ISOMERISM

INTRODUCTION
The word isomerism came from Greek word *isomers* (isos = equal, meros = a share). Two or more compounds having the same molecular formula but different chemical and/or physical properties are called isomers and the phenomenon is known as isomerism.

Isomerism can be broadly divided into two types,
1. Structural isomerism (constitutional isomerism)
2. Stereoisomerism (configurational isomerism)

STRUCTURAL ISOMERISM (CONSTITUTIONAL ISOMERISM)
The isomers in which atoms have a different connectivity are known as structural isomers and the phenomenon is called structural isomerism. In other words, *the isomer having same molecular formula but different structural formula is called structural isomer and the phenomenon is known as structural isomerism.* The isomerism arises due to difference in arrangements of atoms within the molecule without any reference of space.

Types of structural isomerism:
(i) Chain or nuclear isomerism
(ii) Position isomerism
(iii) Functional isomerism
(iv) Metamerism
(v) Tautomerism

Chain or Nuclear Isomerism
Compounds having same molecular formula but different arrangement of carbon chain within the molecule (i.e. they differ in chain length) are called chain or nuclear isomers and the phenomenon is called chain or nuclear isomerism. Example: Butane and 2-methyl propane are chain isomers.

Position Isomerism
Compounds which have the same structure of the carbon chain (carbon length) but differ only in the position of the multiple (double or triple) bond or the functional group or the substituent group are called position isomers and the phenomenon is called position isomerism. Example: 1-butene and 2-butene are positional isomers.

Functional Isomerism
Compounds having the same molecular formula but different functional groups are called functional isomers and the phenomenon is called functional isomerism. Example:
The following classes of organic compounds show functional isomerism among themselves.

(a) Carboxylic acids and esters

\[ \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_2 \text{OH} \quad \text{and} \quad \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_3 \]

acetic acid

methyl formate

(b) Aldehydes and ketones

\[ \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_3 \quad \text{and} \quad \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_2 \text{H} \]

propanone

propanal

(c) 1°, 2° and 3° amines

\[ \text{H}_3\text{C} \overset{\text{N}}{\text{H}} \text{CH}_3 \quad \text{N}\text{-ethyl-N-methylamine} \quad \text{and} \quad \text{H}_3\text{C} \overset{\text{N}}{\text{H}} \text{CH}_3 \]

N,N,N-trimethylamine

Metamerism

Compounds having the same molecular formula but different number of carbon atoms (or alkyl group) on either side of the functional group (i.e. –O–, –S–, –NH– and –CO–) are called metomers and the phenomenon is called metamerism. Metamerism occurs among the members of the same homologous family. Example:

(a)

\[ \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_3 \quad \text{ethoxyethane} \quad \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_3 \quad \text{1-methoxypropane} \quad \text{H}_3\text{C} \overset{\text{O}}{\text{C}} \text{H}_3 \quad \text{2-methoxypropane} \]

(b)

\[ \text{H}_3\text{C} \overset{\text{NH}}{\text{C}} \text{H}_3 \quad \text{N,N-diethylamine} \quad \text{H}_3\text{C} \overset{\text{NH}}{\text{C}} \text{H}_3 \quad \text{N-methyl-N-propylamine} \quad \text{H}_3\text{C} \overset{\text{NH}}{\text{C}} \text{H}_3 \quad \text{N-isopropyl-N-methylamine} \]

Tautomerism

It is the type of isomerism in which two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called tautomers. It arises due to migration of atomic nuclei from one polyvalent atom to the other.
within the same molecule. Example: The compound acetoacetic ester has two tautomers—one has keto group and other has an enol group.

\[
\begin{align*}
\text{ethyl 3-oxobutanoate} & \quad \leftrightarrow \quad \text{ethyl -3-hydroxybut-2-enoate} \\
\end{align*}
\]

The equilibrium between the two forms is dynamic in nature.

There are several types of tautomerism.
(i) Keto–enol tautomerism

Generally, keto form is more stable than enol form because of the fact that C=O bond is stronger than C=C bond, but there are some exceptions to this rule. Example:

(a) 

Reason: Phenol gets aromatic stabilization.

(b) 

Reason: Extended conjugation and intramolecular hydrogen bonding in enol form.

Effect of solvent: Polar protic solvents such as H₂O, CH₃OH etc. which form H– bonds with the carbonyl group of the keto form, decrease the enol content. On the other hand, aprotic solvents such as hexane, benzene etc. increases the enol content. For example, enol form of acetylacetone is available as 76% in ethanol but 92% in benzene.

(ii) Nitro–aci tautomerism

(iii) Oxime–nitroso tautomerism

(iv) Imine–inamine tautomerism

Structural Requirements for Tautomerism

(i) Compound should have an electronegative atom which is bonded with multiple bond (i.e. N and O).
Compound should have at least one acidic hydrogen present on \( \alpha \)-carbon of the molecule. If the above two conditions are fulfilled, then compound will show tautomerism.

Percentage of enolic contents of some common compounds in decreasing order is given below,

\[
\text{OH} > \text{COO} \quad \text{H}_2\text{C}_6 > \text{COOCH}_3 > \text{COOCH}_3 > \text{RO} \quad \text{OR} > \text{COH} > \text{COH}
\]

[Note: Presence of benzene ring adjacent to carbonyl group increases the enol content due to extended conjugated system provided by benzene ring.]

**Difference between Tautomerism and Resonance**

Tautomerism and resonance are two different phenomena and the differences are as follows:

(i) In tautomerism, an atom changes its place but resonance involves a change of position of \( \pi \) electrons or unshared electrons.

(ii) Tautomers are different compounds and they can be separated by suitable methods but resonating structures cannot be separated as they are imaginary structures of the same compounds.

(iii) Tautomers are in dynamic equilibrium but in resonance only one compound exists.

(iv) Resonance in a molecule lowers the energy and thus stabilizes a compound and decreases its reactivity but no such effects occur in tautomerism.

**STEREISOMERISM (CONFIGURATIONAL ISOMERISM)**

Isomers those have the same molecular formula and structural formula but differ in the spatial arrangements of atoms or groups, i.e. such compounds have identical molecular structures but different configurations are called stereoisomers and the phenomenon is known as stereoisomerism.

There are two types of stereoisomerism

(i) Geometrical isomerism

(ii) Optical isomerism

**Geometrical Isomerism**

Isomers which possess the same molecular and structural formula but differ in arrangement of atoms or groups in space around the double bond (or where the rotation is frozen) are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

Compound will show geometrical isomerism if it fulfills the following two conditions:

(i) The rotation about two adjacent atoms in the molecule should be frozen.

