stereochemistry of organic molecules can be well understood with the use of models that give us a three-dimensional view of a molecule. However, the models are not always available or handy to study the three-dimensional structure of molecules. Therefore, it is important to learn the ways of representing the three-dimensional structures of these molecules on a two dimensional surface like the paper or a blackboard or a white board. It is necessary to learn that how to draw three dimensional structures on a two dimensional paper. Drawing of structures of molecules in such a way is called **projection**.

There are five well-known methods for representing the structures. These are divided into following two main categories.

- **Perspective type:** This includes the flying wedge and the zig-zag representation.
- **Projection type:** This includes the Fischer, the Newman and the Sawhorse projections.

The two types of representations of the organic molecules are described in the following subsections.

1.2.1 Perspective Representation of Molecules

The perspective type representation includes the flying wedge and the zig-zag ways as mentioned above. The two types are explained in the following paragraphs.

Flying Wedge representation: You know that the valency of carbon is four and a saturated carbon atom is attached to four groups when joined by single bonds. In flying wedge formula, the two bonds of the carbon atom are shown on the plane of the paper and of the other two; one is shown above the plane and the other below the plane. The bonds which are in the plane are shown by ordinary lines (—) but the bond above the plane is usually shown by a solid cone (▬)and the bond below the plane is shown by a broken line (·''''). For example, methane can be represented by flying wedge structures as shown in Fig. 1.1 given below.

The flying wedge formula or three-dimensional representation is usually done for molecules containing chiral centres. It may also be used for achiral molecules.

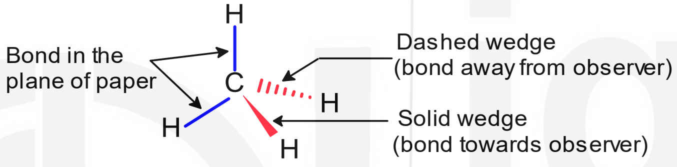


Fig. 1.1: The Flying wedge representation of methane.

Similarly the two isomers of lactic acid can be drawn as shown in Fig.1.2.

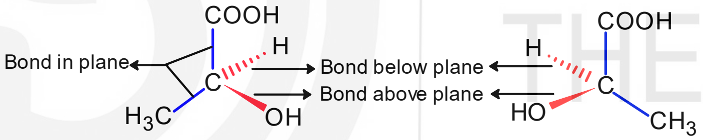
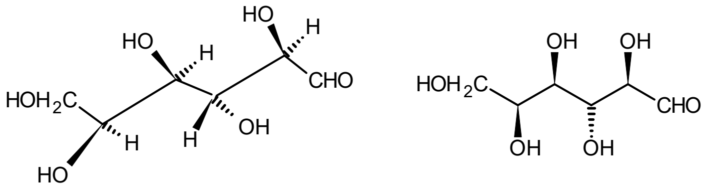


Fig. 1.2: Flying wedge representation of lactic acid.

Zig-Zag Representation: The perspective "zig-zag" structure was devised by Masamune. While drawing these types of structures, carbon and hydrogen atoms are not shown. Carbon atom is considered to be present at the junction of two lines and at the end of the line whereas number of hydrogen atoms is considered such that the valency of carbon is satisfied. Any other atom if present in the chain, is written there. Any substituent or functional group is written at the appropriate carbon with the help of a bond. This representation always denotes a staggered conformation.

Remember that a"zig-zag" formula does not represent an eclipsed conformation.

The flying wedge and "zig-zag" representations of D-glucose are given in Fig.1.3. You should be able to note the difference between these two.



(a) (b)

Fig. 1.3: Flying wedge (a) and Zig zag (b) representation of open chain D-glucose.

1.2.2 Projection Representation of Molecules

The projection type representation includes the Fischer, the Newman and the Sawhorse projections as mentioned above. The three types are explained in the following paragraphs.

Fischer Projections: Fischer projection is a convention for displaying the three-dimensional configurational relationship of a molecule in planar representation. In this representation, the molecule is so oriented that the carbon atom is in the plane of projection (could be paper or blackboard) and the four bonds are shown by two *vertical* and *horizontal* lines which intersect each other. The point of intersection of these lines represents the carbon atom. The horizontal lines of the cross represent bonds projecting outward i.e., above the plane and the vertical lines represent the bonds going below the plane. Fig.1.4 represents a general molecule drawn in wedge formula and its equivalent in Fischer projection. The two groups X and Z are on the plane of paper in wedge and dash representation and the projection is shown under it.

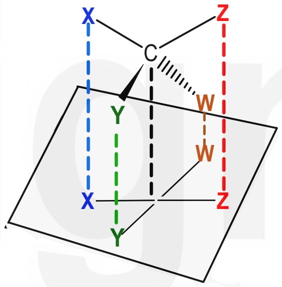


Fig. 1.4: Fischer projection from wedge and dash representation.

For drawing the Fischer projection, a molecule may also be viewed as shown in Fig.1.5 and then writing groups C and D on the horizontal line as they are projecting out of the plane towards viewer.

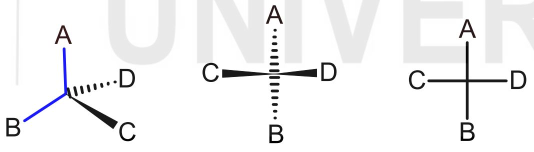
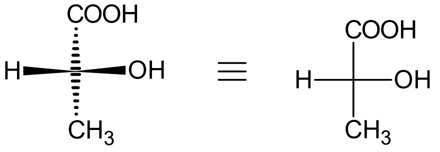


Fig. 1.5: Viewing a molecule for Fischer projection

Fischer projections are normally used to represent compounds with chiral centres. For example one of the isomers of lactic acid can be drawn in wedge and dash formula as 1.6 (a) whose Fischer projection is shown as 1.6 (b).



(a) Wedge formula (b) Fischer projection

Fig. 1.6: Lactic acid: (a) Wedge and Dash (b) Fischer projection formula

We can actually draw many Fischer projections for any stereoisomer because it depends upon the direction of viewing the molecule. As an example the above stereoisomer of lactic acid, can also be represented in different ways as shown in Fig.1.7.

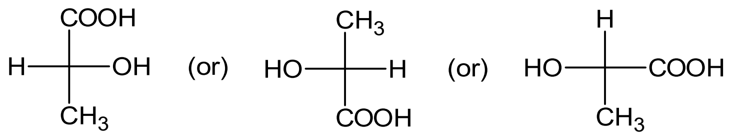


Fig. 1.7. Fischer projections of lactic acid

One can represent complicated carbohydrates like glucose and fructose etc. in a way that communicates their stereochemical information by adhering to the specified guidelines for drawing these projections.

Sawhorse Projection: In this projection, the two key carbon atoms are joined by a diagonal line which is taken to be on the plane of the paper and the remaining bonds are shown by small lines projected above and below that plane. There is a free rotation about C-C bond and the three groups attached to one carbon may be rotated clockwise or anticlockwise in relation to the three groups attached to the other carbon atom. The relative position of various groups attached to these carbon atoms can be easily represented by this type of projection. For example, *n*-butane, $CH_3CH_2CH_2CH_3$, can be represented as shown in Fig. 1.8.

