Stereochemistry: 3-D Chemistry

Enantiomers

If a molecule and its mirror image are not superimposable these molecules are isomers; in particular, these mirror image isomers are called *enantiomers* of each other.

Each of these enantiomers is said to be a *chiral* molecule.





Properties of Enantiomers

<u>Physical</u>- Physical properties include items like melting point, boiling point, color, hardness, density, *etc.*

All physical properties of enantiomers are mirror imaged: the property of one enantiomer is the mirror image of the other.

In practice, this means that all physical properties of both enantiomers, <u>except for one</u>, are the same.



The Nature of Light

Light can be considered to be composed of electromagnetic waves. Like ocean waves, these waves rise and fall.

As ordinary light travels from an object (which is illuminated) to your eyes the waves rise and fall in all directions --- unlike ocean waves, which rise and fall only vertically.





Enantiomers rotate light, *ie* when light passes through them they rotate the direction in which the waves rise and fall. One enantiomer (of a pair) will rotate the light clockwise and the other will rotate the light counterclockwise by an equal amount. <u>This difference in</u> <u>direction of rotation (one is the mirror image of the other)</u> is the only physical property which is different for the two enantiomers. This ability of enantiomers to rotate light is called *optical activity*.

But since the waves are oriented in all directions entering the substance, after being rotated by a certain number of degrees they will emerge oriented in all directions. Thus, it is impossible to detect this effect with ordinary light.

When ordinary light is passed through a polarizer (*eg* a polaroid sheet) *plane polarized light* is what emerges. This light is like ocean waves in that all the waves are oriented in one direction.





With plane polarized light it is possible to observe the optical activity of enantiomers and determine that they rotate the light by equal amounts but in opposite directions. The enantiomer which rotates the light clockwise, looking toward the light, is called <u>dextrorotatory</u> (d or +); the other one, <u>levorotatory (l or -)</u>.







Chemical -

Enantiomers have identical properties, except toward chiral substances where they will behave differently. Reaction between (+)-A and (+)-B will proceed differently from that between (-)-A and (+)-B: frequently the rate of reaction will be different, sometimes drastically different.



(+)-Glucose is metabolized by animals and fermented by yeast, (-)-glucose is not.





(+)-Carvone is the principal constituent of oil of caraway,(-)-carvone is the principal constituent of oil of spearmint.



The Racemic Mixture (Racemic Modification, Racemate)

1:1 mixture of enantiomers, $eg(\pm)$ -carvone.

A racemic mixture is optically inactive because the rotation caused by one isomer is exactly cancelled by its mirror image.

Since the physical properties of enantiomers are the same, a racemate cannot be separated into its components by ordinary physical means. *Resolution* of a racemate into its enantiomers requires a special approach using chiral molecules.



Molecules which are not chiral are *achiral*. Achiral molecules are superimposable on their mirror images. Achiral molecules frequently contain one of the following *symmetry elements* (in at least one conformation):

- 1) Plane of symmetry.
- 2) Center of symmetry.

Either of these symmetry elements is a sufficient, but not necessary, condition to make a molecule achiral.



Plane of symmetry: Bisects molecule into 2 mirror image halves. The plane of symmetry is shown in blue.



trans-trans-1,3-Dibromo-2-chlorocyclobutane

trans-cis-trans-1,3-dibromo-2,4dichlorocyclobutane

Center of symmetry: Point such that if a line is drawn from any atom to this point and then extended an equal distance beyond the point, an identical atom will be found. The center is shown as a red ball at the center of the molecule.



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