(ii) Both substituents on each carbon should be different about which rotation is frozen.
Types of geometrical isomers. The types of geometrical isomers are,
(i) cis–trans isomerism 
(ii) syn-anti isomerism 
(iii) E–Z isomerism

(i) cis–trans isomerism

<table>
<thead>
<tr>
<th>cis form</th>
<th>trans form</th>
</tr>
</thead>
</table>
| a
b       | b
a         |

The isomer in which similar groups are placed on the same side is called cis and the isomer in which the similar groups are on opposite sides is called trans. Example:

H₃C  
\[\text{cis 2 butene}\]  
H CH₃

H \[\text{trans 2 butene}\]  
H CH₃

HOOC

\[\text{cis cyclopropane}\]  
\[\text{cis 1,2 dicarboxylic acid}\]

COOH

\[\text{cis 1,2 dimethylcyclopropane}\]  
\[\text{cis 1,2 cyclohexanol}\]

Geometrical isomerism in nitrogen compounds. Geometrical isomerism due to restricted rotation around > C = N bond. The important class of compounds exhibiting geometrical isomerism due to >C=N bond are (i) oximes (ii) hydrazones and (iii) semi carbazones.

(i) Oximes: In aldoxime, when hydrogen and hydroxyl group are on the same side, the isomer is known as syn (analogous to cis) and when these groups are on the opposite sides, the isomer is known as anti (analogous to trans).

\[\text{syn Benzaldoxime}\]  
\[\text{anti Benzaldoxime}\]

Similarly, azo compounds show geometrical isomerism.

\[\text{anti – azobenzene}\]  
\[\text{syn – azobenzene}\]

[Note: Certain compounds show geometrical as well as optical isomerism such type of isomerism is known as geometrical enantiomerism.]

Distinction between cis and trans isomers. Distinction between cis and trans isomers of a compound can be made on the basis of their physical properties such as melting point, boiling point, solubility, dipole moment etc.
(i) **Melting point:** In general, the melting point of a *trans* isomer is higher than that of the corresponding *cis* isomer. This is due to the reason that the molecules of a *trans* isomer are more symmetrical and hence fit more closely in the crystal lattice as compared to the molecules of a *cis* isomer.

\[
\begin{align*}
\text{Maleic acid (} \text{cis isomer)} & \quad \text{m.p. } 403 \text{ K} \\
\text{Fumaric acid (} \text{trans isomer)} & \quad \text{m.p. } 575 \text{ K}
\end{align*}
\]

(ii) **Solubility:** In general, solubility of a *cis* isomer is higher than that of the corresponding *trans* isomer. This is due to the reason that the molecules of a *cis* isomer are less tightly held in the crystal lattice.

\[
\begin{align*}
\text{Maleic acid (} \text{cis form)} & = 79 \text{ g/100ml} \\
\text{Fumaric acid (} \text{trans isomer)} & = 0.7 \text{ g/100ml}
\end{align*}
\]

(iii) **Dipole moment:** The *cis* isomer has higher dipole moment than the corresponding *trans* isomer.

\[
\begin{align*}
\mu & = 1.85 \\
\mu & = 0 \\
\mu & = 2.54 \text{ D} \\
\mu & = 2.38 \text{ D}
\end{align*}
\]

(iv) **Stability:** The *trans* isomer is more stable than *cis* isomer due to steric hindrance. Intermolecular reactions occur easily when reacting groups are close together. Hence, the *cis* isomer will form cyclic derivatives more readily as against *trans* derivatives. But this reaction will take place in only those *cis* isomers in which the substituents on two double bonded carbons are capable of intramolecular reaction with each other.

Fumaric acid forms anhydride via the formation of maleic acid because at high temperature fumaric acid converts into maleic acid

Fumaric acid \(\rightleftharpoons\) Maleic acid \(\rightarrow\) Maleic anhydride
(v) **Action of heat:** On strong heating cis and trans isomers are interconvertible. This interconversion takes place as follows,

\[ \text{Homolytic bond fission} \]

\[ \text{cis} \rightleftharpoons \text{trans} \]

Thus, *cis* isomer \( \rightleftharpoons \) *trans* isomer.

(vi) **Different chemical properties:** Syn addition to alkene makes *cis* form into meso and *trans* into d and l. Anti addition makes *cis* into d–l and *trans* into meso.

**Number of geometrical isomer in polyenes.** (a) When compound has ‘n’ double bonds and ending groups of a polyene are different, the number of geometrical isomers = 2^n.

\[ \text{C}_6\text{H}_5 – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{Cl} \]

Since, the number of double bonds is four and two ends are different, one is \( \text{C}_6\text{H}_5 \) and other is Cl. Therefore, number of geometrical isomers = 2^4 = 16

(b) When the ending groups of polyene are same.

Case – I: When number of double bonds is even then the number of geometrical isomers = 2^{n-1} + 2^{n/2-1}

\[ \text{Cl} – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{Cl} \]

n = 4, even

No. of geometrical isomers = 2^{4-1} + 2^{4/2-1}

= 2^3 + 2^1 = 10

Case – II: When number of double bond is odd then no. of geometrical isomer = 2^{n-1} + 2^{(n+1)/2-1}

\[ \text{C}_6\text{H}_5 – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{CH} = \text{CH} – \text{C}_6\text{H}_5 \]

No. of geometrical isomers = 2^3 + 2^{2} = 6

**(E) and (Z) system of nomenclature.** The simple *cis*–*trans* nomenclature is not applicable when there are four different substituent groups are present on two doubly bonded carbon atoms. In such cases, a more general system of nomenclature of geometrical isomers has been proposed called the (E) and (Z) system. For naming the compounds by this method, first the groups of highest priority on each carbon atom are identified by using sequence rules. If the highest priority groups on two carbon atoms of the double bond are on the same side the configuration is Z (Zusammen in German means same side) and if they are on opposite sides, the configuration is E (Entgegen in German means opposite). The group/atom attached to carbon–carbon bond is given higher rank, whose atomic weight is higher.

**Exercise:** Assign E–Z configuration to each of the following:
Optical Isomerism

Compounds which rotates the plane of polarized light are known as optically active compounds and the phenomenon is known as optical activity. If a substance rotates the plane of polarized light in clockwise direction then it is dextrorotatory, (+) form or (d) form. If a substance rotates the plane of polarized light in anti-clockwise direction then it is laevorotatory, (-) form or (l) form. (d) form and (l) form can only be known by the use of polarimeter and not by the configuration of the compound.

Specific rotation. The specific rotation of an optically active substance is defined as the degree of rotation observed when the plane polarized light is passed through a tube having a path length of 1 decimetre (10 cm) and a concentration of 1 g/mole of the compound at a specified temperature and wavelength. It is denoted by \([\alpha]_D\), where \(t\) is the temperature and \(D\) is the wavelength of light used.

The specific rotation is calculated as

\[
[\alpha]_D = \frac{\text{observed angle of rotation}(\alpha)}{L \times C}
\]

where, \(L\) = length of polarimeter tube
\(C\) = conc. of the substance

Chirality and asymmetric carbon. A molecule (or an object) is said to be chiral or dissymmetric, if it is not superimposable on its mirror image and the property of non-superimposability is called chirality. On the other hand, a molecule (or an object) which is superimposable on its mirror image is called achiral (non-dissymmetric or unsymmetric).