The sawhorse projections are found to be very convenient to show the spatial relationship between the substituents attached to two adjacent carbon atoms (chiral or achiral).

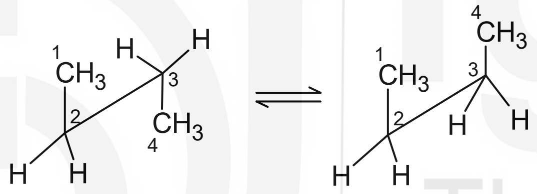


Fig. 1.8: Sawhorse representations of *n*-butane.

Newman Projection: For this type of projection, the molecule is viewed along the bond joining the two carbon atoms. The carbon atom at the back is represented by a circle whereas the front carbon atom is represented by a dot at the centre of the circle. The three groups attached to the front carbon atom are represented by three lines emerging from this point. The circumference of the circle represents the back carbon atom and the three substituents attached to this carbon are shown by three lines emerging from the edge of the circle. These straight lines which represent the bonds are drawn at angles of 120^o. Newman projections are helpful for a better visualization of different conformations of a molecule. For example, the staggered conformation of ethane can be drawn in newman projection as shown in Fig. 1.9.

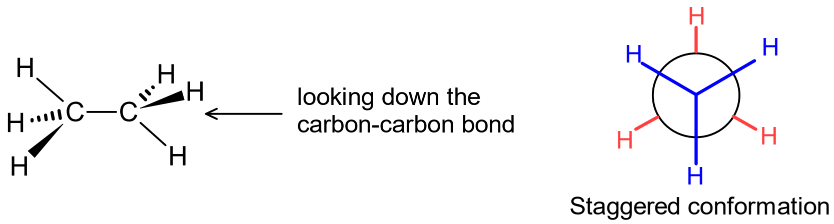
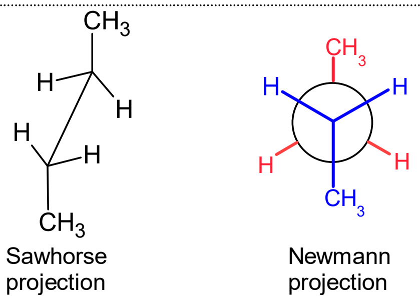


Fig. 1.9: Newman projection of staggered conformation of ethane.

Another example is the staggered conformation of butane that can be represented in sawhorse projection and Newman projection as shown below.



Sawhorse projection

Newmann projection

Fig. 1.10: Sawhorse and Newman projections of butane.

Some of the important points in the context of representing the molecules in two dimensions are mentioned below.

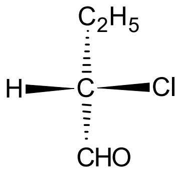
- The “flying wedge” and “zig-zag” formulae have the advantage of showing the molecular backbone in the staggered conformation and entirely on the plane of the paper.
- Fischer formulae depict the molecule in the unrealistic eclipsed conformation while the Newman and sawhorse projections show the molecules in their staggered as well as eclipsed conformations.
- The "flying wedge" and "zig-zag" formulae are useful to show the actual conformation and configuration of compounds having two or more chiral centres.
- Newman and sawhorse formulae are most useful for compounds having two chiral centres.

When solving the stereochemical problems, sometimes it is essential to convert one representation into the other as a particular form is not able to provide the required information. We would explain the interconversions of various representations of molecules in the following subsection.

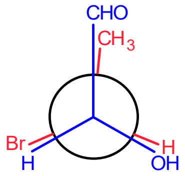
SAQ 1

Draw the correct representation of following compounds in Fischer projection.

a)



b)



1.2.3 Interconversions of Projection Formulae

A few of the simple ways of interconversion of projection formulae from one to the other form are discussed below.

Fischer Projection to Sawhorse

The conversion of Fischer projection to sawhorse projection in eclipsed conformation and then converting it to its staggered conformation with proper numbering of carbon atoms is evident from the examples given in Fig. 1.11.

Fig. 1.11(a) represents an isomer of 2, 3-dibromobutane in Fischer projection. If its sawhorse form is written keeping C-2 in front and C-3 at the back, then the eclipsed sawhorse form becomes 1.11(b). Its staggered conformation is represented as 1.11(c) which is obtained by rotation across the bond between C-2 and C-3.

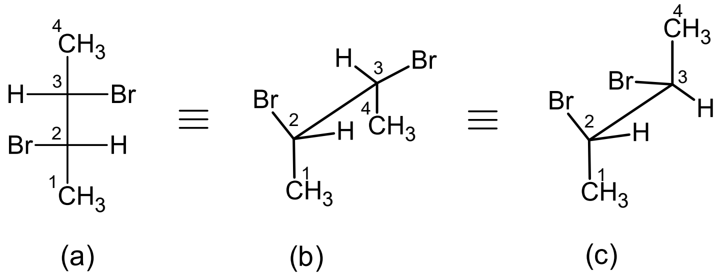


Fig. 1.11: Conversion of Fischer projection to sawhorse.

Sawhorse to Newman to Fischer

The vertical bonds in the eclipsed form of Newman projection may be arranged in such a way that they remain below the horizontal plane shown by dotted line. The transformation to Fischer projection is then carried out keeping the front chiral atom as the lowest chiral centre on counting from the top in the Fischer projection as depicted in Fig. 1.12.

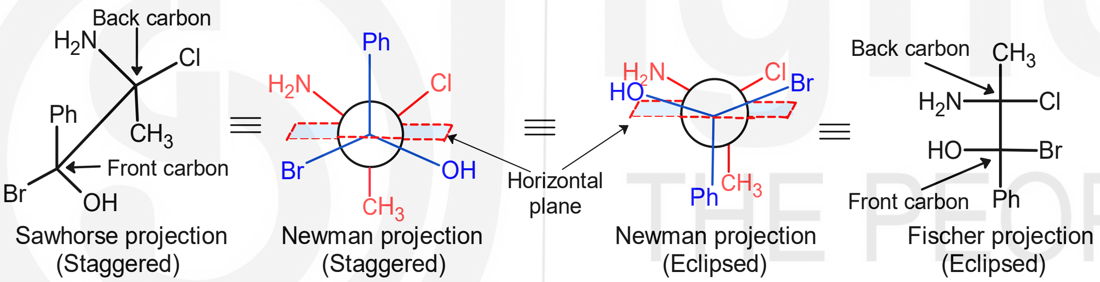


Fig. 1.12: Conversion of sawhorse projection to Newman to Fischer.

Fischer to Newman to Sawhorse

Fig.1.13 shows the conversion of Fischer projection of a molecule into Newman projection and then into sawhorse projection.

