STEREO - ISOMERISM

OPTICAL ISOMERISM

Certain compounds have the property of being able to rotate the plane of polarisation of a beam of polarised light to the right, or to the left. This property is called ***optical activity***, and the compounds possessing it are said to be ***optically active***.

Ordinary light rays vibrate in all planes perpendicular to the direction of travel of the rays. When such light is passed through a polarising prism (polariser), or a piece of polarizing plastic like that used in Polaroid sunglasses, then the emergent light that is transmitted vibrates in a single plane only and is called ***plane - polarised light.*** Optical activity is the ability to rotate the plane of polarisation of plane-polarised light.

Optical activity is detected and measured by using a ***polarimeter***. A polarimeter consists of a light source with a polarizing filter. The resulting polarised light is confined to a single plane and is directed through a chamber containing a solution of the sample in an appropriate solvent (one that dissolves the substance under test but that does not itself have an asymmetric carbon i.e. it is not optically active). The angle of the plane polarised light changes as it passes through the sample, this is measured in degrees (^{0}) and is defined as the observed rotation, α. When the analyser has to be turned to the right (clockwise) the compound is said to be ***dextrorotatory*** and the rotation is $+\alpha^0$; when it has to be turned to the left (anti-clockwise) the compound is said to be ***lavorotatory*** and the rotation is $-\alpha^0$.
The amount of rotation depends upon ...

- i) the particular compound
- ii) the concentration of the compound in th esolution
- iii) the path - length of the beam through the solution
- iv) the solvent , temperature and the wavelength of the light used.

POLARIMETER

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THE BASIS OF OPTICAL ACTIVITY

All known optically active compounds are found to have a molecular structure which is asymmetric, i.e. the atoms in the molecule are arranged so that the original molecule is not superimposable on its mirror image i.e. the molecule lacks symmetry. Another way of expressing this is to say that there is neither a plane of symmetry in the molecule nor a center of symmetry. Example of an asymmetric objects are your left and right hands. Each is the mirror image of the other, try to place one hand above the other so that all parts coincide - it is impossible, therefore non- superimposable.
Superimposable means that if one structure is laid over the other, then the positions of all atoms will match.

The simplest ***asymmetric*** organic molecules are those that contain a ***C - atom bonded to four different*** atoms or groups. A saturated C - atom is linked to four atoms or groups arranged spatially as though they were at the corners of a tetrahedron, with the saturated C - atom at its center.
Example:

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If models are made of the above arrangement and its mirror image, it is found that they are non - superimposable - therefore a ***C - atom bonded to four different atoms or groups is known as as an asymmetric C - atom.*** An asymmetric C atom is sometimes referred to as a ***Chiral*** center and the property is called ***Chirality*** (FYI: Greek for hand). Molecules that are asymmetric and rotate plane polarised light are said to be optically active.

Such compounds, having the same molecular formula but different structural formulas, are therefore isomers; since they contain the same groups of atoms and differ only in their arrangement in space, they are called ***stereoisomers.*** Stereoisomers which are object and mirror - image of one another are also called ***Enantiomers***.
The two isomers differ only in the direction in which they rotate the plane of polarised light.
Example: 3-methyl hexane 2-butanol CHClBr

One optical isomer of limonene occurs in oranges, the other in peppermint oil, and both in turpentine. The two isomers smell different !

Properties of Enantiomers

1. Enantiomers have identical physical properties, except for the direction of rotation of the plane of polarised light (their specific rotations are equal but opposite). Example:

Property	(+) 2-methylbutanol	(-) 2- methylbutanol
specific rotation	+ 5.756 ^{0}	- 5.756 ^{0}
boiling point	128.9 ^{0}	128.9 ^{0}
density	0.189	0.189

