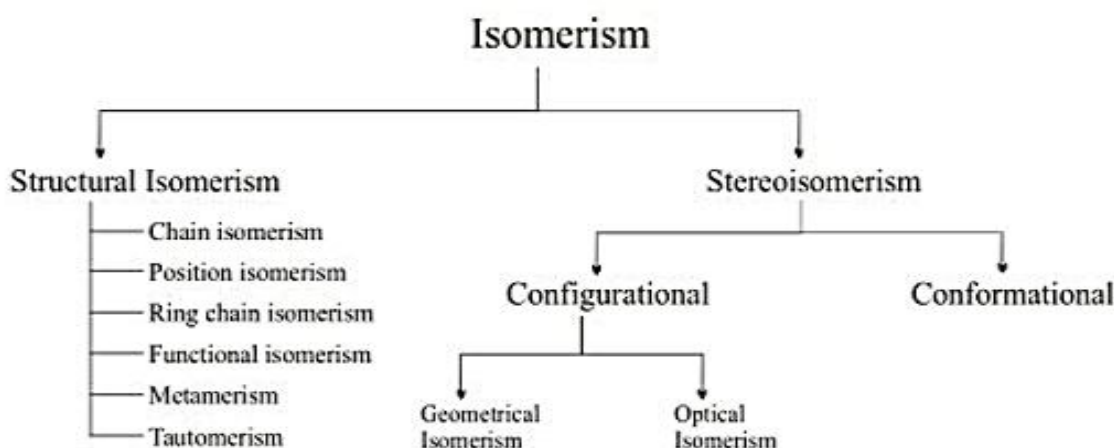


ISOMERISM

INTRODUCTION

- (i) The compound which have the same molecular formula but differ in physical and chemical properties are called as Isomer and the phenomenon is called Isomerism.
- (ii) The term 'isomer' was given by Berzellius.
- (iii) The isomer was derived from Greek word meaning 'equal or like part' (isos= equal; meros = parts)

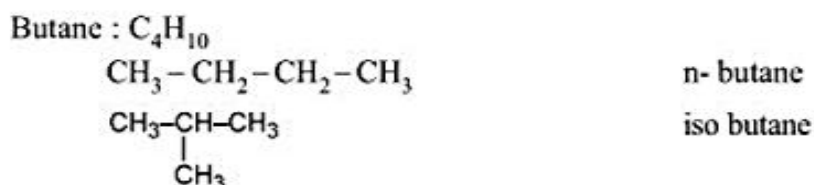


(I) STRUCTURAL ISOMERISM / CONSTITUTIONAL ISOMERISM

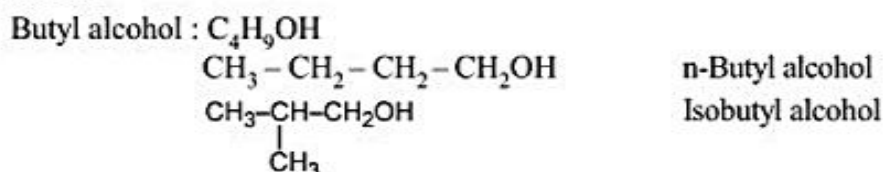
Structural isomers possess the same molecular formula but different connectivity of atoms. The term constitutional isomerism is a more modern term of structural isomerism. It is sub-classified into following types.

(i) Chain Isomerism :

The different arrangement of carbon atoms gives rise to chain isomerism. Chain isomers possess different lengths of carbon chains (straight or branched). Such isomerism is shown by each and every family of organic compounds.



n-butane has the chain of four carbon while isobutane has three in carbon chain. Hence they are chain isomers.

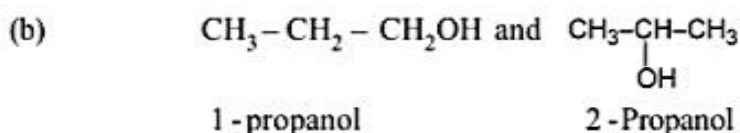
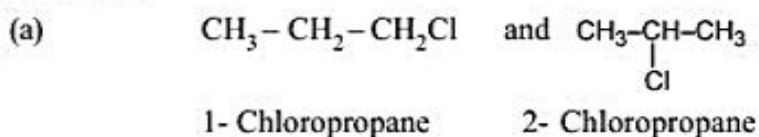


These two butyl alcohols are chain isomers.

To show position isomerism following conditions must be followed

- (i) The same molecular formula
- (ii) The same length of carbon chain
- (iii) The same functional group.

Example :

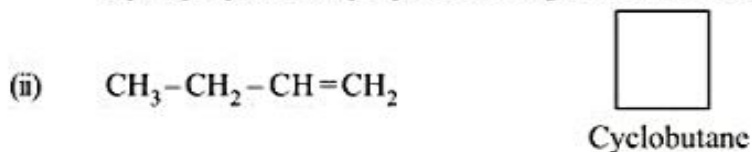


(iii) **Ring chain isomerism**

For example :



Cyclopropane and propene are ring chain isomers.

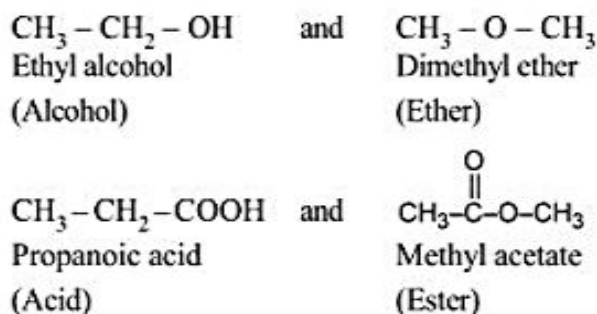


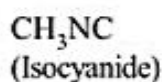
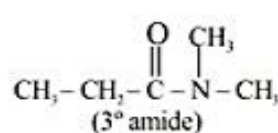
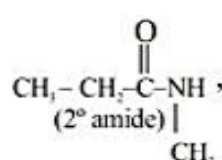
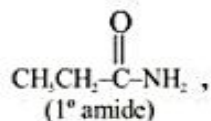
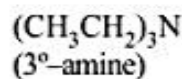
Cyclobutane is the ring-chain isomer of 1-butene.

Note: *Acyclic Alkanes do not exhibit ring-chain isomerism.*

(iv) Functional group isomerism

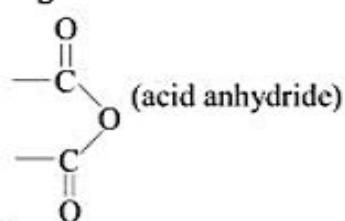
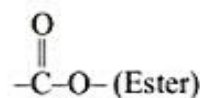
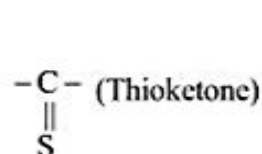
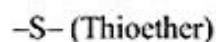
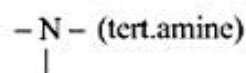
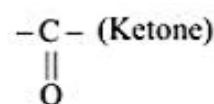
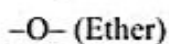
Compounds with the same molecular formula but differing in the type of functional group they possess are classed as functional isomers and isomerism between them is known as functional isomerism. For example:



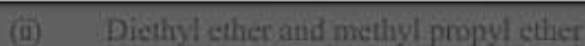
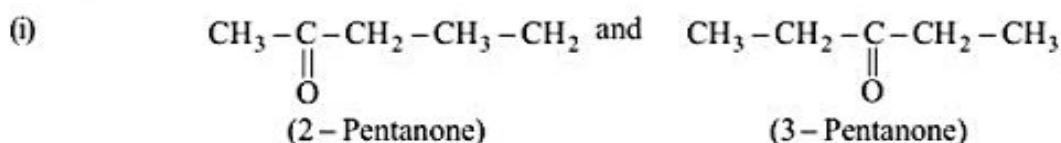


(v) Metamers :

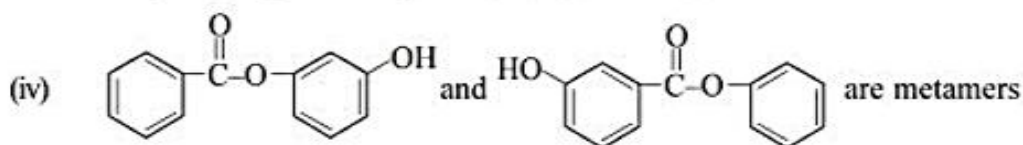
Some example of Polyvalent functional groups.