Example: Alphabet P is chiral and A is achiral.

Thus, for a substance to be optically active, it must be non-superimposable on its minor image.

Chiral carbon atom (chiral centre/stereo centre). Carbon atom bonded to four different atoms or groups is called an asymmetric carbon atom or a chiral atom. A chiral atom is indicated by an asterisk (*). Example:
If a molecule contains only one chiral centre/atom, then the molecule has to be optically active (i.e. non-superimposable on its mirror image) as it will not contain any element of symmetry. Molecules containing two or more chiral centres may or may not be chiral (optically active).

It is necessary to distinguish chiral and chiral centre. The word chiral is used for molecule as a whole which is optically active, whereas chiral centre is for an atom which is attached to form different atoms/groups.

**ELEMENTS OF SYMMETRY**

The types of elements of symmetry are as follows,

1. Plane of symmetry
2. Centre of symmetry
3. Alternate axis of symmetry

**Plane of symmetry.** A molecule is said to possess a plane of symmetry if the atoms or groups on one side of the plane forms the mirror image of those on the other side. In other words, a plane which bisects a molecule/object in two equal halves.

**Centre of symmetry.** A centre of symmetry in a molecule is said to exist if a line is drawn from any atom or group to this point and then extended to an equal distance beyond this point meets the identical atom or group.

A centre of symmetry is usually present only in an even membered ring. Example:
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So, for any compound to be optically active it must not possess any element of symmetry. Example:

Although in mesotartaric acid there are two chiral centres, yet the molecule is optically inactive because it contains plane of symmetry, i.e. presence or absence of symmetries in the molecule can be known by the configuration of the molecule and not by its structure.

Enantiomers

Optical isomers which are non-superimposable mirror images of each other are called enantiomers. The enantiomers have identical physical and chemical properties but rotate the plane of polarized light in opposite directions but to some extent.

Diastereomers

The stereoisomers which are not mirror images of each other are called diastereomers. The properties of diastereomers are different from those of enantiomers (which are mirror images of each other). Example: Stereoisomerism in 2, 3-dibromopentane.

No. of optical isomers possible = \(2^n = 2^2 = 4\)
Meso Compound
An optically inactive compound whose molecule is superimposable on its mirror image inspite of the presence of chiral carbon atoms is called a meso compound. Example: In Tartaric acid.

\[
\text{HOOC} \quad \overset{*}{\text{CHOH}} \quad \overset{*}{\text{CHOH}} \quad \text{COOH}
\]

The molecule contains two chiral carbon and the number of optical isomers should be \(2^n = 2^2 = 4\) but number of optical isomer is reduced to 3 because one molecule has a plane of symmetry.

The stereoisomers of tartaric acid are,

\[
\begin{align*}
\text{(I)} & \quad \text{Mirror} \\
\text{(II)} & \quad \text{Mirror} \\
\text{(III)} & \quad \text{Mirror} \\
\text{(IV)} & \quad \text{Mirror}
\end{align*}
\]

I and II are enantiomers (non-superimposable).
III and IV are meso form (superimposable).

**Calculation of number of optical isomers in compounds (containing ‘n’ chiral atoms)**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>Number of optical active forms (a)</th>
<th>Number of meso forms (m)</th>
<th>Number of racemic mixture (a/2)</th>
<th>Total number of optical isomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The molecule has no symmetry</td>
<td>(2^n)</td>
<td>0</td>
<td>(2^{n-1})</td>
<td>(a + m)</td>
</tr>
<tr>
<td>2</td>
<td>The molecule has symmetry</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Case 1:
When compound has even number of chiral carbon atoms

\[ 2^{n-1} \quad 2^{n/2-1} \quad 2^{n/2} \quad a+m \]

Case 2:
When compound has odd number of carbon atoms

\[ 2^{n-1} - 2^{(n-1)/2} \quad 2^{n-1/2} \quad 2^{n-1} \]

Example:
(i) \[ \text{H}_5\text{C}_6\text{CH}_3 \]
Number of optically active forms = \( a = 2^3 = 8 \)

(ii) \[ \text{HOOC-CHOH-CHOH-COOH} \]
Number of optical isomer = \( a = 2^{2-1} = 2 \)
Number of meso form = \( m = 2^{n/2-1} = 2^0 = 1 \)
Total number of configuration isomer = 2 + 1 = 3

(iii) \[ \text{HOH}_2\text{C}-\text{CHOH-CHOH-CHOH-CH}_2\text{OH} \]
Number of optical isomer = \( 2^{3-1} - 2^{(3-1)/2} = 2^2 - 2^1 = 4 - 2 = 2 \)
Number of meso form = 2
Total no. of configurational isomers = 2 + 2 = 4

OPTICAL INACTIVITY DUE TO COMPENSATION

The optical inactivity is also possible due to compensation. There are two types of compensation. They are,
(a) internal compensation
(b) external compensation.

Internal compensation. If the rotation of polarized light caused by one half of the molecule is exactly cancelled by equal and opposite rotation caused by the other half of the molecule and the molecule becomes optically inactive, then the optical inactivity of molecule is due to internal compensation (within the molecule). Example: Mesotartaric acid.

External compensation. If two enantiomers are mixed together in equimolar amount, then the mixture becomes optically inactive. The rotation caused by one enantiomer is exactly cancelled by other enantiomers and is due to external compensation. The resulting optically inactive mixture is called racemic mixture. Example: Equimolar amount of d and l form of tartaric acid.

Resolution
The process by which a racemic mixture can be separated into its (d) and (l) enantiomers is called resolution.
The racemic mixture can be resolved by following methods namely:
(i) Mechanical separation.
(ii) Biochemical method. Example: \textit{Penicillium glaucum} added to racemic tartaric acid consumes only (+) tartaric acid leaving behind (-) tartaric acid.
(iii) Chemical method
NOMENCLATURE

The arrangement of atoms or group of atoms which characterizes a particular stereoisomer is called its configuration. The two terms which are commonly used to describe the configuration of different stereoisomers are absolute and relative configuration. By absolute configuration we mean the actual arrangement of atoms or groups of atoms in space of a particular stereoisomer of a compound.

The relative configuration means the arrangement of atoms or group of atoms in space of stereoisomer of compound relative to the atoms or group of atoms of another compound chosen as arbitrary standard.

D, L nomenclature or D, L system

Before 1951, there was no method available for determining the absolute configuration of a compound so, the relative configuration were established with respect to glyceraldehyde chosen as the arbitrary standard. The two enantiomers of this compound were designated D and L symbols. In this system, all sugars whose Fischer projection formula shows the –OH group on the chiral carbon atom adjacent to the terminal CH₂OH group on the right hand belong to the D–series.

