CHAPTER 2

Stereochemistry

❖ Chirality

All the crystals or molecular geometries that cannot be superimposed on their mirror images have a special property to rotate the plane of polarized light when passed through them; such compounds are called as chiral compounds and the property is called as chirality or optical activity.

In 1811, a French physicist named François Jean Dominique Arago observed the rotation of the orientation of linearly polarized light when it is passed through quartz. A French physicist, Jean Baptiste Biot, also observed the rotation of the plane of polarized light in 1815 with some liquids and vapors of organic compounds like turpentine. After that, an English astronomer, Sir John F. W. Herschel, found in 1820 that all the different individual quartz crystals were actually the mirror images of each other, and rotated the plane of polarized light by equal magnitude but the directions of rotation were opposite. The crystal that rotates the plane of polarized light towards the right is called dextrorotatory, while the mirror image will rotate to left imparting a label of levorotatory. Now since all the crystals that were capable of rotating the plane of polarized light could not be superimposed on their mirror image crystals by any mean, the term 'chiral' (derived from Greek word, cheir = hand) become extremely popular to define such crystals as our hands also the non-superimposable mirror images of each other.

➢ *Experimental Measurement of Chirality or Optical Activity*

Optical activity or chirality is measured by an instrument called the 'polarimeter'. The basic experimental setup to measure the magnitude of optical activity is shown below.

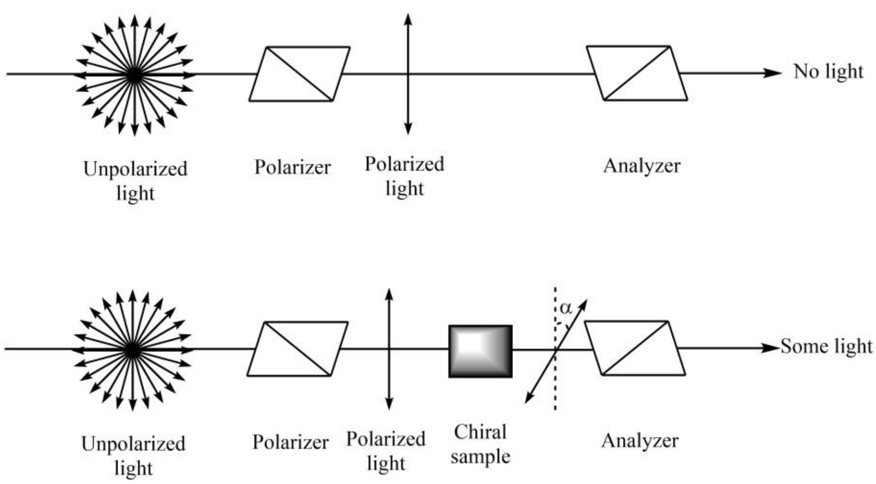


Figure 1. Schematic diagram of a polarimeter to measure chirality.

The angle through which the plane of polarized light gets rotated by the chiral molecules is symbolized by α and can be formulated as given below.

$$\alpha = [\alpha]_{\lambda}^{T}.l.c \quad (1)$$

Where *l* is the path length of the sample in cm whereas *c* represents the concentration of the sample in g/ml. The symbol represents the specific angle of rotation $[\alpha]_{\lambda}^{T}$ at temperature T and wavelength λ. It is also worthy to note that the observed angle of rotation also depends upon the nature of the solvent. Furthermore, the wavelength of the radiation used and the temperature of the system should be kept constant throughout the experiment. In order to determine the specific angle of rotation, use path length and concentration unity in the rearranged form of equation (1), i.e.,

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{l.c} \quad (2)$$

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{1\,cm \times 1\,g/ml} \quad (3)$$

or

$$[\alpha]_{\lambda}^{T} = \alpha \quad (4)$$

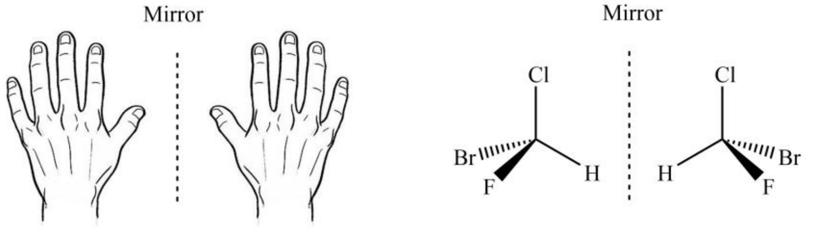
Therefore, the specific angle of rotation of any chiral molecule may simply be defined as the observed angle of rotation when the solution of the same compound with unit concentration and unit path length is placed in the path of polarized light.