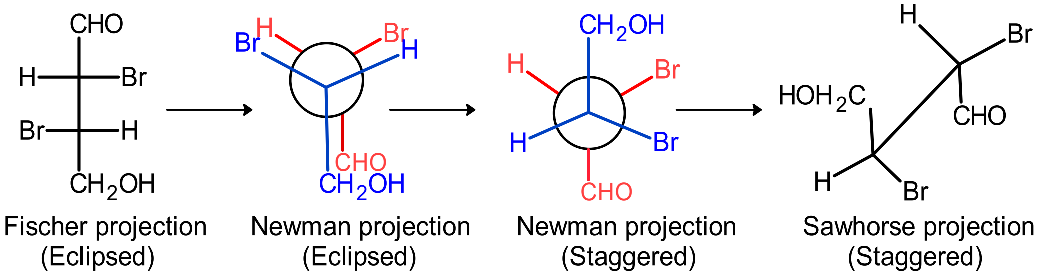
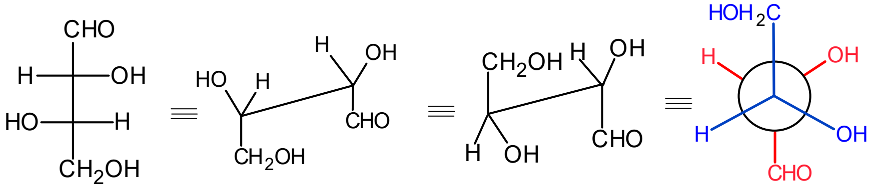


Fig. 1.13: Conversion of Fischer projection to Newman to sawhorse.

Fig. 1.14 (a) shows the Fischer projection of one of the isomers of threose carbohydrate. It can be converted into sawhorse form in eclipsed conformation, Fig. 1.14(b). Its staggered form is represented as 1.14(c) which can be converted into Newman projection as in 1.14(d).



(a) Fischer (b) Eclisped sawhorse (c) Staggered sawhorse (d) Newman

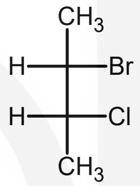
Fig. 1.14: Conversion of Fischer, sawhorse and Newman projections of threose.

After having a clarity of the representation of the organic molecules and their interconversion, we proceed to a recall the types of stereoisomers. In other words we will study the classification of isomers in the next section. Before proceeding try to answer the following SAQs.

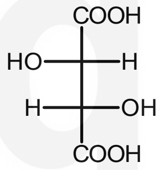
SAQ 2

Draw Newman and sawhorse projection formulae for the following compounds in eclipsed configuration.

a)



b)



1.3 CLASSIFICATION OF STEREOISOMERS

The study of the three-dimensional structures of molecules helps to understand their stereochemical relationships. It is very well known that stereoisomerism exists due to the different spatial arrangement of atoms in a molecule i.e., their three-dimensional structure. The different 3-dimensional structure changes into different stereoisomers. The stereoisomers are classified into two types viz., **configurational** and **conformational isomers**. Configurational isomers are the molecules which have different arrangement of atoms and cannot be converted into each other without breaking a bond. These are further classified as **geometrical** and **optical isomers**. The optical isomers are further classified as **enantiomers** and **diastereomers**. The conformational isomers are different relative arrangements of atoms obtained by the rotation across single bonds in the molecule. We will discuss about conformational isomers in detail in Unit 3.

You have already studied about these types of isomers and, also the IUPAC notations used in their nomenclature in your previous classes. Now we will discuss more about these types of isomers. We start with geometrical isomers in the following subsection.

1.3.1 Geometrical Isomers

The geometrical isomers belong to the configurational type of isomers as mentioned above which depend upon the configuration of the molecules.

Configuration can be defined as the specific arrangement of atoms in space which characterizes a particular stereoisomer. In other words, it can be said that the arrangement of atoms that emerges from the spatial arrangement of its bonds. As per IUPAC (1979), configuration is defined as,
"*The arrangement of the atoms in space of a molecule of defined constitution without regard to arrangements that differ only as after rotation about one or more single bonds*."

There are two necessary conditions that are required to be fulfilled by geometrical isomers.

1. There should be restricted rotation between two atoms under consideration. This can be due to presence of a double bond between the two atoms or when the two atoms are part of the same ring. These two atoms may not necessarily be carbon-carbon only and can be carbon-nitrogen or nitrogen-nitrogen also.

2. Each of the two atoms under consideration should have two different groups linked to these.

You are familiar with *cis* and *trans* notations for geometrical isomers which are based on the presence of identical groups on the same or opposite side of a double bond. If any compound contains four different substituents (e.g., in abC = Cxy) or contains more than one double bond then it cannot be designated as the *cis*/*trans*. In such cases, the *E* and *Z* system of nomenclature is used. The concept in brief can be well depicted by the nomenclature followed in case of 2-butene as depicted in Fig. 1.15.

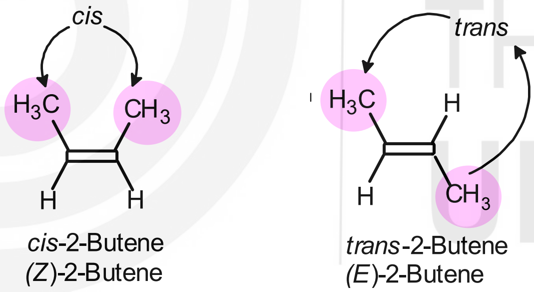


Fig. 1.15: Geometrical isomers of 2-butene.

You will study more about the *E* / *Z* notations of geometrical isomers and the CIP rules for assigning priority of groups attached in detail in Unit 5 of Block 2.

The following subsection explains the other type of configurational isomers viz., the optical isomers.

1.3.2 Optical Isomers

As per the definition given above, optical isomers belong to the type of configurational isomers. It can be said that the molecules that have the same molecular formula but have a different arrangement of the atoms in space are called optical isomers. However, this is not the complete explanation of these molecules. As the name suggests these isomers are optically active or show the property of optical activity. **Optical activity** is a physical property of a molecule like other physical properties which is defined as the property of a molecule to rotate the plane of plane-polarized light. However, all the molecules or compounds do not show this property. Then what type of compounds show optical activity? It is essential to understand the concept of plane polarised light to answer this question and surely you are aware of this concept from your previous classes.

Plane polarised light: when light oscillates in one single direction after passing through a polarising filter.

You know that a molecule containing a carbon atom attached to four different substituents, a, b, c and d results in the existence of non-superimposable mirror images called the **enantiomers** Fig. 1.16. If we try to superimpose structures I and II, we get structure III. It is clear from structure III in figure that the structures I and II are non-superimposable. Such molecules are said to contain an asymmetric carbon atom and are known as **chiral molecules**.

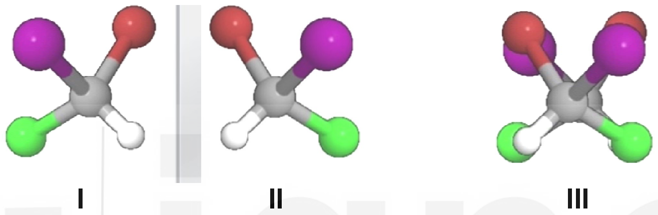


Fig.1.16: Stuctures I and II as the mirror images of a molecule with structure III depicting the non-superimposability of structures I and II.