Example:

![Diagram of D(+)-Glyceraldehyde and D(+)-Glucose]

Similarly, if –OH is on the left hand side, then the sugar belongs to L–series.

![Diagram of L(-)-Glyceraldehyde and L(-)-Glucose]

It is important to mention here that there is relation between configuration and sign of rotation.

R, S nomenclature (absolute configuration)

The limitation of the (D, L) system have however been removed by an unambiguous system developed by R.S Cahn, C.K. Ingold and V. Prelog. This system is called Cahn, Ingold, Prelog system or simply R, S system. R (from Latin rectus means right) and (from Latin sinister means left). Any chiral carbon atom has either (R) configuration or (S) configuration. The configuration is assigned by following steps:

Step – 1: First a priority sequence is assigned to all groups attached to the carbon atom. The priority can be assigned by,

(i) If four atoms attached to chiral atom are different, priority depends upon atomic number. Atom with highest atomic number gets highest priority and the one with lowest atomic number is the lowest priority by assigning number 1, 2, 3 and 4.

(ii) If two or more than two isotopes of the same element is present, the isotope of higher mass gets the highest priority.

(iii) If two or more of the atoms directly bonded to the chiral atoms are identical, the atomic numbers of the next atoms are used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at first...
point of difference along the chain. The atom which has been attached to an atom of highest priority has the higher priority.

(iv) If a double bond or triple bond is linked to a chiral centre the involved atoms are duplicated or triplicated respectively.

Step – 2: The molecule is then visualized so that the group of lowest priority (4) is directed away from us (i.e. the lowest priority at the bottom of the plane). If on going from group of highest priority to the second and then to third, i.e. \((1) \rightarrow (2) \rightarrow (3)\), the eye moves in clockwise direction, then the configuration is specified as \(R\) and if in anti-clockwise direction it is specified as \(S\). Example:

In fisher projection formula
Multiple Choice Questions

1. The possible structural isomers of $C_4H_6$ are
   (A) 9
   (B) 8
   (C) 7
   (D) 6

   **Sol.**
   (A).

   2. The number of functional isomers of $C_3H_6O$ is
   (A) 2
   (B) 3
   (C) 4
   (D) 5

   **Sol.**
   (D).

   3. The number of isomers for the aromatic compound having molecular formula $C_7H_8O$ is
   (A) 2
   (B) 3
   (C) 4
   (D) 5

   **Sol.**
   (D).

   4. Which of the following has the highest enol content?
   (A) $CH_3COCH_2COOC_2H_5$
   (B) $CH_3COCH_2COCH_3$
   (C) $C_6H_5COCH_2COCH_3$
   (D) $C_6H_5COCH_2COOC_6H_5$

   **Sol.**
   (D).

   5. Keto-enol tautomerism is observed in
   (A) $C_6H_5-CHO$
   (B) $C_6H_5COCH_2COCH_3$
   (C) $C_6H_5-CHO-C_6H_5$
   (D) All of the above

   **Sol.**
   (B). $C_6H_5COCH_2CH_2COCH_3$ contains $\alpha$-hydrogen

   6. Only two isomeric monochloro derivatives are possible for
   (A) $n$-butane
   (B) 2,4-dimethyl pentane
   (C) benzene
   (D) 2-methyl butane
7. Geometrical isomerism is shown by

(A) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{H} \\
\text{I}
\end{array}
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{Br} \\
\text{H}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{Br} \\
\text{H}
\end{array}
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{Cl} \\
\text{H}
\end{array}
\]

(C) \[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{Cl} \\
\text{H}
\end{array}
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{C} \\
\text{Br} \\
\text{H}
\end{array}
\]

8. The above structures (A) and (B) represent

(A) resonance structures

(C) enantiomers

(B) tautomers

(D) anomers

9. The following compound can show

(A) optical isomerism

(C) optical and geometrical isomerism

(B) geometrical isomerism

(D) tautomerism

10. The type of isomerism observed in urea molecule is

(A) chain

(B) position

(C) geometrical

(D) tautomerism

11. The following compound can exhibit

(A) geometrical isomerism

(B) geometrical and optical isomerisms
(C) optical isomerism  (D) tautomerism

**Sol.** (C). It contains a chiral atom.

12. *Which of the following compound can exhibit geometrical isomerism?*

(A) \( \text{C}_6\text{H}_5 - \text{CH} = \text{NOH} \)  
(B) \( \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \)

(C) \[
\begin{array}{c}
\text{HOOC} \\
\text{COOH}
\end{array}
\]

(D) All the three

**Sol.** (D).

13. *Which of the following molecule is optically active?*

(A) \( \text{CH}_3-\text{CH}_2\text{CHClCH}_2\text{CH}_3 \)

(B) \[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{H}_3 \end{array}
\]

(C) \[
\begin{array}{c}
\text{NO}_2 \\
\text{COOH}
\end{array}
\]

(D) \( (\text{CH}_3)_2\text{CHCOOH} \)

**Sol.** (B).

The two carbons (1,3) in the structure are not in the same plane.

14. *Which of the following structures are superimposable?*

(A) I and II  
(B) II and III  
(C) I and IV  
(D) I and III

**Sol.** (D).

15. *The number of chiral carbon atoms in*

(A) 2  
(C) 1  
(B) 3  
(D) 4
16. Out of the following compounds, which one would have a zero dipole moment?
(A) 1, 1-dichloroethylene  
(B) cis-1, 2-dichloroethylene  
(C) trans-1, 2-dichloroethylene  
(D) None of the above

Sol. (C).

17. Which of the following hydrocarbon has the lowest dipole moment?

(A) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{H}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

(C) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_2
\end{array}
\]

(D) \[
\begin{array}{c}
\text{H}_2\text{C} \\
\text{C}
\end{array}
\]

Sol. (B). Linear structure so dipoles cancel each other.

18. The enolic form of acetone contains:
(A) 9 sigma bonds, 1 pi bond and 2 lone pairs
(B) 8 sigma bonds, 2 pi bonds and 2 lone pairs
(C) 10 sigma bonds, 1 pi bond and 1 lone pair
(D) 9 sigma bonds, 2 pi bonds and 1 lone pair

Sol. (A).

19. Tautomerism is exhibited by

(A) \[
\begin{array}{c}
\text{Ph} \\
\text{CHO}
\end{array}
\]

(B) \[
\begin{array}{c}
\text{Ph} \\
\text{CO}
\end{array}
\]

(C) \[
\begin{array}{c}
\text{Ph} \\
\text{KH}
\end{array}
\]

(D) \[
\begin{array}{c}
\text{Ph} \\
\text{KO}
\end{array}
\]

(A) 1, 2, 3  
(C) 1, 2, 4

Sol. (B).

20. Which of the following compounds will show geometrical isomerism?

1. 2-Butene  
2. Propene  
3. 1-Phenylpropene  
4. 2-Methylbut-2-ene

(A) 1, 2  
(B) 3, 4  
(C) 1, 2, 3  
(D) 1, 3

Sol. (D).