➢ ***Conditions for Chirality***

In order to be optically active, any one of the following conditions can be used to define the chirality of a molecule to somewhat less or more strictly.

Condition 1: Since All the crystals or molecular geometries that are capable of rotating the plane of polarized light could not be superimposed on their mirror images, the primary condition for a molecule to be optically active or chiral can be summarized as follows.

If a molecular geometry wants to be optically active, it must not be superimposable on its mirror image.

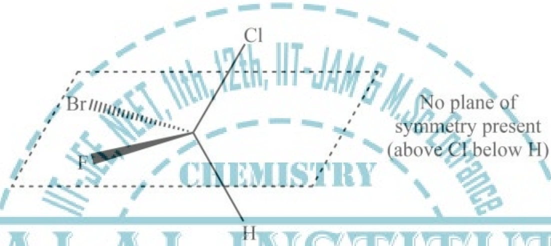


Non-superimoposable mirror images Non-superimoposable mirror images

This condition defines chirality in an absolute sense and will be chiral if it is satisfied.

Condition 2: Now although the first condition is successful in defining chirality, its application is quite difficult. This is because it is very difficult to imagine the mirror image of the molecular geometry in three dimensions (especially complex molecules), and then the confirmation of their superimposition is even more difficult to tackle for human imagination. Therefore, an alternate route is necessary to check the first condition. This problem can be solved by the fact that any molecular geometry lacking plane of symmetry cannot be superimposed on its mirror image; and therefore, the problem of 'visualizing the mirror image and its subsequent superimposition' is reduced to finding the plane of symmetry only. If a plane of symmetry is present, the molecule would be superimposable of its mirror image, and hence, will be achiral. Conversely, if a plane of symmetry is absent, the molecule would not be superimposable of its mirror image, and hence, will be chiral. Hence, this condition of chirality can be summarized as follows;

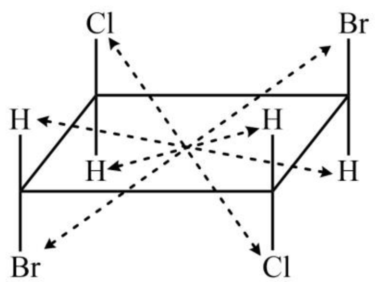
If a crystal molecular geometry wants to be optically active (or chiral), there should be no plane of symmetry.



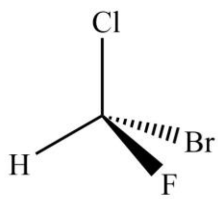
This condition defines chirality in part because there are molecules that don't have any plane of symmetry but still inactive.

Condition 3: Since there are molecules that don't have any plane of symmetry but still inactive, a more inclusive approach is needed to confirm the optical activity with ever treating mirror images. This problem can be solved by the fact that any molecular geometry lacking secondary symmetry elements (plane of symmetry, inversion center, and alternating axis of symmetry) can never be superimposed on its mirror image; and therefore, will be achiral. Hence, this condition of chirality can be summarized as follows;

If a crystal molecular geometry wants to be optically active (or chiral), there should secondary symmetry elements i.e., plane of symmetry (σ), center of symmetry (i), and alternating axis of symmetry (S_n).



No plane of symmetry present
yet achiral due to inversion (i.e. *i* or S_2)



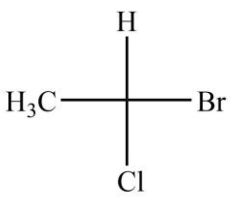
No secondary symmetry element (σ, *i*, S_n) present;
and therefore, chiral in nature.

This condition defines chirality in an absolute sense and will be chiral if it is satisfied.

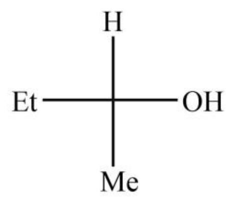
➢ ***Types of Chirality***

Depending upon the geometrical profile of molecular species, chiral compounds or chirality can primarily be divided into four categories as given below.