Example :-



- (iii) Diethyl amine and methyl propylamine
 $\text{CH}_3\text{CH}_2 - \text{NH} - \text{CH}_2\text{CH}_3$ (Diethyl amine);
 $\text{CH}_3\text{CH}_2\text{CH}_2 - \text{NH} - \text{CH}_3$ (Methyl propyl amine)



(vi) **Tautomerism :**

- Tautomerism is a special type of functional group isomerism which arises due to the transfer of hydrogen atom as proton from a polyvalent atom to other polyvalent atom.
- Such isomers are directly and readily inter convertible under ordinary conditions, and the isomers are called tautomers.
- Tautomers exist in dynamic equilibrium.
- The other names of tautomerism are 'desmotropism' or 'prototropy'.
- Tautomerism is thus the property shown by certain compounds exhibiting different properties, as if they possess different structures and these constitutional isomers are called tautomers.
- If the hydrogen atom oscillates between two polyvalent atoms linked together, the system is called as *Diad*.



- (vii) Hydrogen atom oscillates in between first and third atoms in a chain, the system is called as triad.



(a) **Keto - Enol Tautomerism -**

- When the tautomers exist in the two forms keto & enol then, such type of tautomerism is called keto-Enol tautomerism'.
- It was discovered by the scientist 'Knorr' in 1911 in acetoacetic ester.
- The Keto means the compound has a Keto group $> \text{C} = \text{O}$, and the enol form has both double bond and OH (hydroxy) group Joined to the same carbon.

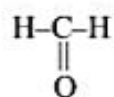


Conditions for tautomerism

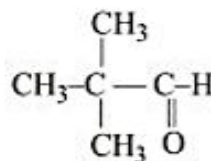
- Presence of groups like $> \text{C} = \text{O}$, $-\text{N} = \text{O}$, $> \text{C} = \text{N}-$ & $\alpha\text{-H}$ with respect to these groups.
- In order for conversion of a keto form to its enol form it must have an α -hydrogen (i.e., hydrogen attached to the carbon adjacent to the carbonyl group). Thus benzaldehyde, m-chlorobenzaldehyde (in general, aromatic aldehydes) formaldehyde, trimethylacetaldehyde do not exist as their enol forms.



Benzaldehyde m-Chlorobenzaldehyde



Methanal



Trimethyl-acetaldehyde

- (iii) Keto enol tautomerism can occur both in acidic and basic medium.

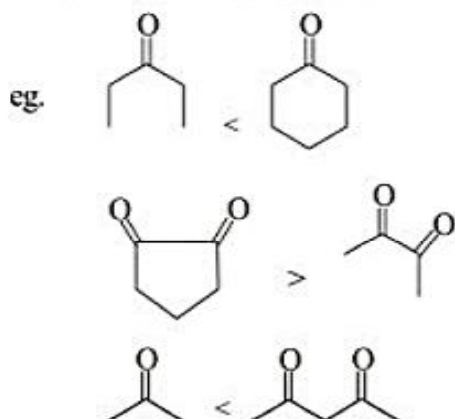
Example of Keto enol tautomerism :-

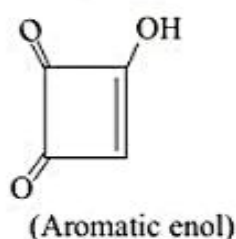
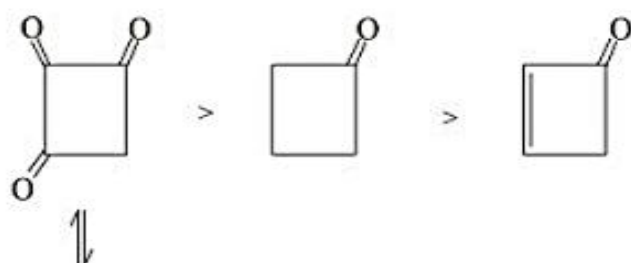
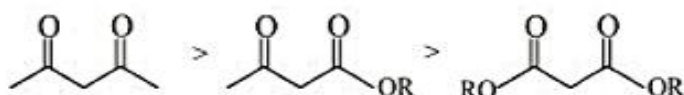
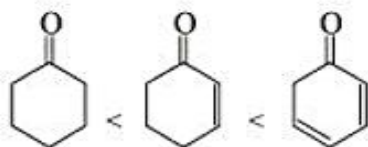
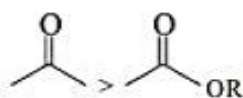


Enol – Contents : It is the % amount of enol in keto enol system usually keto content is generally more than Enol. contents.

Enol contents: \propto Stability of enol
 \propto aromatic in enol
 \propto conjugation in enol
 \propto Hydrogen bonding in enol
 \propto Acid strength of α -H of keto form
 \propto Presence of electron withdrawing group

Normally Enol content of cyclic system is greater than corresponding a cyclic system as insertion of π -bond is easier in cyclic system.





MCQ

Q.1 $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Cl}$ and $\text{CH}_3\text{-CH(Cl)-CH}_3$ shows which type isomerism

(A) Chain isomers
(C) Functional isomers

(B) Position isomers
(D) Metamers

Q.2 $\text{CH}_3\text{CH}_2\text{CH}_2\text{-OH}$ and $\text{CH}_3\text{-CH(OH)-CH}_3$ shows which type of isomerism

(A) Chain isomers (B) Position isomers (C) Functional isomers (D) Metamers

Q.3 $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{-O-CH}_3$ express which type of isomerism

(A) Functional isomers (B) Chain isomers (C) Metamers (D) Position isomers

Q.4 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ and $\text{CH}_3\text{-CH(CH}_3\text{)-CH}_3$ shows which type of isomerism



(A) Chain isomer (B) Position isomer (C) Functional isomer (D) Metamers

Q.5 Alcohol and ether express which type of Isomerism

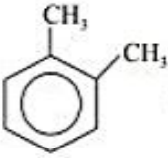

(A) Position isomers (B) Chain isomers (C) Metamers (D) Functional isomers

Q.6 How many position isomers are shown by $\text{CH}_3\text{-CH=CH-CH}_3$

(A) 2 (B) 3 (C) 4 (D) 5

Q.7 How many position isomers are shown by $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$


(A) 5 (B) 3 (C) 4 (D) 2

Q.8  and  shows which type of isomerism.

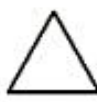
(A) Position isomers (B) Chain isomers (C) Functional isomers (D) Metamers

Q.9 How many Ring chain isomers are possible for C_3H_6 .

(A) 2 (B) 3 (C) 4 (D) 5

Q.10 $\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$ and  express which type isomerism.