21. Which of the following compound will exhibit geometrical isomerism?

(A) 1-Phenyl-2-butene  
(B) 3-Phenyl-1-butene  
(C) 2-Phenyl-1-butene  
(D) 1, 1-Diphenyl-1-propene

Sol. (A).
22. Which of the following have asymmetric carbon atoms?

1. ClCH₂ - CH₂ Br
2. CH₃ - CHCl₂
3. CH₃ - CH₂ DCl
4. CH₂ Br - CHOH - CH₃

(A) 1, 2, 3
(B) 1, 3, 4
(C) 2, 3
(D) 3, 4

[IIT – 1989]

Sol. (D).

23. How many chiral carbon atoms are present in 2, 3, 4-trichloropentane?

(A) 3
(B) 2
(C) 1
(D) 4

[IIT – 1990]

Sol. (A).

24. An organic molecule necessarily shows optical activity if it

(A) contains asymmetric carbon atoms
(B) is non-planar
(C) is non-superimposable on its mirror image
(D) is superimposable on its mirror image

[IIT – 1993]

Sol. (C).

25. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is

(A) 2
(B) 3
(C) 4

[IIT – 1997]

Sol. (D).

26. The correct statement about the compounds A, B and C

(A) A and B are identical
(B) A and B are diastereomers
(C) A and C are enantiomers
(D) A and B are enantiomers

[IIT – 1997]

Sol. (B). Rotating (B), we get the mirror image of (A).

27. How many optically active stereoisomers are possible for Butane -2,3-diol?

(A) 1
(B) 2
(C) 3
(D) 4

[IIT – 1997]

Sol. (C).

28. The optically active tartaric acid is named as D (+) tartaric acid because it has a positive

(A) optical rotation and is derived from D - glucose
(B) pH in an organic solvent
(C) optical rotation and is derived from D (+) glyceraldehyde
(D) optical rotation only when substituted by deuterium

[IIT – 1999]

Sol. (C).

29. Which of the following compound exhibit stereoisomerism?

(A) 2-methylbutene-1
(B) 3-methylbutyne-1
(C) 3-methylbutanoic acid
(D) 2-methylbutanoic acid

[IIT – 2002]

Sol. (D). 2-methylbutanoic acid contain chiral centre CH₂CH₂ CH(CH₃)COOH.
30. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be
   (A) optically active mixture          (B) pure enantiomer
   (C) meso compound                    (D) racemic mixture

   [IIT-2003]

Sol. (D).

**Fill in the Blanks**

1. Alkenes can exhibit position, chain, ................... and ................... isomer. (geometrical, functional)
2. Carboxylic acids and esters are example of ................... isomerism. (functional)
3. Ketones must contain at least ........... carbon atoms in order to exhibit metamerism. (five)
4. Ethyl cyanide and ethyl isocyanide are .......... isomers. (functional)
5. The structure of enol form of CH₃COCH₂COCH₃ with intramolecular hydrogen bonding is .................
   \[
   \begin{array}{c}
   \text{H₃C} \\
   \text{O} \\
   \text{H} \\
   \text{O} \\
   \text{CH₃} \\
   \text{CH₃} \\
   \end{array}
   \]
6. Geometrical isomerism is due to ........... rotation of ........... bond. (restricted, double)
7. ........... cannot be resolved into d and l form. (meso form)
8. ‘E’ and ‘Z’ system of naming geometrical isomers is based on ........... rules. (sequence)
9. Fisher projection is a ............... representation of the three dimensional structure. (planar)
10. Amongst the three isomer of nitrophenol, the one that is least soluble in water is ...........
    (o-nitrophenol)
Short Answer Type Questions

Prob.1. Write all possible structural isomers of the compound with molecular formula $C_4H_{10}O$.

Sol. Total number of structural isomers = 7

(i) $\text{CH}_3\text{C}-\text{CH}_3\text{OH}$

(ii) $\text{H}_3\text{C}-\text{OH}$

(iii) $\text{H}_3\text{C}-\text{CH}_3\text{O-CH}_3$

(iv) $\text{CH}_3\text{O-CH}_3$

(v) $\text{H}_3\text{C}-\text{O-CH}_3$

Prob.2. Write structural formula of all the isomeric alcohols having the molecular formula $C_4H_{10}O$.

Sol. (A) $\text{H}_3\text{C}-\text{OH}$

(B) $\text{CH}_3\text{OH}$

(C) $\text{H}_3\text{C}-\text{O-CH}_3$

Prob.3. Write all possible isomers of the compound having molecular formula $C_3H_8O$.

Sol. (A) $\text{H}_3\text{C}-\text{OH}$

(B) $\text{H}_3\text{C}-\text{O-CH}_3$

Prob.4. How many isomers are possible with the formula $C_2\text{ClBrF}$?

Sol. Six isomers are possible

Prob.5. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III.
ISOMERISM

BY

NKB.CO.IN

Prob. 6. What is the relation between following pairs of structure, indicate whether they are identical or enantiomers?

(a)

(b)

Sol. (a) Enantiomers.
(b) Pair of identical molecules.

Prob. 7. What do you think about the following compounds optically active or not? Support your answer.

(a)

(b)

(c)

(d)

Sol. (a) It is optically inactive due to presence of two chlorine in same carbon.
(b) It has two chiral carbon atoms but due to plane of symmetry it is optically inactive.
(c) It has two chiral carbon and don’t have any plane of symmetry, so it is optically active.
(d) There is no chiral carbon but the molecule is chiral (an allene), so it is optically active.

Prob. 8. Calculate total number of optically active isomers of the compound COOH(CHOH)$_2$COOH
When the molecule can be divided into two equal halves (i.e. has symmetry), number of asymmetric carbon atoms is even, then
Number of optically active isomers, \( a = 2^{n-1} \)
Number of meso forms, \( m = 2^{(n/2)-1} \)
Total number of optical isomers = \( a + m \)
Where \( n \) = number of chiral carbon atoms
Here \( n = 2 \)  \( \therefore \) \( a = 2 \), \( m = 1 \)
Total optical isomers = \( 2+1=3 \)

Prob. 9. How many total stereoisomers are possible for butane-2, 3-diol and how many of them are optically active?

Sol.

<table>
<thead>
<tr>
<th>CH₃</th>
<th>OH</th>
<th>*</th>
<th>CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2, 3- dihydroxybutane

Chiral centre present = 2
Plane of symmetry is present
\( \therefore \) total no. of stereo isomer present = 3

I meso compound  (optically inactive)
II enantiomers  (optically active)

Prob. 10. Write down the structures of the stereoisomers formed when cis 2 butene is reacted with bromine.  
[IIT-JEE-1995]

Sol.

The addition of bromine to cis 2-butene involves anti-addition and thus racemic 2, 3-dirbromo butane is formed.
1. Members belonging to same class of compound are called isomers.

