B.SC PART I PAPER ORGANIC

Topic:- Stereochemistry (Isomerism)

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ISOMERISM

These compounds have the same molecular formula but differ from each other in physical or chemical properties, and are called Isomers and the phenomenon is called Isomerism. Since isomers have the same molecular formula, the difference in their properties must be due to different modes of combination or arrangement of atoms within the molecule. These are two main type of isomerism:

(1) Constitutional Isomerism
(2) Stereoisomerism

(1) Constitutional Isomerism:-

When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called Constitutional Isomerism. In other words, **Constitutional isomers are compounds that have the same molecular formula but different structural formulas.** Constitutional isomerism is of five types:

(a) Chain Isomerism
(b) Position Isomerism
(c) Functional Isomerism
(d) Metamerism
(e) Tautomerism

(2) Stereoisomerism:-

When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called Stereoisomerism. The stereoisomers have the same structural formulas but differ in arrangement of atoms in space. In other words, stereoisomerism is exhibited by such compounds which have the same structural formula but differ in configuration. (The term configuration refers to the three-dimensional arrangement of atoms that characterizes a particular compound). Stereoisomerism is of two types:

(a) Geometrical or Cis-Trans Isomerism

(b) Optical Isomerism

ISOMERS

(Same molecular formula)

Constitutional Isomers

(Different connectivity among atoms)

Different carbon skeletons :

$CH_3CH_2CH_2CH_3$ and $CH_3CH(CH_3)CH_3$

Different functional groups :

CH_3CH_2OH and CH_3OCH_3

Different position of functional groups :

$CH_3CH(NH_2)CH_3$ and $CH_3CH_2CH_2NH_2$

Stereoisomers

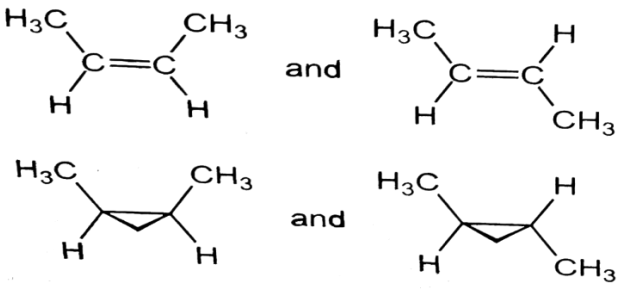
(Same connectivity, different arrangement in space)

Diastereomers

(Nonsuperimposable, non-mirror images)

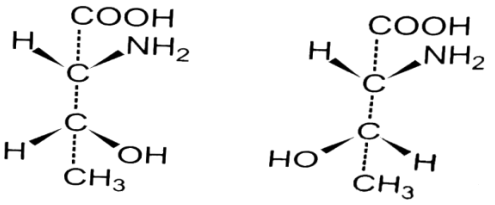
Cis-trans Diastereomers

(Double bond or Ring)



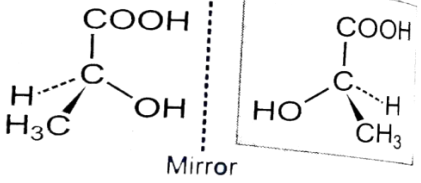
Chiral Diastereomers

(Multiple Chiral centers)



Enantiomers

(Nonsuperimposable, mirror images)



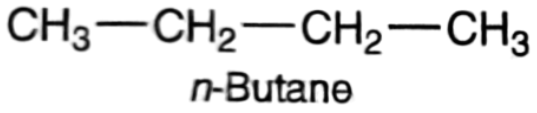
CONSTITUTIONAL ISOMERISM (STRUCTURAL ISOMERISM)

In constitutional isomerism the isomers have the same molecular formula but differ in constitutional formula, that is, in the order in which the different atoms are linked in the molecule. Constitutional isomerism is of five type:-

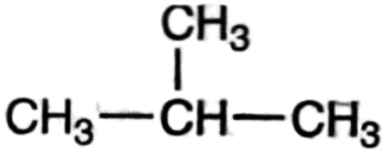
(1) Chain Isomerism

Chain isomers (also called skeletal isomers) have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other.

Example:- n-Butane and Isobutane



n-Butane



Isobutane

(2) Position Isomerism

Position isomers have the same molecular formula but differ in the position of a functional group on the carbon chain.

Example:- 1-Bromobutane and 2-Bromobutane

(3) Functional Isomerism

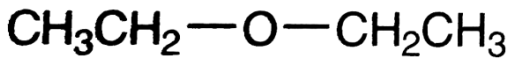
Functional isomers have the same molecule formula but different functional groups.