(A) Ring chain isomers (B) Metamers (C) Position isomers (D) Chain isomers

Q.11 $\text{CH}_3\text{-CH=CH}_2$ and  express which type of isomerism

(A) Ring chain isomers (B) Chain isomer (C) Position isomers (D) Metamers

Q.12 $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{NHCH}_3$ and $\text{CH}_3\text{-N(CH}_3\text{)-CH}_3$ express which of Isomerism



(A) Functional Isomers (B) Chain Isomers (C) Metamers (D) Position isomers

Q.13 $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{-C(=O)-O-CH}_3$ express which of isomerism

(A) Position isomers (B) Chain Isomers (C) Metamers (D) Functional Isomers

Q.14 Alkynes and Alkadienes express which type of isomerism

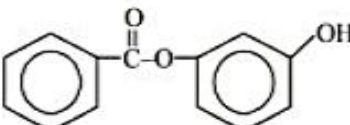
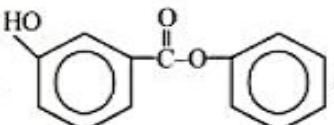
(A) Position isomers (B) Chain isomers (C) Metamers (D) Functional isomers

Q.15 The type of isomerism observed in urea and $\text{NH}_2\text{-CH=NOH}$

(A) Chain isomers (B) Position isomers
(C) Geometrical isomers (D) Functional isomers

- Q.16 $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{CH}_3$ and $\text{CH}_3\text{-O-CH}_2\text{CH}_2\text{CH}_3$ express which type of Isomerism
 (A) Metamers (B) Functional isomers (C) Tautomerism (D) Functional isomers

- Q.17 $\text{CH}_3\text{-}\overset{\text{CH}_3}{\underset{\text{O}}{\parallel}}{\text{C}}\text{-CHCH}_3$ and $\overset{\text{CH}_3}{\text{CH}_2}\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_2\text{CH}_3$ express which type isomerism
 (A) Metamers (B) Tautomers (C) Functional isomers (D) Position isomers

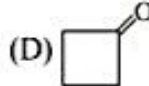
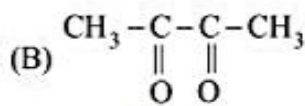
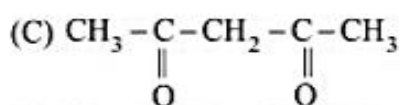
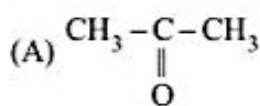
- Q.18  and  express which type of isomers
 (A) Metamers (B) Tautomers (C) Functional Isomers (D) Chain Isomers

- Q.19 Diethyl amine and methyl propyl amine express which type of Isomers.
 (A) Functional isomers (B) Position isomers (C) Metamers (D) Chain isomers
- Q.20 The molecules which exhibit metamerism are
 (A) $\text{C}_4\text{H}_{10}\text{O}$ (ethers) (B) C_4H_8 (alkene) (C) $\text{C}_5\text{H}_{10}\text{O}$ (ketone) (D) $\text{C}_4\text{H}_{11}\text{N}$ (amine)

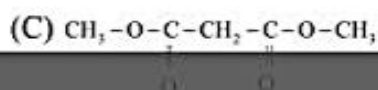
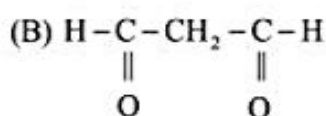
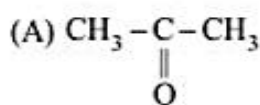
- Q.21 Which molecule does not express Tautomerism
 (A) $(\text{CH}_3)_3\text{CCHO}$ (B) CH_3CHO (C) $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$ (D) $\text{CH}_3\text{-CH}_2\text{CHO}$

- Q.22 Which form is more stable for $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}{\text{C}}\text{-CH}_3$
 (A) enol-form (B) keto form
 (C) both form are equally stable (D) keto and enol form does not exist

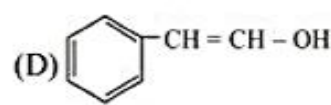
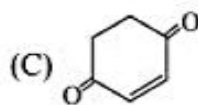
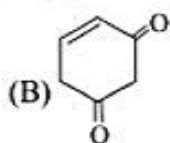
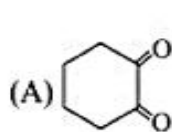
- Q.23 Which molecule has higher enol content



- Q.24 Which molecule has higher keto-contents



Q.25 Which of the following compounds can exhibit tautomerism



Q.26 The number of structural isomer shown by C_6H_{14}

(A) 6

(B) 5

(C) 6

(D) 8

Q.27 How many chain isomers are shown by C_4H_{10}

(A) 3

(B) 2

(C) 4

(D) 5

Q.28 How many chain isomers are shown by C_4H_9OH

(A) 2

(B) 3

(C) 4

(D) 5

Q.29 Number of structural of isomers shown by C_6H_{14} :

(A) 4

(B) 5

(C) 8

(D) 6

ANSWERS

Q.1	B	Q.2	B	Q.3	A	Q.4	A	Q.5	D	Q.6	A
Q.7	D	Q.8	A	Q.9	A	Q.10	A	Q.11	A	Q.12	A
Q.13	D	Q.14	D	Q.15	D	Q.16	A	Q.17	A	Q.18	A
Q.19	C	Q.20	A, C, D	Q.21	A	Q.22	B	Q.23	C	Q.24	B
Q.25	A, B, C, D	Q.26	B	Q.27	B	Q.28	A	Q.29	B		

(II) STEREOISOMERISM / SPACE ISOMERISM

Compounds having same molecular formula, same connectivity and structural formula but differ due to spatial arrangement of group or atom are said to be stereo isomers and phenomenon is termed as stereoisomerism.

It is divided into two parts : (1) Configuration isomerism (2) Conformational isomerism

1. **Configuration isomerism** : Stereoisomers which are not interconvertible at room temperature are known as configurational isomers

Configurational isomerism is further divided into two parts

(A) Geometrical isomerism

(B) Optical isomerism

GEOMETRICAL ISOMERISM

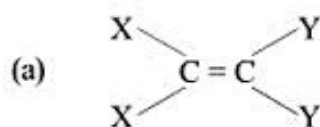
It is type of configurational isomerism which arises due to restricted rotation of atoms or groups around a double bonded system or cyclic system.

Conditions

(i) Restricted rotation

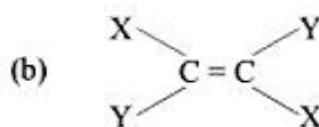
(ii) Different functional groups or atoms which is showing geometrical isomerism.

For example:



Not showing G.I.

(Because same group X and Y present on each carbon)

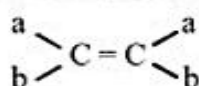


Showing G.I.

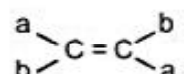
Geometrical isomers are named as

(a) cis- trans isomers (b) E and Z isomers (c) Syn-anti isomers

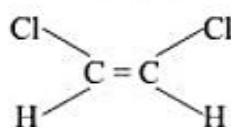
- (a) *Cis- trans isomers.* When like atoms or groups attached at the same side of double bonded C-atom-called as cis. isomers. When like atoms or groups are on the opposite sides of doubly bonded carbon, are called. trans isomers.



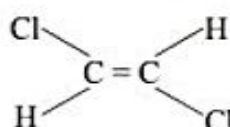
cis isomers



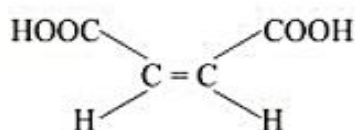
trans isomers



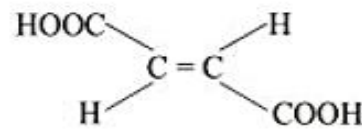
cis isomer



trans isomer



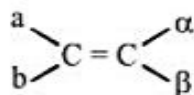
Maleic acid
(cis isomer)



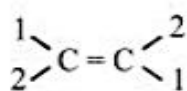
Fumaric acid
(trans isomer)

- (b) E and Z isomers,

- (i) The above system is used for derivatives of alkenes in which all the four substituents should be different

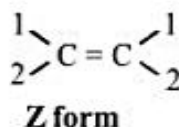


- (ii) Following a set of rules (Cahn - Ingold-Prelog rules) the substituents on a double bond are assigned priorities.
- (iii) The double bond is assigned the configuration E (From entgegen, the german word for opposite) if the two groups of higher priority are on the opposite sides of the double bond.



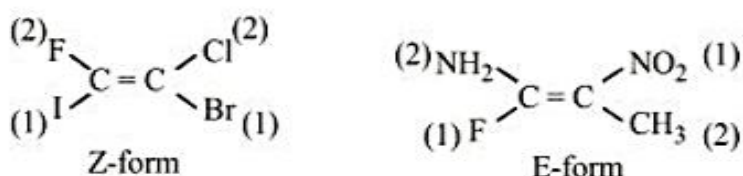
E form

- (iv) On the other hand, the double bond is assigned the configuration Z (From zusammen, the German word for together) if the two groups of higher priority are on the same side of the double bond.