**Sol. False**, are called homologues.

2. Chain isomerism is observed in hydrocarbons only.

**Sol. False**

3. m-chlorobromobenzene is an isomer of m-bromochlorobenzene.

**Sol. False**, same compound.

4. Ethyl alcohol and dimethyl ether are position isomers.

**Sol. False**, functional isomers.

5. Optically active compound may exist in four forms.

**Sol. True**, laevo, dextro, racemic, meso.

6. Compounds containing asymmetric carbon atoms are always optically active.

**Sol. False**, meso form contains plane of symmetry.

7. The arrangement in space of the atoms or groups that characterizes a stereoisomer is called its configuration.

**Sol. True**

8. Diastereomers have different physical properties and similar but not identical chemical properties.

**Sol. True**

9. Ethane 1,2-diol is optically inactive.

**Sol. True**

10. Cyclic compounds can also exhibit geometrical isomerism.

**Sol. True**
SECTION – B

Subjective Problems

Prob.1. Write structural formula for each of following:
(a) A cyclic ester with the formula C₄H₄O₄.
(b) An unsaturated dibasic acid of zero dipole moment with formula C₄H₄O₄.

Sol. (a)

(b)

Prob.2. Write structures that corresponds to following description:
(a) A tertiary amine with the formula C₄H₁₁N.
(b) A cyclic ester with the formula C₆H₈O₄.

Sol. (a)

(b)

Prob.3. What are the possible types of compounds that can have a molecular formula C₃H₆O?

Sol.  C₂H₅ - CHO, CH₃ - C - CH₃, CH₂ = CH - CH₂ - OH, CH₂ = CH - O - CH₃, etc.

Prob.4. Write the structure of a tautomeric isomer for each of the following compound:

Sol. (a)

(b)

(c)

(a)

(b)

(a)

(b)
Prob.5. Assign E and Z configuration to the following alkenes.

(a) 2-pentene

(b) 2-methylbut-2-ene

(c) 3-methylpent-2-ene

(d) 4-methylpent-2-ene

(e) 2-methyl-1-butene

Sol.  
(a) E  
(b) Not possible  
(c) Z  
(d) E  
(e) Not possible

Prob.6. C₄H₈ can have so many isomers. Write their structures. What are different tests to make distinction between them?

Sol.  
C₄H₈ can have following structures:

(a) CH₃—CH₂—CH=CH₂ 1-butene

(b) CH₃—CH=CH—CH₃ 2-butene (cis and trans)

(c) CH₃—C=CH₂ 2-methyl-1-propene

(d) Cyclobutane

(e) Methyl cyclopropane

The tests used for distinction between above isomers are,

(i) Ozonolysis of (a) forms CH₃CH₂CHO and HCHO, (b) forms CH₃CHO and (c) forms

(ii) CH₃—C—H \[ \xrightarrow{+ \text{alkaline KMnO}_4} \] CH₃—C—OH

\text{cis 2-butene}  
\text{Meso-isomer}
CH\_3–C–H + alkaline KMnO\_4 \rightarrow \begin{array}{c} \text{trans 2-butene} \\ \text{d-and l-butane-2,3-diol} \end{array}

Prob. 7.

Which enol form will be favoured and why?

Sol.

(II) will be favoured because it is more stable due to extended conjugation than (I).

Prob. 8. For each of the following addition, predict the regiochemistry of each adduct and determine whether the product mixture is optically active. If not, determine whether the inactivity results from the absence of chiral centre; the formation of equal amounts of enantiomers or formation of a meso compound.

(a) DCI \rightarrow 

Sol. (a) chiral 

(b) HBr \rightarrow 

Sol. (b) a chiral and enantiomer

Prob. 9. For each of the following reactions, predict whether the desired stereochemistry and regiochemistry can be attained with the acid-catalysed hydration, hydroboration-oxidation, or not at all.
Sol. (a) acid-catalysed hydration
(b) Not at all
(c) hydroboration-oxidation
(d) hydroboration-oxidation

Prob. 10. Assign R, S configuration to the product when cyclopentene reacts with
   (a) cold KMnO₄
   (b) Br₂, water

Sol. (a)  

(b)  

Prob. 11. (a) Would you expect the following compound to be optically active? Explain.

Sol. No, the compound is optically inactive as it contains plane of symmetry.

Prob. 12. How many optically active forms are possible for the following compounds:

(i)  
(ii)  

Sol. (i) Two   (ii) Achiral (due to symmetry)

Prob. 13. In the following compounds, identify those that are optically active and meso compound.

Sol. (a) Meso
(b) Optically active
Prob. 14. A racemic mixture of (±) 2-phenyl propanoic acid on esterification with (+) 2-butanol gives two esters. Mention the stereochemistry of the two esters produced.

Sol.

The bonds attached to the chiral carbon in both the molecules are not broken during the esterification reaction. (+) acid reacts with (+) alcohol to give an (++) ester while (−) acid reacts with (+) alcohol to give (+−) ester. These two esters are diastereoisomers.

Prob. 15. The structure of D-Glucose is as follows:

(a) Draw the structure of L-Glucose.
(b) Give the reaction of L-Glucose with Tollen’s reagent.

Sol.
ASSIGNMENT PROBLEMS

SECTION – A

Multiple Choice Questions

1. The maximum number of cyclic isomers possible for the compound having molecular formula C₄H₈O is
   (A) 8  
   (B) 6  
   (C) 7  
   (D) 5

2. Tautomeration is not exhibited by
   (A) 
   (B) 
   (C) 
   (D) 

3. The enol form of acetone, after treatment with D₂O, gives:
   (A) 
   (B) 
   (C) 
   (D) None of the above

4. Tautomeration is not exhibited by
   (A) 
   (B) 
   (C) 
   (D) 

5. Tautomeration is not exhibited by
   (A) 
   (B) 
   (C) 
   (D) 

6. Which of the following will give the least stable enol?
7. Among these ketones which of the following is the correct order of the case of their enolizations:
   (A) I > II > III
   (B) III > II > I
   (C) II > I > III
   (D) III > I > II

8. CH₃CHOHCHBr have
   (A) 2 optical isomers
   (B) 2 geometrical isomers
   (C) 4 optical isomers
   (D) none of the above

9. Which will form geometrical isomers?
   (A) 
   (B) 
   (C) 
   (D) All of the above

10. Which one of the following will show geometrical isomerism?
    (A) CH₂C≡CCH₃
    (B) CH₃CH=CHCH₃
    (C) CH₂CH₂CH=CH₂
    (D) CH₂CH₂CH=CCl₂

11. Which of the compound will exhibit geometrical isomerism?
    (A) 2-butene
    (B) 2-butyne
    (C) 2-butanol
    (D) butanal

12. Which of the following compound is optically active?
    (A) 1-butanol
    (B) 2-butanol
    (C) 2-butene
    (D) 2-butyne