Example:- Ethyl alcohol and Dimethyl ether

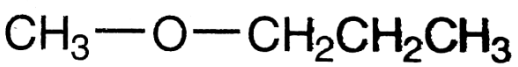
(4) Metamerism

This type of isomerism is due to the unequal distribution of carbon atoms on either side of the functional group. Members belong to the same homologous series.

Example:- Diethyl ether and Methyl propyl ether



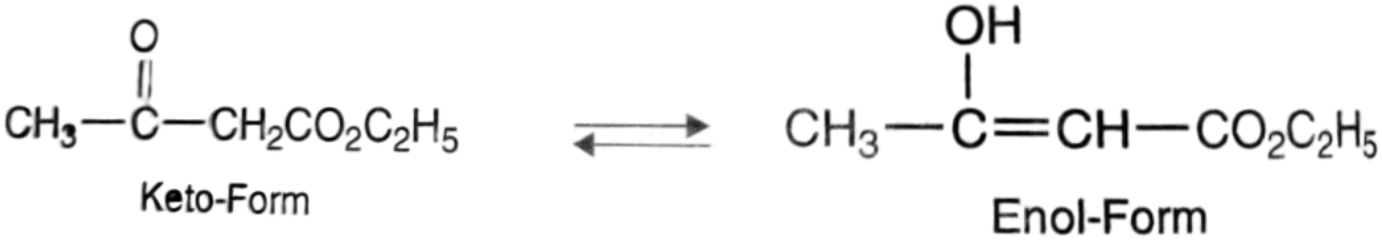
Diethyl ether



Methyl propyl ether

(5) Tautomerism

It is a special type of functional isomerism in which the isomers are in dynamic equilibrium with each other. For example, ethyl acetoacetate is an equilibrium mixture of the following two forms. At room temperature, the mixture contains 93% of keto-form plus 6% of the enol-form.

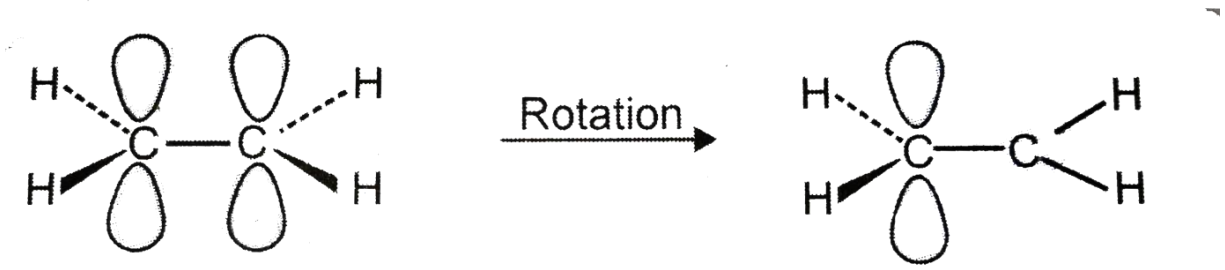


GEOMETRICAL ISOMERISM

Geometrical isomerism (also called cis-trans isomerism) result from a restriction in rotation about double bonds, or about single bonds in cyclic compounds.

(1) The carbon atoms of the carbon-carbon double bond are sp^2hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the overlap of sp^2 hybrid orbitals. The π bond is formed by the overlap of p orbital. The presence of the π bond locks the molecule in one position. Two carbon atoms of the C=C bond and the four atoms that are

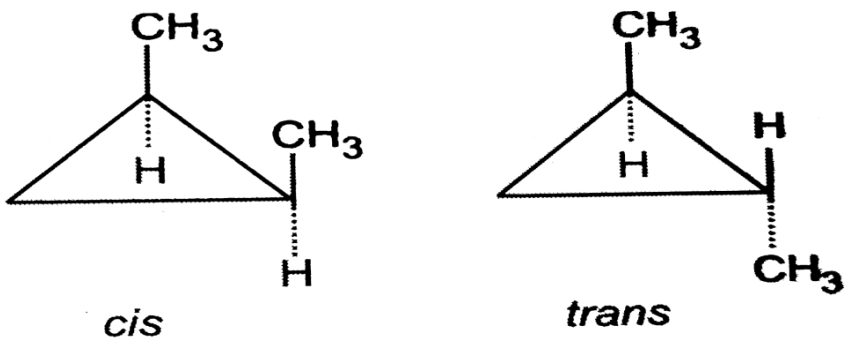
attached to them lie in one plane and their position in space are fixed. Rotation around the C=C bond is not possible because rotation would the π bond



(2) Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break the ring.

Example:- 1,2-dimethylcyclopropane exists in two isomeric forms.



OPTICAL ISOMERISM

Optical isomerism is a type of stereoisomerism. The outstanding feature of optical isomers is that they have the ability to rotate plane-polarized light. This property is often referred to as optical activity