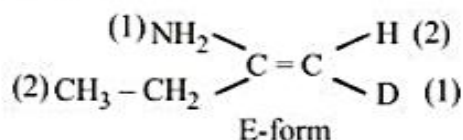


Priority rule : cahn, ingold & prelog proposed a sequence rule.

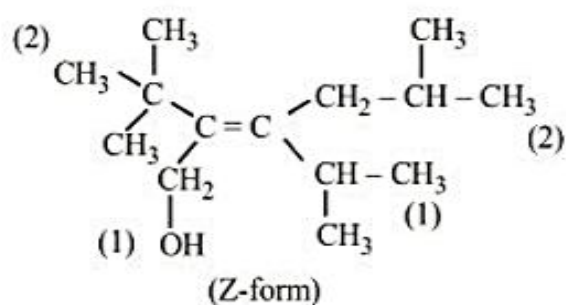
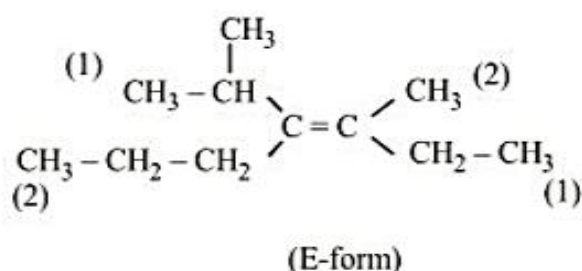
Rule-1 When atom or group of atom which are directly attach to the stereogenic centre have higher atomic number will have higher priority. Example



Rule-2 When the atomic number will be same, priority assigned on basis of atomic weight.



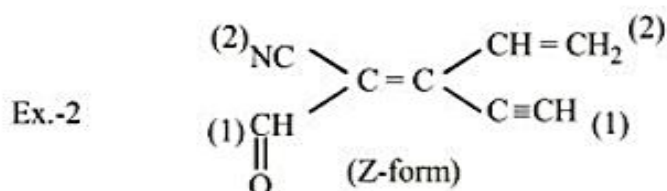
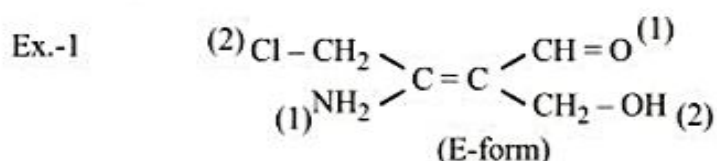
Rule-3 When both atomic number and atomic weight are same then priority will be decided by the next joining atom.



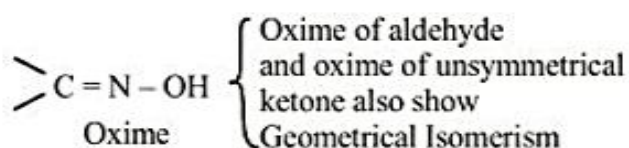
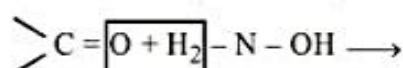
Rule-4 If multiple bonded group attach to the double bonded carbon, then they are considered in following manner.



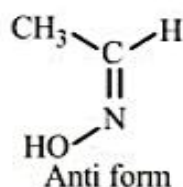
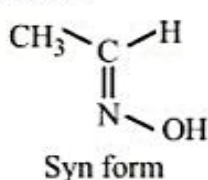
For example :



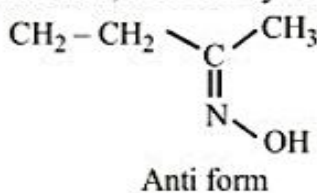
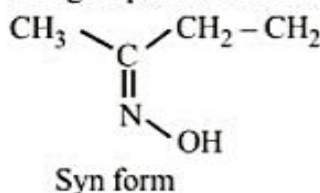
- (c) **Syn-anti isomers** This type of isomerism exhibit by oximes and Azo compound. Oximes are the compounds formed by the reactions of aldehydes or ketones with hydroxyl amine. The products obtained have all the necessary conditions for Geometrical isomerism. i.e. restricted rotation they can be represented by the general formula



Aldoximes

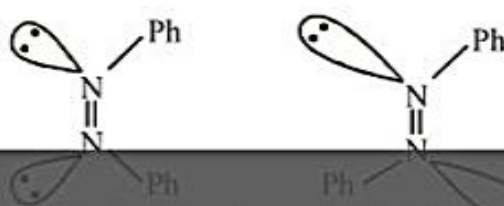


When -OH group and H atom is same side, then it is syn form otherwise anti form



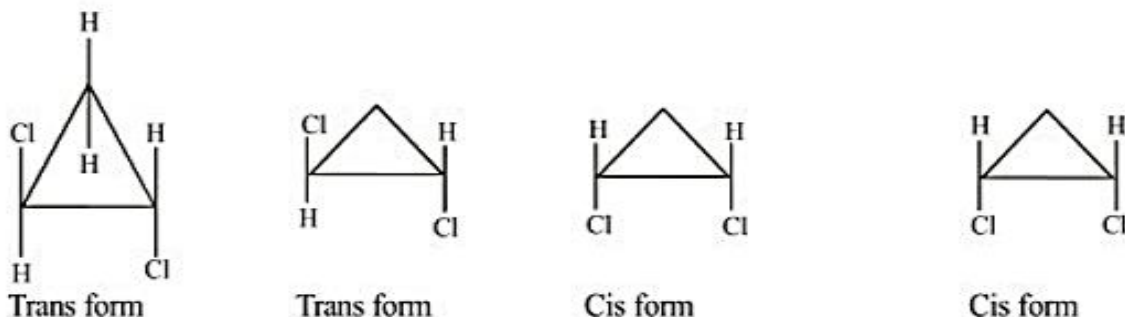
In unsymmetrical Ketoxime, if -OH and the alphabetically alkyl present on the same side of double bond, then it is called as syn form and other isomer is anti form

Geometrical Isomerism in Azo compound :



Geometrical Isomerism in cyclo alkane :

In cyclic compound the rotation about C – C single bond is not free because of the rigidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical Isomerism. The substituents on the same side are cis-isomers while the substituents on opposite sides represent trans-isomers.



No. of geometrical isomers in polyenes :

Case-1 In case of unsymmetric alkene. If $R_1 \neq R_2$ ($R_1 - CH = CH - CH = CH - R_2$)

$$\text{no. of G.I.} = 2^n$$

$n \rightarrow$ number of double bond showing geometrical isomerism

Ex.- $CH_3 - CH = CH - CH = CH - CH_2 - CH_3$

$$N = 2^n = 2^2 = 4.$$

Case-2 In case of symmetric alkene. If $R_1 = R_2$ ($R_1 - CH = CH - CH = CH - R_2$)

$$\text{no. of G.I.} = 2^{n-1} + 2^{p-1}$$

if n is even no. then, $P = \frac{n}{2}$

if n is odd no. then, $P = \frac{n+1}{2}$

Ex.- $CH_3 - CH = CH - CH = CH - CH = CH - CH_3$

$$\text{here } \begin{cases} n = 3 \\ P = \frac{3+1}{2} \end{cases}$$

$$N = 2^2 + 2^1 = 6$$

MCQ

Q.1 Which of the following compounds exhibits geometrical isomers -

- (A) C_2H_5Br (B) $(CH_2)(COOH)_2$ (C) CH_3CHO (D) $(CH_2)_2(COOH)_2$

Q.2 The number of geometrical isomers of

$CH_3CH = CH - CH = CH - CH = CHCl$ is -

- (A) 2 (B) 4 (C) 6 (D) 8

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- Q.3 Maleic and fumaric acids are:
 (A) Geometrical isomer (B) Tautomers (C) Optical isomers (D) Metamers
- Q.4 Which of the following can exhibit cis-trans isomerism –
 (A) $\text{HC} = \text{CH}$ (B) $\text{ClCH} = \text{CHCl}$ (C) $\text{CH}_3\text{CHClCOOH}$ (D) $\text{ClCH}_2 - \text{CH}_2\text{Cl}$
- Q.5 Geometrical isomerism is possible in case of:
 (A) Pent-2-ene (B) Butane (C) 2-Butene (D) Ethene
- Q.6 Give the E-Z designation of the following compound -
- $$\begin{array}{c} \text{C}_6\text{H}_5 \quad \quad \text{I} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{C} = \text{C} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{CH}_3\text{NH} \quad \quad \text{Br} \end{array}$$
- (A) E (B) Z (C) E-Z (D) E-E
- Q.7 Which of the following compounds will exhibit trans (geometrical) isomerism?
 (A) 2-butene (B) 2-butyne (C) 2-butanol (D) butanal

ANSWERS

Q.1	B	Q.2	D	Q.3	A	Q.4	B	Q.5	A, C	Q.6	A
Q.7	A										

OPTICAL ISOMERISM

Configurational isomers which differ in their optical activity.