13. The total number of isomeric optically active monochloro isopentane is:
    (A) two
    (B) three
    (C) four
    (D) one

14. Isopentane, (CH₃)₂CH₂CHCH₃ can form four isomeric monochloro derivatives. How many of these are optically active?
    (A) 1
    (B) 2
    (C) 3
    (D) 4

15. Each of the following compound is expected to be optically active except
    (A) HO
    (B) H₃C
    (C) methyl-2-methyl propanoate
    (D) methyl-2-chloro propanoate
16. Configurations:

(I) \[
\text{Me} \quad \text{COOEt} \\
\text{Br} \quad \text{H} \\
\text{Br} \quad \text{H} \\
\text{I} \quad \text{COOEt}
\]

and

(II) \[
\text{Me} \quad \text{COOEt} \\
\text{Br} \quad \text{H} \\
\text{Br} \quad \text{H} \\
\text{I} \quad \text{COOEt}
\]

(A) represent same compound
(B) represent two different molecules which are mirror-images of one another
(C) represent two different molecules which are diastereomeric pair
(D) represent two different molecules whose equimolecular mixture will be racemic

17. A compound contains two dissimilar asymmetric carbon atoms. The numbers of possible stereoisomers are
(A) 2  
(B) 3  
(C) 4  
(D) 5

18. Which of the following is chiral?

(A) \[
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\]

(B) \[
\text{C} \\
\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\]

(C) \[
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\]

(D) \[
\text{H}_3\text{C} \\
\text{H} \\
\text{H} \\
\text{H}
\]

19. Which of the following can exhibit optical isomerism?

(A) \[
\text{H}_3\text{C} \rightarrow \text{N} \\
\text{C}_2\text{H}_5
\]

(B) \[
\text{H} \\
\text{C} \rightarrow \text{C} \\
\text{H} \\
\text{Cl} \\
\text{Cl}
\]

(C) \[
\text{H}_3\text{C} \\
\text{H}
\]

(D) \[
\text{Cl} \\
\text{C} \rightarrow \text{C} \\
\text{Cl} \\
\text{H} \\
\text{Cl}
\]

20. Which of the following compound is not optically active?

(A) \[
\text{Cl} \\
\text{H} \\
\text{Cl} \\
\text{Br} \\
\text{H}
\]

(B) \[
\text{Cl} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Cl}
\]

(C) \[
\text{Cl} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Br}
\]

(D) \[
\text{Cl} \\
\text{H} \\
\text{Br} \\
\text{H} \\
\text{Br}
\]

---

Fill in the Blanks

1. \(\alpha\)-chloro toluene and benzyl chloride are .......... isomers.

2. d and l-forms of an optically active compound differ in .................

3. The isomerism shown by lactic acid is .............

4. The isomerism not found in alkenes is .................
5. The type of isomerism observed in urea molecule is .................

6. The number of isomers shown by C\textsubscript{7}H\textsubscript{8}O is .................

7. Monosubstituted naphthalene has ................. position isomers.

8. Ethyl benzene is ................. isomer to xylenes.

9. Glucose has ................. optical isomers.

10. An organic compound with molecular formula C\textsubscript{2}H\textsubscript{5}NO contains doubly linked atoms, it shows ................. and ................. isomerism.

**Short Answer Type Questions**

1. Write the structural formula of all the isomers having molecular formula C\textsubscript{8}H\textsubscript{12}.

2. Write the possible isomers of the formula C\textsubscript{5}H\textsubscript{10}O\textsubscript{2}.

3. Explain that enol form of acetoacetic ester is said to be more volatile than keto form.

4. Allocate the symbol E and Z to each of the following:
   
   (i) \[\text{H}_3C\quad\text{Cl}\quad\text{H}\quad\text{Br}\]
   
   (ii) \[\text{H}_5\text{C}_6\quad\text{COOH}\quad\text{H}\quad\text{C}_6\text{H}_5\]

5. Discuss isomerism in lactic acid.

6. Discuss the optical activity of 2,3 pentadiene.

7. Why does 2-butene exhibit cis–trans isomerism but 2-butyne does not?

8. How can you distinguish between the following?

   \[\text{HOOC}\quad\text{H}\quad\text{COOH}\]

9. Assign R or S configuration to the following:

   (i) \[\text{HOOC}\quad\text{CH}_3\quad\text{CH}_2\text{OH}\quad\text{CCl}_3\]

   (ii) \[\text{HOOC}\quad\text{CH}_3\quad\text{CH}_2=\text{CH}_2\quad\text{CH}_3\]

10. What is the relation between the members of the following pairs of structures? Are they identical, structural isomers, geometrical isomers or resonance contributors?
True or False Type Questions

1. CHClBr(OH) is optically active as it do not contain any element of symmetry.
2. Only organic molecules can be optically active.
3. Sign of rotation of an enantiomer is related to its configuration.
4. 2, 3, 4-trichloropentane has three chiral carbon atom.
5. To be optically active a molecule must contain chiral carbon.
6. The dipole moment of trans form of geometrical isomerism is always zero.
7. d and l form of optical isomers can be interconverted by heating.
8. A molecule containing only one chiral centre always exhibit optical activity.
9. Stereoisomers have same structural formula but different configurations.
10. Tartaric acid shows the presence of three optical isomers.
1. Write the structures that correspond to the following description:
   (a) Four esters with the formula C₄H₈O₂.
   (b) Two aldehydes with the formula C₄H₆O.
   (c) Three ketones with the formula C₅H₁₀O.

2. Write structural formula for each of the following:
   (a) Three primary alcohols and one tertiary alcohol with formula C₄H₈O
   (b) A secondary alcohol with formula C₃H₆O

3. Write the structure of a tautomeric isomer for each of the following compounds:
   (a) [Structure image]
   (b) [Structure image]
   (c) [Structure image]

4. Assign E and Z configuration to the following alkenes:
   (a) Hexa-1,4-diene
   (b) Stilbene
   (c) Stilbene

5. 'Enol' percentage, I > II
   (I) [Structure image]
   (II) [Structure image]
Enol form of I is more stabilized due to resonance, hence have higher percentage than enol form of II at equilibrium. In enol form there are greater numbers of resonating structures and hydrogen bonding also exists, so enol form is more stable than keto form.

6. Draw structures of all stereoisomers of
(a) 1, 2-dichlorocyclobutane
(b) 1, 3-dichlorocyclobutane

7. In each of the following molecules, indicate the presence of a centre of chirality with an asterisk (*).

8. For each of the following pairs of structures, identify the relation between them. Are they enantiomers, diastereomers, geometrical isomers or same structures?
9. (a) Make structures of 2, 3-dibromobutane and assign R and S configuration.
(b) Draw the enantiomers of 3-bromocyclohexane and give R/S designation for each.