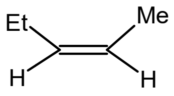
For a molecule to show optical activity, non-superimposability of mirror images or chirality or presence of asymmetric carbon atom is required. However, it becomes difficult to find out the superimposability of molecules with more than one asymmetric carbon atoms. This raises questions like why some molecules are chiral while others are not? How do we check chirality or asymmetry in a molecule? These questions are addressed by the presence of some symmetry elements in the molecule under consideration. The symmetry is a geometric feature which can be a point, line or plane. The process for finding the presence of any such element in a molecule involves few steps called symmetry operations, which are discussed in following section. Before proceeding you can check your understanding of the configurational isomers by answering the following SAQs.

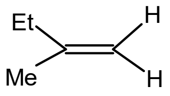
SAQ 3

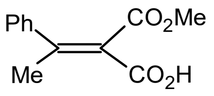
Draw the possible geometrical isomers for 1-bromo-1,2-dichloroethene and assign *E/Z* configuration to each of these.

SAQ 4

Which of the following will form geometrical isomers and why?







1.4 SYMMETRY ELEMENTS AND SYMMETRY OPERATIONS

You have read just above that the symmetry of a molecule is described in terms of **symmetry elements**. The operations performed to determine the presence of symmetry elements are called **symmetry operations**. A symmetry element can be a geometric line, plane or point with respect to which one or more symmetry operations are performed. The symmetry elements are of four types. These are:

- Rotational or proper axis of symmetry (C_n)
- Plane of symmetry (σ)
- Centre of symmetry or centre of inversion (i)
- Alternating or improper axis of symmetry (S_n)

These types are explained in the following subsections.

1.4.1 Rotational Axis of Symmetry

It is denoted by the symbol C_n (Latin word *Circulate*) and is also called **proper axis of rotation**. The subscript 'n' denotes the *fold* or *order* of rotation. It is defined as, "an *n* fold axis of symmetry, when a structure possessing this axis is rotated by an angle of 360°/n around the axis, the structure which results is superimposable with the original one". It is also called **symmetry axis** or **simple axis of symmetry**. The value of *n* can never be a fraction, because in such a case every C_n operation will not give superimposable structure, that is, equivalent structure. If a molecule possesses more than one simple axis of symmetry with different values on *n* then the C_n axis having maximum value of *n* (fold) is called the **principal axis**. When there are several C_n axes with same value of *n*, then the principal axis is one that involves maximum number of atoms of the molecule.

We consider the example of *cis*-1,3-dichlorocyclobutane. It can be depicted by its enantiomers as shown in Fig.1.17. Let us see if it has any symmetry element. Rotation by 90° about the axis shown in the figure gives a molecule which is not identical to the starting compound but a rotation of 180° gives an identical molecule indicating the existence of a two-fold rotational axis of symmetry ($360^{\circ}/180^{\circ} = 2$). Thus, it has a two fold rotational axis of symmetry.

A plane of symmetry is an imaginary plane passing through an object dividing it such that one half is the reflection of the other half.

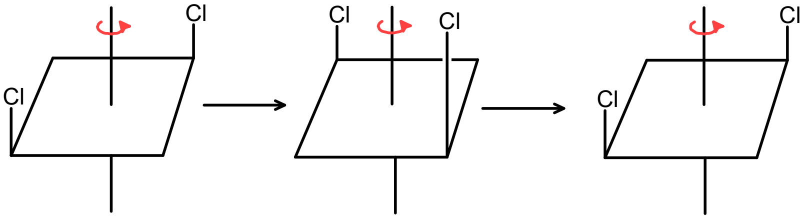


Fig. 1.17: Two fold rotational axis of symmetry

1.4.2 Plane of Symmetry

A plane of symmetry is a plane such that if a line from any element on one side of the plane is drawn perpendicular to the plane and the line extended to an equal distance on the other side of the plane, an identical element is found at the end of the line. In other words, we can say that one half of the molecule is mirror image of the other half. It is because of this property; a plane of symmetry is also called the **mirror plane**. It is designated as sigma (σ) that comes from the German word *spiegel,* meaning mirror.

You might be familiar with the famous monument of India, Taj Mahal. It is very symmetrical, one half of the building is symmetrical to another half.

We find the plane of symmetry not only in organic molecules but in many objects that we see around, e.g., a butterfly. We see that in the butterfly one half of the body and the wings is identical to the other half. The cube shown in Fig. 1.18 has several planes of symmetry. Both the beaker and the compound bromochloromethane have only one plane of symmetry.

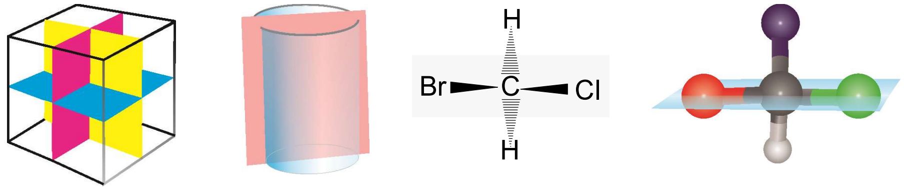
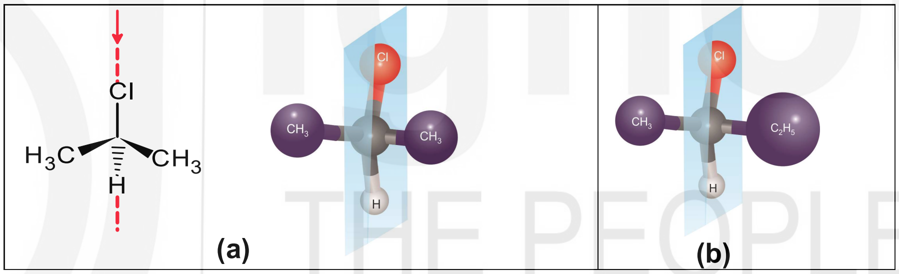


Fig. 1.18: Plane of symmetry depicted by some objects and molecules.

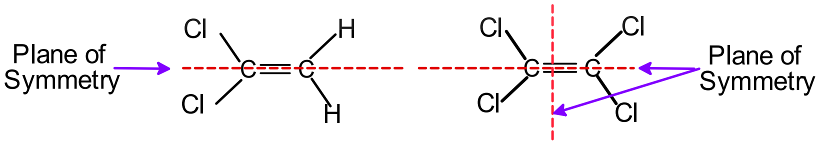
The plane may pass through atoms, between atoms, or both. For example, 2-chloropropane has a plane of symmetry, Fig.1.19 (a), the 2-chlorobutane molecule does not possess a plane of symmetry, Fig.1.19 (b).



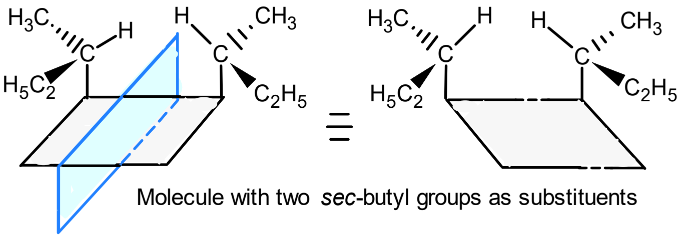
(a) (b)

Fig. 1.19: Plane of symmetry in (a) 2-chloropropane and (b) 2-chlorobutane.