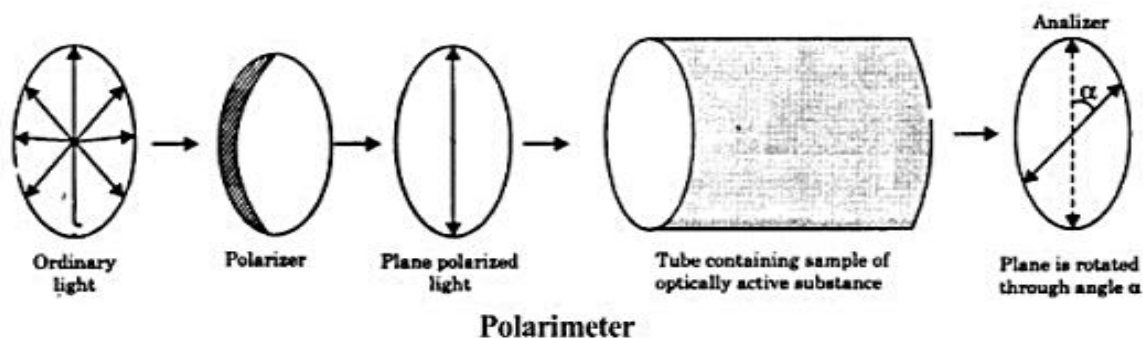
Optical Activity : The ability of optically active substances to cause rotation in the plane of oscillations of polarized light is called optical activity. The substances which do not have any interaction with plane polarized light are called optically inactive substances.

Following experiment was conducted to determine the optical activity of a substance

- Under ordinary conditions, the light waves oscillate in infinite number of planes passing through the line of propagation at right angle.
- Plane polarized light is a light whose vibrations take place in only one of these possible planes.
- Ordinary light can be turned into plane polarized light by passing it through Nicol prism (made up of calcite, a special crystalline form of CaCO_3)
- When plane polarize light is passed through the liquid or dissolved state of such substances.
- The plane of oscillation gets rotated through some angle towards left or right of the original plane of oscillations. The substances which rotate the plane of polarized light are called optically active substances.
- The substances which rotate the plane of polarized light in the clockwise direction, i.e., towards right are called dextrorotatory substances (Latin : dextro means right). This is indicated by putting a better d or (+) sign before the name of the substances.
- The substances which rotate the plane of polarized light in the anticlockwise direction, i.e., towards left are called leavorotatory substances (Latin : laevus means left). This is indicated by putting letter 'l' or (-) sign before the name of the substance.

(h) The angle through which the plane of polarized light is rotated is represented by α and is called observed angle of rotation.

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(i) The amount of rotation caused by an optical active compound depends on various factors-

- (a) Wavelength of light beam
- (b) Temperature
- (c) Density or concentration
- (d) Length of the solution through which light beam has been passed.

Specific Rotation : The specific rotation of optically active compound can be defined as the amount of optical rotation observed when plane polarised light is passed through a solution of 1 gm per ml concentration solution in a 1 dm long tube.

$$\text{Specific rotation} = [\alpha]_D^t = \frac{\alpha}{l \times C}$$

Cause of optical activity:-

- (a) In order to exhibit optical activity, an object or molecule must be chiral.
- (b) Any molecule or object is said to be chiral if does not have any element of symmetry i.e. a plane of symmetry or a centre of symmetry.

Plane of symmetry:- A 'Plane' of symmetry' is a plane which divides an object in such a way that the part of it on one side of the plane is the mirror image of that on the other side for eg. a ball is symmetrical while a hand is asymmetric



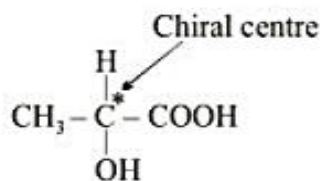
A chiral molecule or object is non-super imposable on its mirror images.

- (c) Hence, chiral objects or molecules are also called dissymmetric objects or molecules the word chiral in fact is derived from the Greek word cheir, meaning hand.

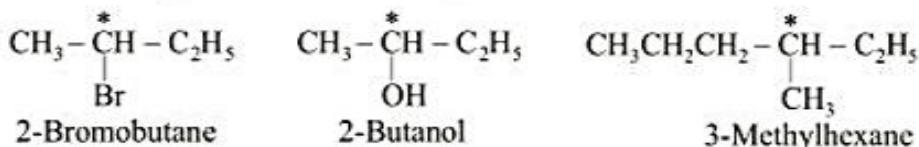
Chiral centre:-

(i) A carbon atom bonded to four different atoms / groups in the molecule is called Chiral centre.

(ii) The chiral centre in the molecule is represented by asterisk (*). For example, the second carbon in lactic acid is chiral centre because it is bonded to four different groups (– H, – CH₃, – OH and – COOH).

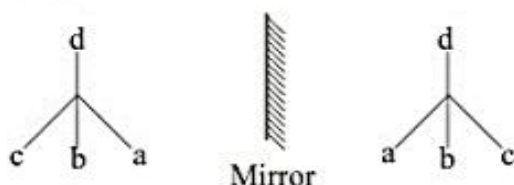


(iii) Some more examples of molecules having one chiral centre are



- (d) Compounds which are mirror images of each other and are not superimposable are termed *enantiomers* and the phenomenon is described as *enantiomerism*.

Enantiomers : Enantiomers are molecules which are mirror images of each other i.e. they should be non-superimposable.



Characteristics of Enantiomers :

Some of the important characteristics of enantiomers are as given below :

- (i) Enantiomers have identical physical properties such as melting point, boiling point, density, refractive index etc.
- (ii) Enantiomers are optically active substances. They rotate the plane of polarized light in opposite directions but to the equal extent.
- (iii) Enantiomers have identical chemical properties. This means that they form same products as a result of chemical combination. However, their reactivity, i.e., rates of reaction with other optically active substances are different.
- (iv) Enantiomers have different biological properties. For example (+) -sugar plays significant role in animal metabolism. On the other (–) -sugar does not play any role in metabolism.

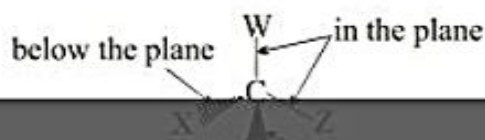
Representation of Enantiomers :

(a) Wedge and dash formulae

(b) Fischer Projection Formulae

(a) Wedge and dash formulae :

- (i) In this method, the four groups bonded to the chiral centre are represented by different means.
- (ii) A normal line represents the bond lying in the plane of paper.
- (iii) A broken line represents the bond going behind the plane of the paper and a solid wedge represents the bond projected out towards the viewer.