10. \( \text{C}_4\text{H}_8\text{O}_2 \) (A) reacts with Na but does not give colour with neutral \( \text{FeCl}_3 \). (A) by iodoform test is converted into iodoform and sodium salt of dibasic acid (B). (B) can decolourize \( \text{KMnO}_4 \) and gives white ppt. with \( \text{CaCl}_2 \) solution in acetic acid. Identify (A) and (B) write all isomers of A.

11. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly.

12. Explain that \( \alpha \)-methyl acetyl acetone undergoes enolization to a smaller extent than acetyl acetone.

13. Molecular formula \( \text{C}_4\text{H}_8\text{O}_4 \) can have isomers A, B, C and D:
   (a) is dicarboxylic acid giving racemic tartaric acid with alk. \( \text{KMnO}_4 \).
   (b) is dicarboxylic acid giving meso tartaric acid with alk. \( \text{KMnO}_4 \).
   (c) is also dicarboxylic acid giving another monobasic acid on heating.
   (d) is cyclic ester.

14. How many asymmetric carbon atoms are created during the complete reduction of benzyl, \((\text{PhCOCOPh})\) with Li\( \text{AlH}_4 \)? Also write the number of possible stereoisomers of the product.

15. \( \text{C}_4\text{H}_8 \) has 4 isomers, A, B, C and D. A, B, C decolourizes \( \text{Br}_2 \) water but D does not. A gives optically inactive meso form, while B forms optically inactive mixture in equal amounts. Identify A, B, C and D.
ANSWERS TO ASSIGNMENT PROBLEMS

SECTION – A

Multiple Choice Questions

1. (D)  2. (B)  3. (A)  4. (D)  
5. (A)  6. (A)  7. (A)  8. (C)  
9. (D)  10. (B)  11. (A)  12. (B)  
13. (A)  14. (B)  15. (C)  16. (A)  
17. (C)  18. (C)  19. (D)  20. (D)  

Fill in the Blanks

1. functional  2. specific rotation  
3. optical isomerism  4. metamerism  
5. tautomerism  6. five  
7. Two  8. chain  
9. sixteen  10. geometrical, functional  

Short Answer Type Questions

1. 

\[ \text{pentane, isopentane, neopentane} \]

2. Isomer of carboxylic acid, esters, hydroxy aldehyde, hydroxy ketones etc.

3. Due to intramolecular H-bonding in enolic form which reduce the intermolecular association and lowers the boiling point.

4. (i) E  (ii) Z  

5. 

It shows optical isomerism  
In lactic acid number of chiral carbon = 1  
Total number of optical isomers = \( 2^1 = 2 \)

6. The given compound is \( \text{CH}_3-\text{CH} = \text{C} = \text{CH}-\text{CH}_3 \).  
In this compound both \( \pi \) bonds are perpendicular to each other, it will have the following geometry.
Thick bonds represent the bonds coming towards the viewer while the thinner represent the bonds going away from the viewer. Thus, mirror image of this compound is not superimposable.

Thus, compound is optically active and one is (+) isomer and other is (−) isomer. They are not interconvertible because of restricted rotation about a double bond.

7. 2-butene has two dissimilar groups attached to each unsaturated carbon, 2-butyne is linear so it cannot have geometrical isomer.

8. On heating, cis form will give anhydride at comparatively lower temperature.

9. (i) S  (ii) R

10. (a) Geometrical  
     (b) Resonance contributors

**True or False Type Questions**

1. True
2. False, inorganic molecule can also show optical activity.
3. False
4. False, 2 chiral atoms.
5. False, e.g. allenes.
6. False
7. True
8. True
9. True
10. False, only two but has three configurations (d, l and meso form)

**Subjective Problems**

1. (a) (i) H₃C\[\begin{array}{c}O\end{array}\]CHₑ₃OCH₃  (ii) H₃C\[\begin{array}{c}O\end{array}\]CHₑ₃
ISOMERISM

2. (a) (i) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (ii) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (iii) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (b) (i) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (ii) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]
   (iii) 
   \[
   \begin{array}{c}
   \text{CH}_3 \\
   \text{OH}
   \end{array}
   \]

3. (a) 
   \[
   \begin{array}{c}
   \text{C} \\
   \text{OH}
   \end{array}
   \]
   (c) None

4. (a) E at C₄
   (b) E
   (c) Z

5. 

6. (a) 
   \[
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl}
   \end{array}
   \]
   Same structure
   \[
   \begin{array}{c}
   \text{Cl} \\
   \text{Cl}
   \end{array}
   \]
   enantiomers
7. (a) Achiral

(c) Achiral

(e) 

8. (a) Identical, (b) Same structure, (c) enantiomer, (d) Structural, (e) same structure, (f) geometrical (Z,Z) and (Z,E), (g) geometrical (Z,Z) and (E,E), (h) cis and trans (Z and E) at C₃, (i) diastereomers, (j) diastereomers, (k) diastereomers and (l) enantiomers.

9. (a) 

(b) 

(R) 

(S)

10. A = \[
\begin{align*}
&\text{CH}_3 \\
&\text{CH}_3 \\
&\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

B = \[
\begin{align*}
&\text{Na} \\
&\text{O} \\
&\text{O} \\
&\text{Na}
\end{align*}
\]

\[
\text{CaCl}_2 \xrightarrow{\text{ACOH}} \text{CaC}_2\text{O}_4 \text{ (white ppt.)}
\]

11. The breaking and reforming of C – I bonds occur. This results into two enantiomers, which forms racemic mixture and does not show optical activity due to external compensation.

(Racemic mixture)
12. Enolization (greater due to less strain)

\[ \text{H}_3\text{C} - \text{O} - \text{O} \text{CH}_3 \leftrightarrow \text{H}_3\text{C} - \text{C} = \text{C} = \text{CH}_3 \]

Enolization (smaller due to higher strain)

\[ \text{H}_3\text{C} - \text{O} - \text{O} \text{CH}_3 \leftrightarrow \text{H}_3\text{C} - \text{C} = \text{C} = \text{CH}_3 \]

13. (a) Fumaric acid

\[ \text{HOOC} - \text{CH} = \text{CH} - \text{COOH} \]

(b) Maleic acid

\[ \text{HOOC} - \text{CH} = \text{CH} - \text{COOH} \]

(c) Methylene malonic acid

\[ \text{H}_2\text{C} = \text{CH} - \text{COOH} \]

(d) Cyclic ester of oxalic acid and Glycol

\[ \text{HOOC} - \text{O} - \text{O} - \text{O} - \text{O} - \text{O} - \text{HCOOH} \]

14. The reaction is

\[ \text{Ph} - \text{O} - \text{O} \text{Ph} \xrightarrow{\text{LiAlH}_4} \text{Ph} - \text{OH} \]

Two asymmetric carbons are created on complete reduction of benzil. Therefore, these stereoisomers are meso, d and l.

15. A = \text{CH}_3 - \text{CH} = \text{CH} = \text{CH}_2

B and C = \text{cis} and \text{trans} forms of \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3

D = cyclobutane