Some more examples of compounds having a plane of symmetry can be given to have a clear understanding. These are 1,1-dichloroethene, 1,1,2,2-tetrachloro ethene, and molecules with two secondary butyl groups as shown in Fig.1.20.



1,1-Dichloroethene 1,1,2,2-Tetrachloroethene



Molecule with two *sec*-butyl groups as substituents

Fig.1.20: Examples of molecules with Plane of symmetry.

It should be remembered that every planar molecule necessarily has a plane of symmetry, namely the *molecular plane*. The symbol σ is usually found to carry three subscripts indicating the position of symmetry plane/planes relative to the principal axis (C_n). These are explained below and depicted in Fig.1.21.

- **Horizontal (σ_h)** represents the reflection in the plane containing the principal axis of rotation, that is, axis with highest value of '*n*'.
- **Vertical (σ_v)** represents the reflection in the plane containing the principal axis.
- **Diagonal (σ_d)** represents reflection in the plane, which contains the principal axis and bisects the angle between the two C_2 axes.

When both σ_v and σ_d planes are present, then the σ_v plane contains the greater number of atoms.

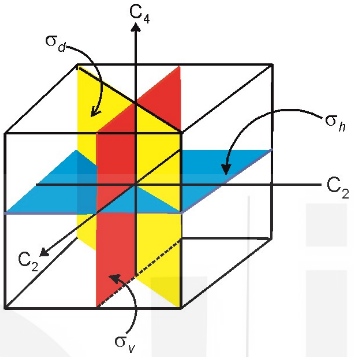


Fig.1.21: Different planes of symmetry.

SAQ 5

Give the order of the simple/proper axis of symmetry, C_n, for the following molecules.

a) CH_4 b) CH_3Cl c) $CHCl_3$ d) Benzene

1.4.3 Centre of Symmetry

Centre of symmetry is defined as "a point in space such that if a line is drawn from any part or atom of the molecule to that point and then extended an equal distance beyond it, an analogous part or atom will be encountered." In other words, inversion of all atoms in the molecule through the point results in an arrangement indistinguishable from the original one. The point is also called a **centre of inversion**.

The centre of symmetry is represented as '***i***'. All C_n and σ elements, if present in addition to *i,* must pass through *i.* Let us understand it with the help of a molecule of 2,4-dimethylcyclobutane-1,3-dicarboxylic acid. It has got two carboxyl groups at two positions and two methyl groups at other two positions. Let us focus on the structure for this molecule given in Fig. 1.22.

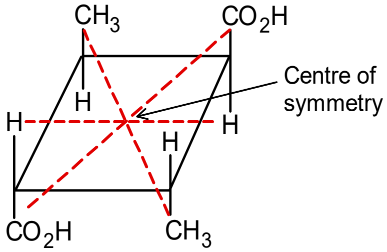


Fig.1.22: 2,4-Dimethylcyclobutane-1,3-dicarboxylic acid.

We draw a line from the carboxyl group, pass it through one point as shown in the structure and extend beyond. On doing so, we meet another carboxyl group after the same distance. When we start from the hydrogen, move through the centre point and extend this line beyond we meet another hydrogen. Similarly for methyl group we find that after an equal distance passing through this point we get a methyl group.

Some other examples of compounds which have a centre of symmetry are ethane(a), *trans*-1,2-dichloroethene(b) shown in Fig. 1.23 (a) and (b) respectively. A molecule shown in 1.23 (c) contains two secondary butyl groups at 1 and 3 position of a cyclobutane ring also possesses a centre of symmetry.

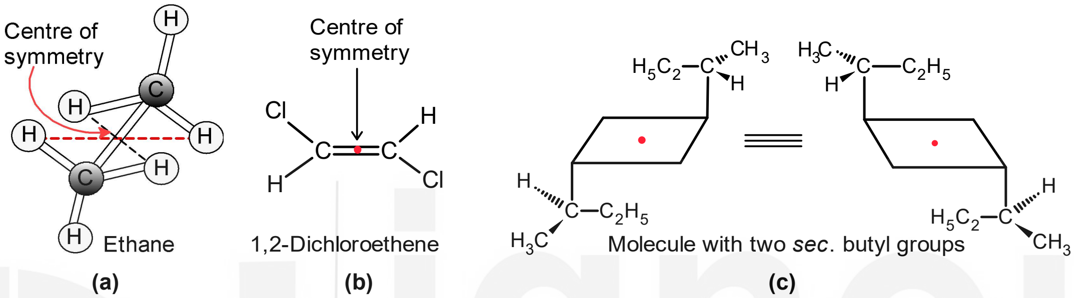


Fig. 1.23: Some molecules showing centre of symmetry.

1.4.4 Alternating Axis of Symmetry

Alternating axis of symmetry is designated as S_n. It is also known as **improper axis of rotation** or also **rotation-reflection axis of symmetry**. A molecule is said to possess an *n*-fold alternating axis of symmetry if rotation through an angle of 360°/*n* about an axis followed by reflection in a plane perpendicular to the axis gives the molecule which is indistinguishable from the original molecule. The alphabet *n* is arrived by the rotation of the molecule. If the molecule is rotated by 90° the value of *n* will be 4. Suppose we get the above explained observation after 180° rotation, the value of *n* will be 2. Hence, we say that the molecule possesses a **two-fold alternating axis of symmetry** or **four-fold alternating axis of symmetry** if the value of *n* is 4. When the rotation is by 60°, the molecule is said to possess a **six-fold alternating axis of symmetry** and so on.

We can understand the symmetry operation by taking 1,3-dichlorobutane molecule. If we try a 90° rotation to get the position for a similar group we will not be able to achieve this. However rotation of 180° makes this possible. We can say that the molecule has two-fold alternating axis of symmetry and not a simple axis of symmetry. Thus, in rotation around the axis, the Cl group appears twice but one of them appears above the plane of the molecule and the other appears below the plane. You can try to visualise this in Fig. 1.24.

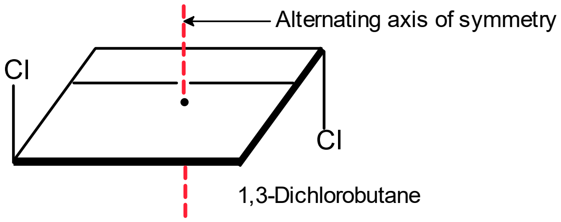


Fig. 1.24: Alternating axis of symmetry in 1,3-dichlorobutane.

In order to understand the operations, let us consider an isomer of 1,2,3,4-tetramethylcyclobutane that has the methyl groups alternately above and below the plane, structure I in Fig. 1.25. Let us see the result of rotation of 90° on structure I. We get structure II. The reflection of structure II in the plane of the ring gives structure III which if you see carefully, resembles structure I. We can say that the molecule has a 360º/90º = 4 i.e., a four-fold alternating axis of symmetry. This is depicted in the figure given for this molecule.