(b) Fischer Projection Formulae

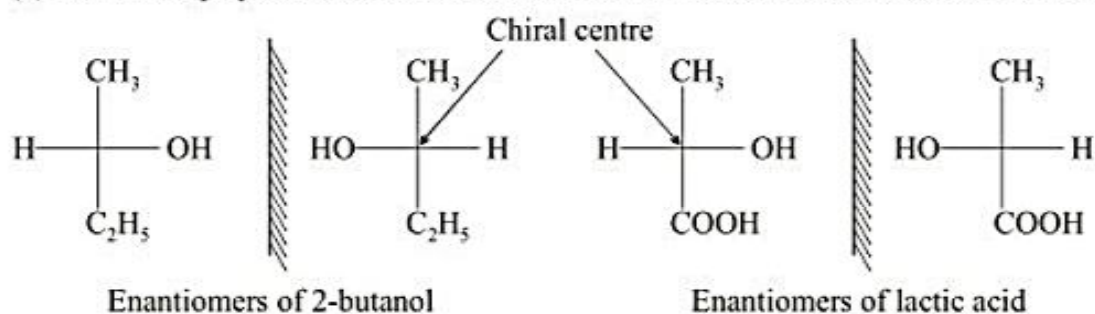
(i) Emily Fischer devised a most simple and convenient method to represent the three dimensional arrangement of groups bonded to chiral centre.

(ii) He used the point of intersection of two perpendicular lines to represent the chiral centre.

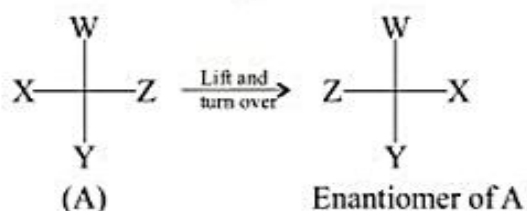
(iii) Horizontal lines represent the bonds projected out of the plane of the paper towards viewer.

(iv) Vertical lines on the other hand, represented the bonds projected back from the plane of the paper away from the viewer.

(v) The Fischer projection formulae of enantiomers of 2-butanol and lactic acid are as under

**Important Points About Fischer Projection Formula :**

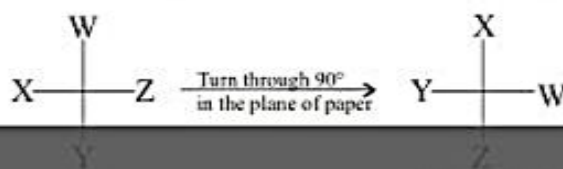
- (1) Fischer projection of a stereoisomer must not be lifted from the plane of the paper and turned over. Such an operation would result into an arrangement which is enantiomer of the original stereoisomer.



- (2) Fischer's projection can be rotated in the plane of the paper about the chiral centre through 180° or its whole number multiple. Such an operation produces the same arrangement



- (3) Fischer projection should not be turned in the plane of the paper through angle of 90° about the chiral centre. Such an operation also produces enantiomer of the original compound.

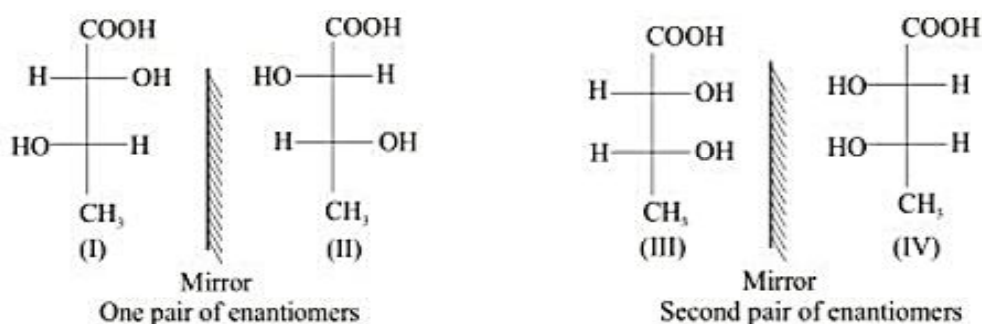


- (4) Keeping one group as steady, the other groups in the Fischer projection can be rotated clockwise or anticlockwise simultaneously. Such operation would give same arrangement as the original.



Diastereomers :

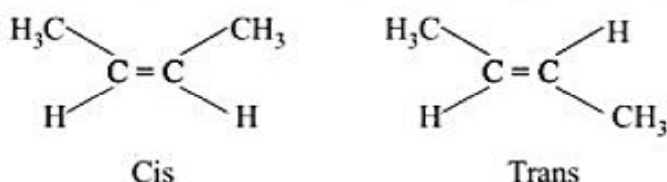
The stereoisomers which are non-superimposable and do not bear mirror image relationship are called diastereomers. For Example, a compound having two asymmetric carbon atoms can have four stereoisomers as shown below in the case of tartaric acid :



(I) is mirror image of (II); similarly (III) and (IV) are mirror images of each other. Thus, the four isomers are two pairs of enantiomers. Now compare (I) with (III); they are neither superimposable nor they are mirror images. They are called *diastereomers*. (I) and (IV) are also diastereomers, as are (II) and (III) and (II) and (IV).

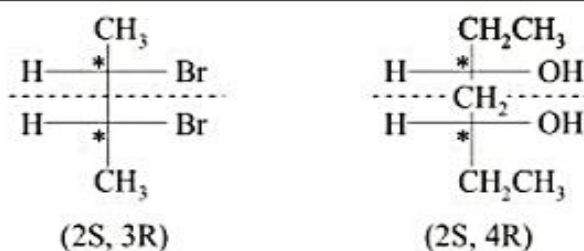
Characteristics of Diastereomers are :

- (i) They show similar but not identical chemical properties. The rates of reactions are different.
- (ii) They have different physical properties, such as melting points, boiling points, densities, solubilities, refractive indices, etc.
- (iii) They can be easily separated through fractional crystallization, fractional distillation, chromatography, etc.
- (iv) Diastereomers are also encountered in the case of geometrical isomers :



MESO COMPOUND

- (a) The compounds containing two or more chiral centres but possessing achiral molecular structure because of having plane of symmetry, are called meso compounds.

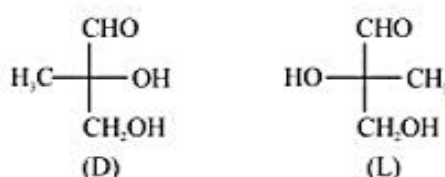


Meso Compound
Plane of symmetry is represented by dotted line

- (b) Meso compounds do not rotate the plane of polarized light in any direction, i.e., they are **optically inactive**.
- (c) This is because of achiral nature of their molecules. Because of the present of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half.
- (d) This cancellation of rotation within the molecule is referred to as **internal compensation**.
- (e) In short, the meso compounds are optically inactive due to internal compensation.

CONFIGURATION

- (i) Three dimensional arrangement of groups about the chiral centre is called configuration
- (ii) There are two methods for assigning configuration to a molecule :
 - (a) Relative method
 - (b) Absolute method.
- (1) **Relative method of configuration (D, L System) :**
 - (a) It uses D-Glyceraldehyde and L-Glyceraldehyde as the basis for the configuration determination.
 - (b) The stereochemical descriptor D refers to the arrangement in which –OH group attached to the chiral centre is on the right side of Fischer projection, whereas descriptor L refers to arrangement in which –OH group is on the left side of the Fischer projection of glyceraldehyde.



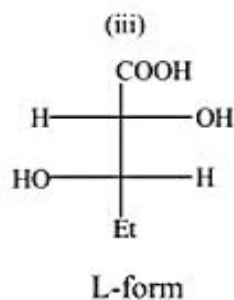
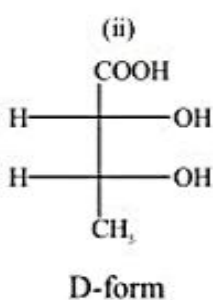
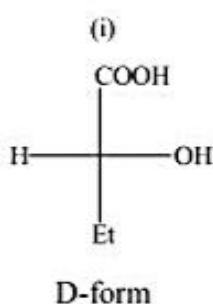
- (d) This method was found suitable for the study of optically active sugars as the sugars are defined as *poly hydroxy aldehydes and ketones*.
- (e) Glyceraldehyde also contains hydroxy and aldehyde groups but this method cannot be used for those molecules which do not possess hydroxy aldehyde groups like CFCl BrI.
- (f) If two or more than two –OH groups are present then D, L configuration is decided on basis of –OH group of lowest chiral in the Golden rule following fischer projection

Golden Rule

usually, the Fischer projection is drawn, so that the longest carbon chain in the molecule is vertical with the highly oxidised function at the top.

