Quadrant II – Notes

Programme: Bachelor of Science (First Year)

Subject: Chemistry

Paper Code: CHC 101

Paper Title: DSC: Inorganic and Organic chemistry (Section B)

Unit: Unit 2 – Stereochemistry

Module Name: Configuration: Geometrical and Optical Isomerism

Module No: 27

Name of the Presenter: Dr. Durga P. Kamat, Ph.D., Assistant Professor, Dhempe College of Arts & Science, Miramar Goa



Conformational isomers: differ only by rotation around Carbon-Carbon single bond. No bonds are broken or made for interconversion.

Configurational isomers: are stereoisomers that do not readily interconvert under normal conditions and thus can be separated and isolated. Their configuration is fixed and interconversion in these stereoisomers usually involves a bond breaking process.

Configuration: is the particular arrangement of atoms in space which characterises a particular isomer.

Configurational isomerism can exist as a result of geometrical isomerism or optical isomerism.

Geometrical isomerism: describes the orientation of functional groups within a molecule that occur as a result of **restricted rotation** & different configurations can be interconverted only by breaking and reforming covalent bonds.

Geometrical isomers can be broadly classified as:

- Compounds having double bonds
- Cyclic compounds

Geometric Isomerism in Compounds having double bonds

Stereoisomerism about double bonds originates because of the restricted rotation (C=C, C=N & N=N) keeping the substituents fixed relative to each other.

1. For the **geometrical isomers resulting from C=C**, an important condition besides the restricted rotation is that, each of the doubly linked (sp²) carbon atoms should be attached to 2 different univalent atoms or groups. *cis*-But-2-ene and *trans*-but-2-ene are the examples of geometrical isomers as they differ in the relative position of substituents across the double bond, also each of the two sp² carbon atoms of the double bond is attached to two different substituents or groups. In case of *cis*-But-2-ene, the identical groups are on the same side of the double bond whereas in case of trans isomer the identical groups are on the opposite side of the double bond.





In case of E isomer the groups with higher priority are on the opposite side whereas in case of Z isomer, groups with higher priority are on same side of the double bond.



(*Z*)-1-bromo-1-chloropropene



(E)-1-bromo-1-chloropropene

2. Geometrical isomers resulting from the -C=N- (eg. Oximes-aldoximes/ketoximes)

An aldoxime obtained from an aldehyde can be either syn or anti. The Nitrogen atom has a lone pair of electrons in one of the sp^2 orbitals and thus the position of the hydroxyl group is fixed. In case of the syn isomer the hydroxyl group is on the same side as that of the hydrogen attached to carbon of the C=N (double bond). In case of the anti-isomer the hydroxyl group is on the opposite side as that of the hydrogen attached to carbon of the C=N (double bond).



3. Geometric isomers resulting from the -N=N- (eg. Azo compounds)

In case of substituted azo compounds, each Nitrogen atom has a lone pair of electrons and a group. In case of syn isomer the two groups are on the same side of the N=N (double bond). In case of anti-isomer the two groups are on the opposite side of the N=N (double bond).





syn-azobenzene

anti-azobenzene

4. Geometric Isomerism is also observed in **Cyclic compounds** (monocyclic (alicyclic), fused ring systems), due to restricted rotation. In general if any two sp³ carbons in a ring have 2 different substituents, stereoisomerism is possible. In case of *cis*- cyclopropane-1,2-dicarboxylic acid, the two carboxylic acid groups are on the same side i.e. either above or below the plane of a 3-membered ring. In case of *trans*- cyclopropane-1,2-dicarboxylic acid, the two carboxylic acid groups are not on the same side of the plane of the 3-membered ring.



The Effect of Geometrical Isomerism on Physical Properties:

Generally, geometrical isomers have different physical properties such as different melting points, boiling points, densities etc. Generally the cis isomer has a higher boiling point than the trans isomer and the trans isomer has higher melting point than the cis isomer.

lsomer	Melting point (°C)	Boiling point (°C)
cis-1,2-dichloroethene	-80	60
trans-1,2-dichloroethene	-50	48

cis-but-2-ene	-139	4
trans-but-2-ene	-106	1

The geometrical isomers have the same functional groups, however they are not identical, they tend to react with the same reagents but at different rates. For eg. fumaric acid requires higher temperature to form maleic anhydride compared to that required for maleic acid.



On the basis of differences in their properties geometrical isomers can be separated and their configuration can be determined.

Optical isomerism: Two isomers are called enantiomers or optical isomers if they are mirror images of each other and differ in their optical activity. Such a phenomenon is known as optical isomerism.

Optical activity: is the property of a molecule to rotate the plane of plane-polarized light.

Light has oscillating electric and magnetic fields, the electric field of light oscillates in all planes. When a beam of ordinary light is passed through a nicol prism or polarizer in polarimeter only the light waves oscillating in single plane are allowed to pass through. This light emerging from polariser is said to be plane polarised. The plane polarised light is allowed to pass through a sample tube containing the solution of a compound which may rotate the plane of plane polarised light and the magnitude of this rotation (α) is directly proportional to the concentration of the sample and length of the sample tube.



Diagrammatic representation of polarimeter

 $\alpha = [\alpha] c |$

 $[\alpha]$ = constant called specific rotation.

Each optically active compound has a characteristic specific rotation. Specific rotation of a compound is the rotation of plane polarised light caused by solution of 1 gram of compound dissolved per mL of the solution, placed in a sample tube of 1 dm long length at a specified temperature and wavelength.

Specific rotation can be calculated from the observed rotation using the following formula.

$$\left[\alpha\right]_{\lambda}^{t} = \frac{\alpha}{1 \, x \, c}$$

t = temperature in ° C, λ = wavelength of light [usually it is sodium D line (590nm)], α = experimentally measured optical rotation (°), l = length of liquid or solution column (dm), c = concentration of the sample (g/mL) in solution.

The compounds which rotate plane of plane polarized light in the clockwise direction or to the **right** are called **dextrorotary** compounds, (+) or (d). The compounds which rotate the plane of plane polarized light in the anti-clockwise direction or to the **left** are known as the **laevorotatory** compounds, (-) or (l).

The compounds which rotate the plane of plane polarised light are said to be optically active. For compounds to be optically active they need to be chiral.

You have learnt in the previous modules that a chiral compound has a nonsuperimposable mirror image, like our hands.



chiral

The very basic cause of chirality in a molecule is the presence of an asymmetric centre. 2-Bromobutane is eg. of a molecule with one asymmetric carbon atom. Two stereoisomers are possible for this compound $(2^n = 2^1 = 2 \text{ stereoisomers})$.



Enantiomers (optical isomers) of 2-bromobutane

Enantiomers or optical isomers are non superimposable mirror images of each other. Enantiomers share many of the same physical and chemical properties.

In fact all the physical properties of enantiomers are the same except their optical activity. The two enantiomers/optical isomers have different configuration.





(R)- 2-Methyl -1- butanol shows specific rotation = + 5.75, whereas (S)- 2-Methyl -1- butanol shows specific rotation = - 5.75. The magnitude of rotation is same but in opposite direction.

Mixture of 2 enantiomers in the same ratio is called racemic mixture. In a racemic mixture each enantiomer rotates the plane of polarized light in equal & opposite directions, thus the net resultant is zero optical activity.

For a mixture of enantiomers to be optically active, one enantiomer has to be in excess over the other.