2. Enantiomers have identical chemical properties except towards optically active reagents. Only in the special case of when the reagent is optically active will there be any differences in chemical reactions ex. in biological systems, the enzyme catalyst are optically active, and therefore often catalyse the reaction of only one enantiomer. Example:

i) The sugar (+) glucose is converted into ethanol by the enzymes in yeast, whereas (-) glucose is not.
ii) Only one isomer of morphine acts as an addictive but efficient pain killer!
iii) Only one isomer of DOPA called L - DOPA is effective in the treatment of Parkinson's disease.
(iv) The drug thalidomide used in the 1950s and 1960s to treat morning sickness in pregnant women was a mixture of two optical isomers. One is a safe and effective drug, the other caused some children to have birth defects.
(v) Chiral molecules are also produced by plants and these substances have a variety of properties, including those which behave as defensive substances or attractive substances.

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RACEMIC MIXTURES OR RACEMATES

1. Enantiomers rotate the plane of polarised light by equal but opposite amounts, therefore a ***mixture of equal amounts of enantiomers will be optically inactive***, i.e. the rotation of this mixture is zero! (The rotation caused by one enantiomer being cancelled by the opposite rotation of the other).

2. Such a mixture, containing equal amounts of two enantiomers, is known as a ***racemic mixture or racemate (±)***.

3. Racemates are usually obtained when preparing optically active compounds.

4. Normal methods of separation (fractional distillation, crystallisation, solvent extraction) will ***not*** separate racemic mixtures, because of the identical physical properties of the enantiomers. The separation of enantiomers from racemic mixtures requires special techniques and is called ***resolution of a racemic mixture.***

5. The most generally applicable method of resolution is to react the racemic mixture with another pure, optically active compound. The products then are not enantiomers (they are no longer mirror images), therefore they have different physical properties and can be separated by the usual methods. Finally, the original enantiomers are regenerated from the products.

NOTE:

1. C - atoms which form part of an aromatic ring cannot exhibit optical activity.
2. When a molecule has two or more chiral centres there are many more possibilities for stereoisomers. In general, for a chiral molecule with 'n' chiral centres, there will be a maximum of 2^n stereoisomers. Thus, if a compound has two chiral C-atoms, it has four possible stereoisomers. Diastereomers are not mirror images , but are optical isomers, meso compounds have a mirror image that is superimposable, .: not optically active.

HOMEWORK

1. Which of the following compounds can exhibit optical isomerism (i.e. which has an asymmetric C - atom). Write the structural formula for the optically active compound and indicate the asymmetric C - atom by an * :

1) $CH_3CHBrCH_2CH_3$ 2) $CH_2BrCH_2CH_2CH_3$ 3) $CH_2 = CHCHClCH_3$
4) $CH_3CHClC_2H_5$ 5) 2- hydroxypropanoic acid 6) 2-chloropropane
7) chloro,iodomethane sulphonic acid 8) 2-butanol
9) $C_8H_{11}N$, containing an aromatic ring (10) $C_8H_{10}O$, containing an aromatic ring
11) Hexan-1,3-diol (12) $C_6H_5CH_2CH(NH_2)COOH$

2. Alanine, an amino acid, has the formula $H_2NCH(CH_3)COOH$. Construct a model of the molecule. Do you think that alanine should be optically active? Replace the — CH_3 by — H. This is the formula of the amino acid, glycine. Do you think that glycine should be optically active. Justify your response.

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3. What is optical activity? How could you demonstrate that a compound is optically active? Draw structural formulae for the optical isomers of molecular formula $C_3H_6O_3$.

4. (a) Explain the term 'chiral molecule'.
(b) The compound $CH_3CHBrCOOH$ exists as two optical isomers. Draw the structure of the two isomers.
(c) How do optical isomers compare in their chemical reactions?

5. Say which of the following structures may show stereoisomerism. State what kind of stereoisomerism is involved, and draw the stereoisomers:
(a) $CH_3CH_2CH_2CHOHCH_3$
(b) $CH_3CH_2CHOHCH_2CH_3$
(c) $CH_3CH = CHCOOH$