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Examples:



R-S system (Absolute configuration)

R → Rectus (Right)

S → Sinister (Left)

R-S nomenclature is assigned as follow :

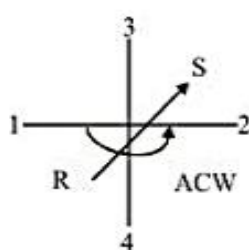
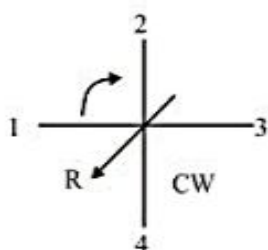
Step-I :- By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

Step-II :- If atom/group of minimum priority present on the vertical line, then

Movement of eyes in clockwise direction = R

Movement of eyes in anticlockwise = S

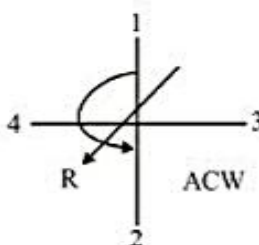
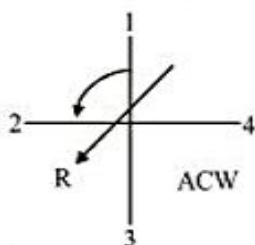
Movement of eyes taken from 1 → 2 → 3 through Low molecular weight group (if needed)



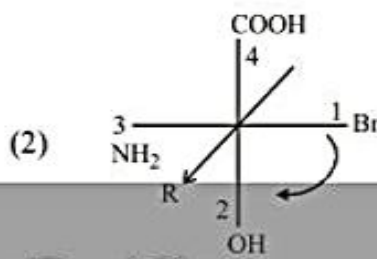
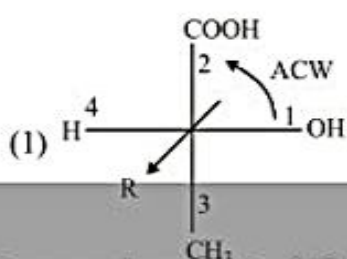
Step III :- If minimum priority group present on the horizontal line, then

clockwise rotation ⇒ S

anticlockwise rotation ⇒ R



Example:-



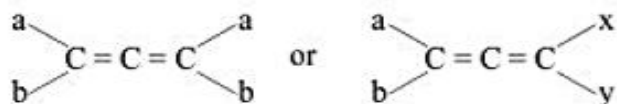
Optical Isomerism in compound containing no chiral carbon atom

Various types of compounds belonging to this group are allenes, alkylidene cycloalkanes, spiro compounds (spiranes) and properly substituted biphenyls.

- (i) **Allenes** These are the organic compounds of the following general formula.

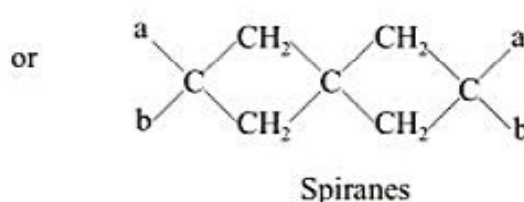
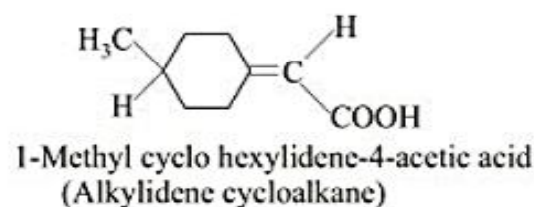


Allenes containing even number of double bonds exhibit optical isomerism provided the two groups attached to each terminal carbon atom are

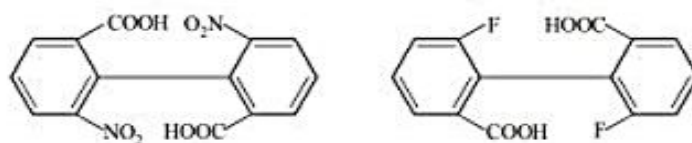


- (ii) **Alkylidene, cycloalkanes and spiro compounds :**

When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spiranes.



- (iii) **Biphenyls :** Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other.



Number of optical isomers :

Case - 1 When the molecule is unsymmetrical. (It cannot be divided into two halves)

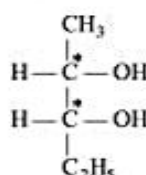
Number of *d* and *l* isomers = 2^n

Number of meso form = 0

Total number of optical isomers = 2^n

Where *n* is the number of chiral carbon atoms.

For eg. 2, 3 - Pentane diol



d and *l* isomers = $2^2 = 4$

Case - 2 When the molecule is unsymmetrical, number of chiral carbon = even number

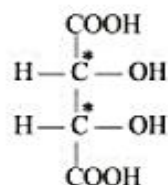
Number of *d* and *l* forms = $2^{(n-1)}$

Number of meso form = $2^{(n/2-1)}$

Total number = addition of the above

$$= 2^{n-1} + 2^{\frac{n}{2}-1}$$

For eg.: Tartaric acid



Number of d and l forms = $2^{(n/2 - 1)} = 2$

Number of meso form = $2^{(2/2 - 1)} = 2^0 = 1$

Total optical isomers = 3

- Case- 3.** When the molecule is symmetrical,
 number of d and l form = $2^{(n - 1)} - 2^{(n/2 - 1/2)}$
 Number of meso form = $2^{(n/2 - 1/2)}$
 Total number of isomers = 2^{n-1}

RACEMIC MIXTURE

- An equimolecular mixture of a pair of enantiomers is called racemic mixture or racemic modification.
- A racemic mixture is optically inactive. This is because of the fact that in equimolecular mixture of enantiomeric pairs, the rotation caused by the molecules of one enantiomer is cancelled by the rotation caused by the molecules of other enantiomer.
- This type of compensation of optical rotation in a racemic mixture is referred to as **external compensation**. Thus, racemic mixture becomes optically inactive because of external compensation.
- Representation of Racemic mixture : The racemic mixture of a particular sample is indicated by using the prefix (d, l) or (\pm). For example, racemic mixture of lactic acid is represented as (\pm) lactic acid.

RACEMIZATION

It is a process of conversion of an optically active compound into the racemic modification. Both (+) and (–) forms of the compound are capable of racemizations under the influence of heat, light or chemical reagents.

RESOLUTION

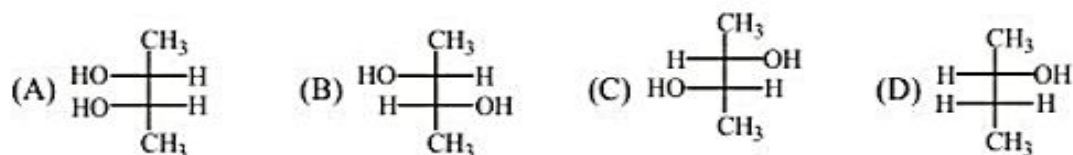
The process of separation of constituent enantiomeric forms from the racemic mixture is known as resolution.

- Chemical method :** This is probably the best method of resolution. The racemic mixture is to combine with another optically active compound and the resulting products (salt - formation) differ in properties, particularly in solubility in various solvents. By fractional crystallization from a suitable solvent, they can be separated.
- Mechanical method :** If the d and l-forms of a substance exist in well defined crystalline forms, the separation can be done by hand picking with the help of magnifying lens and a pair of tweezers.
- Biochemical method :** In this method, the resolution is done by use of micro-organisms, when certain bacteria or moulds are added to a solution of a racemic mixture, they decompose one of the optically active forms more rapidly than the other.