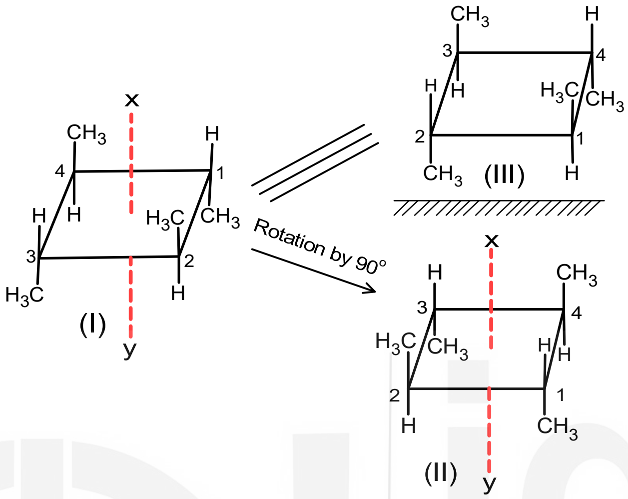


Fig.1.25: Four fold alternating axis of symmetry.

The molecule (1) shown in Fig. 1.26 contains four *sec* butyl groups (each of which contains one asymmetric carbon atom) but is not chiral because it possesses a fourfold alternating axis of symmetry. Structure (2) which is the mirror image of (1) becomes superimposable over it by turning the ring upside down and then rotating it by 90° along the axis shown in the figure. You should try it yourself to show the existence of alternating axis of symmetry.

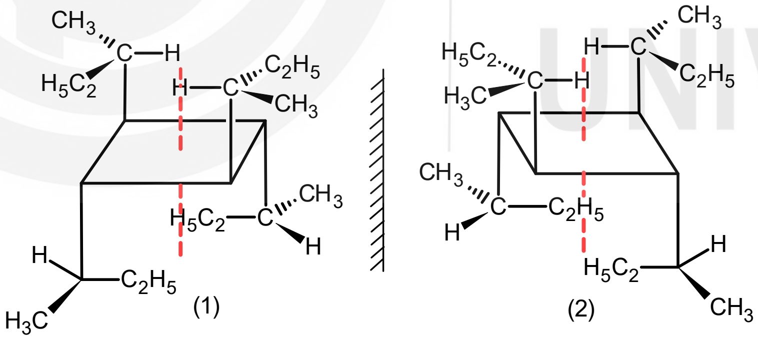
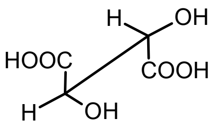


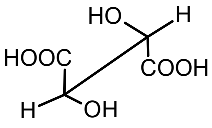
Fig.1.26: Molecule with twofold alternating axis of symmetry.

SAQ 6

The diastereomers, A and B of tartaric acid are shown in the staggered conformation. Find out the element/s of symmetry present in each of them.



A



B

1.4.5 The Identity Element

The identical operation (E) is the process of doing nothing to a molecule, and the corresponding symmetry element is the **identity element** (E). If no change is made to a molecule (or any other object), then it will always be identical to the original structure, so all the molecules (and all objects) possess the identity element and the corresponding identical operation.

1.4.6 Asymmetric and Disymmetric Molecules

Chiral molecule exists in two stereoisomeric forms, known as enantiomers in which the mirror images are nonsuperimposable with each other. It is clear from the above given description that a molecule would be chiral if it is devoid of symmetry elements which include plane of symmetry, centre of symmetry and alternating axis of symmetry. It is appropriate to mention at this stage that one-fold alternating axis of symmetry corresponds to plane of symmetry. Similarly, a twofold alternating axis of symmetry corresponds to centre of symmetry.

If a molecule contains any of these elements of symmetry it will be called a **symmetric molecule.** If the symmetry elements are missing, such molecules were earlier called **asymmetric** molecules. If alternating axis of symmetry and simple axis of symmetry, both are absent, these molecules are called as asymmetric and they are usually active. But if simple axis of symmetry is present and alternating axis of symmetry is absent then such molecules are now given the name as **dissymmetric** and they are usually active. The general points to remember are summarised below in Table 1.1.

Table 1.1: Symmetry designations of chiral molecules

Term	Alternating axis	Simple axis	Optical activity
Symmetric	Present	May or may not be present	Inactive
Dissymmetric	Absent	Present	Usually active
Asymmetric	Absent	Absent	Usually active

The molecular properties of molecules are based on the molecular structure that is directly or indirectly related to the symmetry of the molecules. You will study about this relationship in the following section.

1.5 SYMMETRY AND MOLECULAR PROPERTIES

The physical properties of a compound are dependent on molecular structure and to a good extent the symmetry is responsible for the difference in their properties. The properties that are discussed in the following subsections are the ability to rotate the plane of polarized light, the ability to display permanent dipole moment.

1.5.1 Rotation of Plane Polarised Light

You are familiar with the fact that ordinary light consists of oscillating electrical and magnetic fields or we can say the waves vibrate in all directions perpendicular to the direction of the beam of light beam. On passing the ordinary light through a device called **polarizer** its oscillations in all but one direction are blocked and the light emerging from the polariser oscillates in only one plane. This is called the **plane polarised light**. When this plane polarised light is passed through solution of any optical active substance the plane gets rotated by some angle. The compounds those rotate the plane of plane polarised light to the right are called **dextrorotatory** and those which rotate it in the left direction are called **laevorotatory**. You have studied why compounds exist as optical isomers. The answer is known to you: it is because of the chirality in the molecule.

You have studied how chirality relates to the symmetry in the molecule. The molecules those are chiral, can rotate the polarised light. The property remains unchanged under a proper operation (rotation) but changes sign under an improper operation (reflection). We can say that an improper operation (reflection) transforms one enantiomer into another.

1.5.2 Dipole Moment

You know that the dipole moment of a chemical compound is due to a difference in the charge distribution in its molecules which is due to the difference in the electronegativities of the constituent atoms. The molecule as a whole will have a dipole moment only if the local dipole of a group in one region is not compensated by an opposite local dipole elsewhere in the molecule. Symmetry properties are responsible for indicating whether this will or will not be the case. Specifically, if a molecule has a centre of symmetry then to each local dipole there will be a corresponding equal and opposite one, and the overall dipole moment will be zero. If a molecule has a C_n axis, the component of the dipole moment vector at right angles to the axis averages to zero and the molecule can, at best, have a moment along the direction of the axis. However, this component of the moment will also vanish if there is a symmetry plane perpendicular to the axis or there is at least one other axis perpendicular to the first.

1.6 SYMMETRY AND CHIRALITY

You have read some of the important concepts associated with molecular symmetry and symmetry elements. This is very significant as the understanding of symmetry helps to determine whether or not a molecule will be chiral. We will first recall the concept of chirality and then relate it to the symmetry in a molecule.

1.6.1 Chirality

The term chirality has been derived from a term called **chiral** and the term chiral is derived from a Greek word *Cheir* which means hands. What has chiral and chirality got to do with the hands?