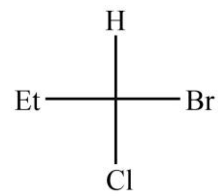
1. Chirality arising from a center (chiral center): This type of chirality arises when all the four groups around tetrahedrally coordinated carbon atom become different. In other words, an organic molecule can no longer be superimposed on its mirror image if it has a center with all different groups.



1-bromo-1-chloroethane



butan-2-ol

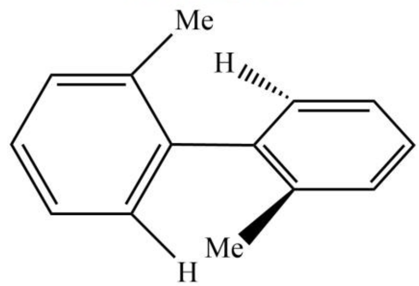


1-bromo-1-chloropropane

Some of the most simple examples of organic molecules with this type of chirality are CH_3-CHClBr, butan-2-ol, and 1-bromo-1-chloropropane.

2. Chirality arising from an axis (chiral axis): This type of chirality arises when a tetrahedrally coordinated prochiral molecule becomes chiral by extending the center along an axis. In other words, a prochiral molecule can no longer be superimposed on its mirror image if its center has been extended to a line with same groups at different ends.

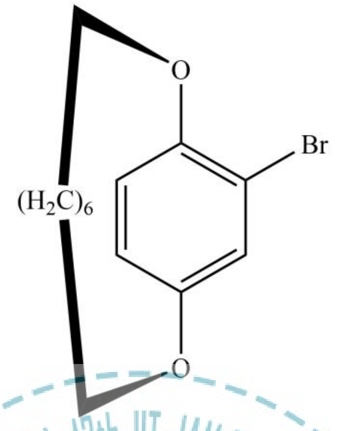
(*R*)-penta-2,3-diene



2,2'-dimethyl-1,1'-biphenyl

Some of the most simple examples of organic molecules with this type of chirality are penta-2,3-diene and 2,2'-dimethyl-1,1'-biphenyl (a biphenyl derivative).

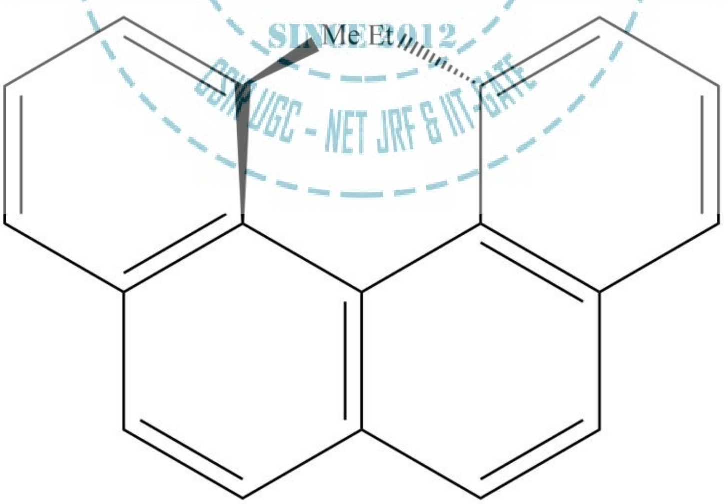
3. Chirality arising from a plane (chiral plane): This type of chirality arises when relacing a group in a plane makes the molecule chiral. In other words, an organic molecule can no longer be superimposed on its mirror image if the replacement of a particular group induces chirality.



13-bromo-1,10-dioxa[8]paracyclophane

Some of the most simple examples of organic molecules with this type of chirality are ansa compounds like 13-bromo-1,10-dioxa[8]paracyclophane.

4. Chirality arising from a spiral (helical chirality): This type of chirality arises when the molecule has a helical structure. In other words, an organic molecule can no longer be superimposed on its mirror image if its geometry resembles a helix.



1-ethyl-12-methylbenzo[*c*]phenanthrene

Some of the most simple examples of organic molecules with this type of chirality are helical compounds like 1-ethyl-12-methylbenzo[c]phenanthrene.

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Volume I

MANDEEP DALAL

First Edition

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ISBN: 978-81-952427-3-3
9 788195 242733
MRP: Rs 800.00

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