You are familiar with another concept, viz. **non-superimposability**. We observe that our two hands are identical, but they are non-superimposable. This property was given the name as **handedness** or **chirality**. Thus, chirality is a property exhibited by two substances made up of identical parts but are not superimposable on each other. The objects which cannot be superimposed on their mirror images are called **chiral**. Some other examples are hand gloves, screw, scissors as shown in Fig.1.27 and many more observed every day.

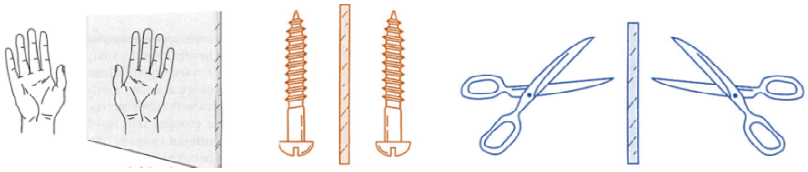


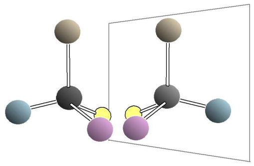
Fig.1.27: Some chiral objects

Let us consider some objects which can be **superimposable**. For example, let's take a chair and its mirror image as shown below. If the mirror image is picked and put it over the chair, it will be exactly super imposable. We can say that the chair is achiral. Some other examples of this type include letter A, number 8, a butterfly etc. These objects which can be superimposed over each other are called **achiral**. You will be able to appreciate the concept of chirality in organic molecules by taking suitable examples.

Fig.1.28: Some achiral objects.

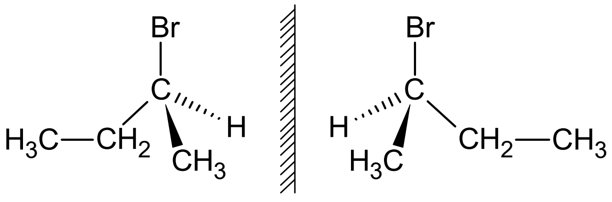
In 1815, the physicist Jean-Baptiste Biot predicted that the ability to rotate the plane of polarization was attributable to some asymmetry in the molecules. Van't Hoff and Le Bel later determined that the molecular asymmetry was associated with compounds having one or more asymmetric carbons.

You have read above that chirality is non-superimposability of mirror images. You analysed and observed that non-superimposability arises due to the presence of an asymmetric carbon atom or the absence of some symmetry elements (Table 1.1). Hence it can be inferred that disymmetry or asymmetry is a necessary and sufficient condition for a molecule to show optical activity and hence optical isomerism. The pair of optically active isomers is called **enantiomers.** Two enantiomers have identical physical properties, except for the direction in which they rotate the plane of plane polarised light. One rotates the plane of plane polarised light to the right hand side whereas the other rotates to the left hand side by an exactly same magnitude.



Nonsuperimposable mirror images

Thus a compound with one asymmetric carbon atom, for example 2-bromobutane, can exist as two different stereoisomers. Imagine a mirror between the isomers; notice that they are mirror images of each other which are non-superimposable i.e., they are different molecules. These two are the enantiomers. The molecule has an asymmetric carbon atom which is responsible for the chirality of 2-bromobutane as shown in Fig.1.29.



2-Bromobutane

Fig. 1.29: Two isomers of 2-bromobutane.

1.6.2 Chirality vis-a-vis Symmetry Elements

Let us now see how the symmetry relates to chirality. By definition, a chiral object is not superimposable on its mirror image, where the mirror image of an object is its reflection. You have read that for any molecule which contains a plane of symmetry (σ) or the corresponding symmetry operation, the reflection operation (σ) will superimpose the molecule on its reflection. Thus, any molecule which contains a plane of symmetry must be achiral.

In fact, any molecule which contains in improper axis of rotation (S_n axis), will be achiral. The reason for this is that an improper axis of rotation is the product of a proper rotation (C_n) followed by a reflection (σ) as dealt in subsection 1.4.4. It was also shown in subsection 1.4.6 that a plane of symmetry (σ) and centre of inversion (i) are just special cases of an S_n axis (S_1 and S_2 respectively). The reflection part of these operations will always cause the molecule to be superimposable on its mirror image and hence achiral. This provides an alternative definition of chirality:

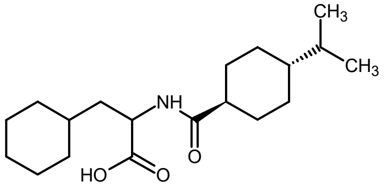
Any molecule (or other object) which in all accessible conformations do not contain an improper axis of rotation (S_n, $n > 0$) is chiral.

A consequence of the dependence of chirality on the absence of an S_n axis is that any molecule that possesses an S_n axis (or a plane of symmetry or center of symmetry) will be achiral, and a molecule in which S_n axis is absent will be chiral.

Molecules containing a single chiral centre are always optically active and lead to a pair of enantiomers. There are compounds which contain more than one chiral centre but still are optically inactive. Any pair of configurational stereoisomers that are not enantiomers are classified as '**diastereoisomers'**. Enantiomers, diastereoisomers differ in physical and chemical properties and behave as different compounds. We will discuss more about enantiomers and diastereoisomers in the next unit.

SAQ 7

Identify the number of chiral centres in the nateglinide molecule, given below, which is an antidiabetic drug.



Nateglinide

In the following last section let us summarise what all you have learnt in this unit about symmetry and chirality.

1.7 SUMMARY

- The unit on molecular symmetry and chirality pertains to the stereochemistry of organic molecules that has direct relationship with the 3 dimensional structures. There are two main types of representing the

3 dimensional structures of these molecules on a 2 dimensional surface like the paper or a blackboard or a white board. These are perspective type that includes the flying wedge and the zig-zag representation and projection type that includes the Fischer, the Newman and the Sawhorse projections.

- The interconversion of the projections is essential for getting a required information. Thus conversion of Fischer projection to sawhorse and *vice versa,* sawhorse to Newman to Fischer and *vice versa* i.e. conversion of Fischer to sawhorse and Newman projections has been dealt by taking relevant examples.
- The study of the three-dimensional structures of molecules describes the stereochemistry of molecules and their existence as stereoisomers. The stereoisomers are classified into two types, viz., configurational and conformational isomers. Configurational isomers are the molecules which have different arrangement of atoms and cannot be converted into each other without breaking a bond. These are further classified as geometrical and optical isomers. The molecules that have the same molecular formula but have a different arrangement of the atoms in space are called optical isomers. The optical isomers are further classified as enantiomers and diastereomers. The conformational isomers are different relative arrangements of atoms obtained by the rotation across single bonds in the molecule.
- The symmetry of a molecule is described in terms of symmetry elements. The operations performed to determine the presence of symmetry elements are called symmetry operations. A symmetry element can be a geometric line, plane or point with respect to which one or more symmetry operations are performed. The symmetry elements are of four types. These are: Rotational or proper axis of symmetry (Cn), Plane of symmetry (σ), Centre of symmetry or centre of inversion (i), Alternating or improper axis of symmetry (Sn). The identical operation (E) is the process of doing nothing to a molecule, and the corresponding symmetry element is the identity element (E).
- A molecule contains any of the elements of symmetry (σ, i or Sn), it will be called a symmetric molecule. If alternating axis of symmetry and simple axis of symmetry, both are absent, these molecules are called as asymmetric and they are usually active. But if simple axis of symmetry is present and alternating axis of symmetry is absent then such molecules are given the name as dissymmetric and they are usually active.
- The physical properties of a compound are dependent on molecular structure and to a good extent the symmetry is responsible for the difference in their properties. Two such properties are, rotation of plane polarised light and dipole moment.
- Chirality is a property exhibited by two substances made up of identical parts but are not superimposable on each other. The objects which cannot be superimposed on their mirror images are called chiral. Any molecule which contains a plane of symmetry must be achiral. In fact, any molecule which contains in improper axis of rotation (S_n axis), will be achiral.

1.8 TERMINAL QUESTIONS

1. Draw the structures and show the principal axis in each of the compounds.

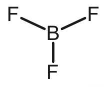
   a) CH_4 b) CH_3Cl c) $CHCl_3$ d) Benzene

2. Write the structural formula for the following isomers.

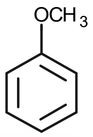
   (a) (*z*)-3-chloro-4-methyl-3-hexene (b) (*E*)-3,4,4-trimethyl-2-pentene

3. 2,4-Dinitrophenylhydrazone derivative of acetone and oxime of formaldehyde do not show geometrical isomerism. Explain.

4. Which of the following molecules has the 'centre of symmetry (i)'? Show the position of centre of inversion/symmetry, if present, in the molecules shown below.



1



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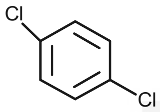

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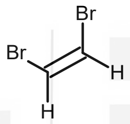

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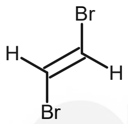

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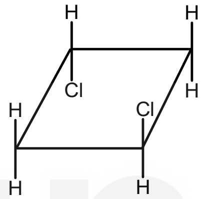


6

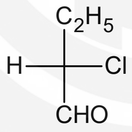
5. Which symmetry element is present in bromobenzene? Illustrate your answer with suitable structures.

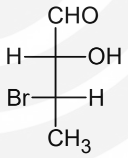
6. What are the symmetry elements in *cis*-2-butene and *trans*-2-butene? Illustrate your answer with suitable structures.

1.9 ANSWERS

Self Assessment Questions

1.





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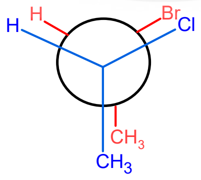

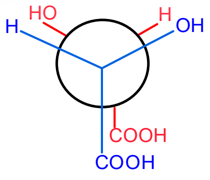

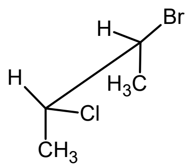

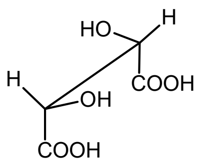

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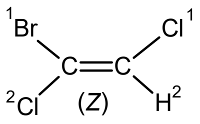
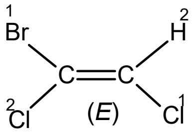
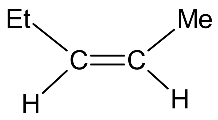
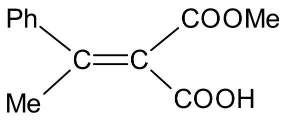




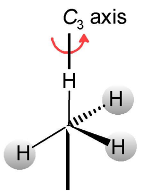
4. These will show geometrical isomerism as these contain two different groups attached to double bonded carbon atoms.



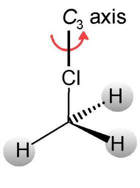
and



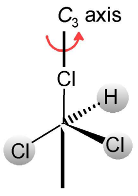
5. a) CH_4 b) CH_3Cl c) $CHCl_3$ d) Benzene



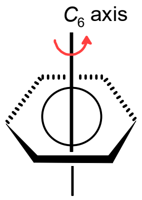
Methane



Chloromethane



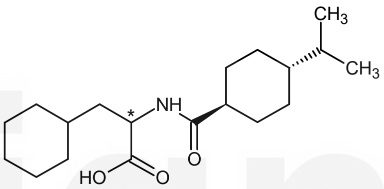
Trichloromethane



Benzene

6. The B diastereomer has inversion symmetry (i) and S_2 symmetry. The A diastereomer has C_2 symmetry.

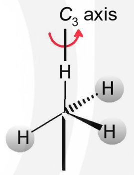
7. The nateglinide molecule has 1 chiral centre with which is shown by an asterisk. The substituted 1, 4-carbon on cyclohexane will generate geometric isomers only, here trans-substituted isomer is given.



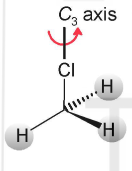
Nateglinide

Terminal Questions

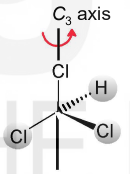
1.



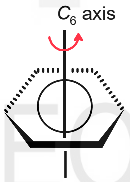
Methane



Chloromethane

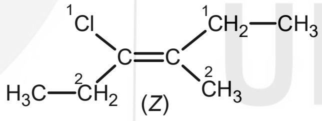


Trichloromethane

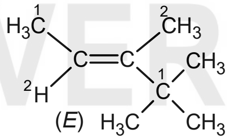


Benzene

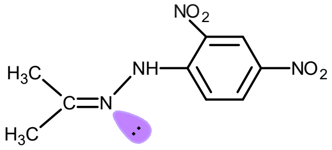
2. a)



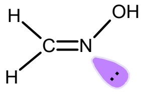
b)



3.



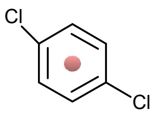
2,4-Dinitrophenylhydrazone of acetone



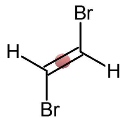
Oxime of formaldehyde

Both of these cannot show geometrical isomerism because the two groups attached to doubly bonded carbon are identical.

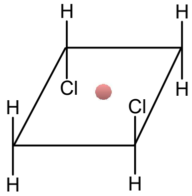
4. Molecular structures 3, 5, and 6 have centre of inversion/ symmetry as shown below. The shaded circle represents centre of inversion/symmetry.



3

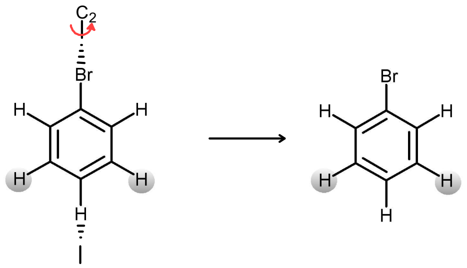


5



6

5. The molecule bromobenzene has simple axis of symmetry C2.



6. Both the molecules contain C_2 axis. Both of these also contain a plane of symmetry as shown below.