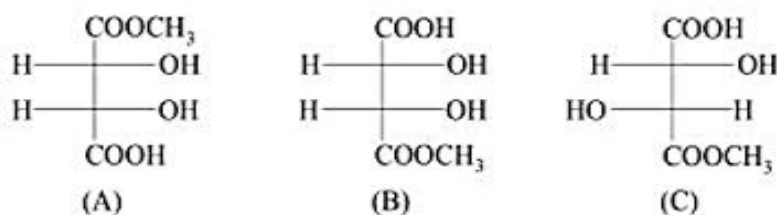
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MCQ

Q.1 A Fischer projection of (2R, 3S)-2,3-butanediol is :-



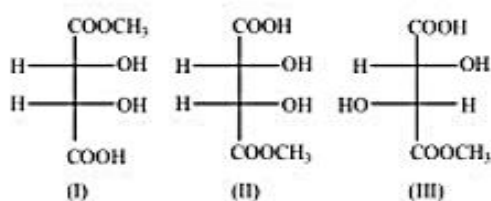
Q.2 The correct statement about the compound A, B and C.



(A) 'A' and 'B' are identical
(C) 'A' and 'C' are enantiomers

(B) 'A' and 'B' are diastereomers
(D) 'A' and 'B' are enantiomers

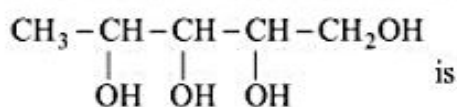
Q.3 The correct statement about the compounds I, II and III



(A) I and II are identical
(C) I and III are enantiomers

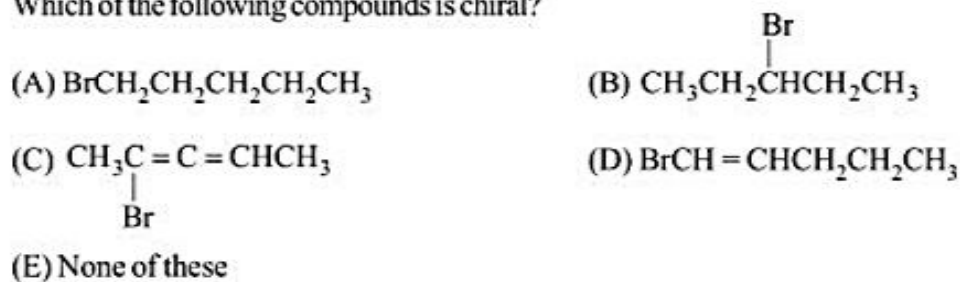
(B) I and II are diastereomers
(D) I and II are enantiomers

Q.4 The number of optically active isomer possible for

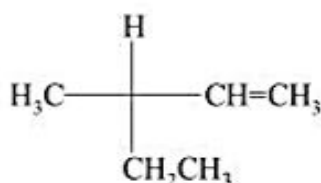


(A) 2 (B) 4 (C) 6 (D) 8 (E) 10

Q.5 Which of the following compounds is chiral?

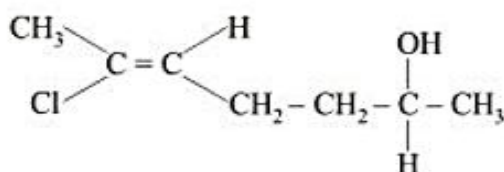


Q.6 The following hydrocarbon can exhibit.



- (A) Geometrical isomerism (B) Optical isomerism
(C) Both geometrical and optical isomerism (D) Tautomerism

Q.8 The compound whose stereochemical formula is written below exhibits x geometrical isomers and y optical isomers.



The values of x and y are

- (A) 4 and 4 (B) 2 and 2 (C) 2 and 4 (D) 4 and 2

ANSWERS

Q.1	A	Q.2	B	Q.3	A	Q.4	D	Q.5	E	Q.6	B
Q.7	B	Q.8	B								

2. CONFORMATIONAL STEREOISOMERISMS

Different non-identical arrangement of atoms or group in a molecule that result by the rotation about a single bond and that can easily be reconverted at room temperature are known as conformational stereo isomers of conformers.

Conformation isomerism :

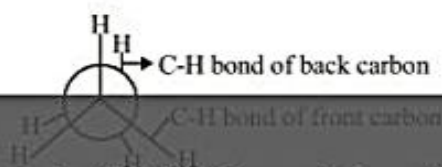
The different arrangement of atoms in space that result from the free rotation of group about C–C bond axis are called conformers, and this phenomenon is called conformation isomerism. The basic structure of the molecule various bond length and bond angle remain the same. There are infinite no. of conformers of any molecule two out of them are defined as staggered and eclipsed.

Condition of conformation :

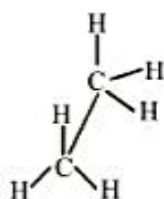
There should be three σ -bond present in a molecule.

Projection of Tetrahedral Carbon Atom :

Newman projection : In this method the molecule is observed along the central carbon-carbon bond. a circle is drawn and centre of the circle represents the front carbon. the bonds of the front carbon are drawn from the centre of the circle while the bonds at the back carbon are drawn from the periphery.

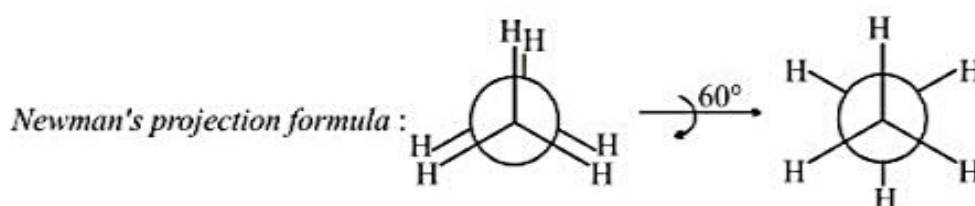
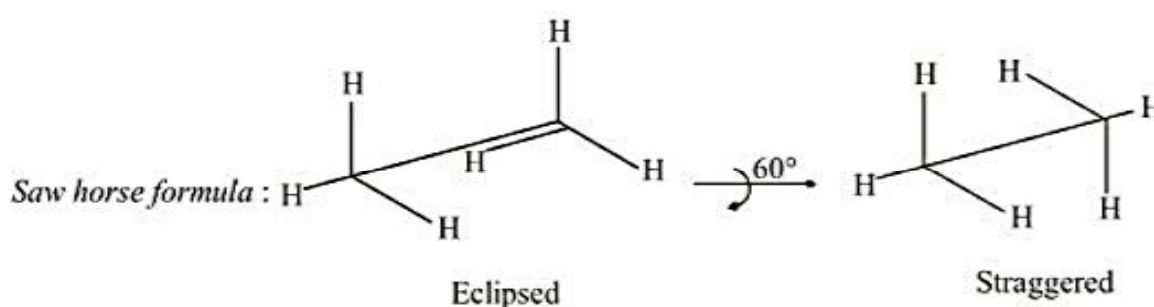


Saw horse projection : In this method, central carbon-carbon bond of the molecule is represented by a straight line written in bond of the molecule is represented by a straight line written in slightly tilted manner and the molecule is observed from the right side.



Dihedral angle :- Angle between valencies of two adjacent atoms

Conformation in ethane ($\text{CH}_3\text{-CH}_3$)

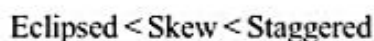


Eclipsed form : When H-atoms of one carbon are directly behind the other is called eclipsed form.

Staggered form : The hydrogen of two atoms are maximum distance with respect to one another.

Skew form : The different forms which exist between 0° to 60° .

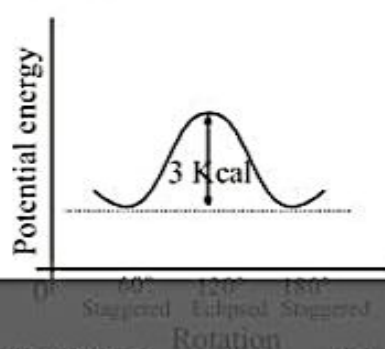
Stability : The eclipsed form is less stable than staggered due to Vander Waal repulsion and torsional strain.

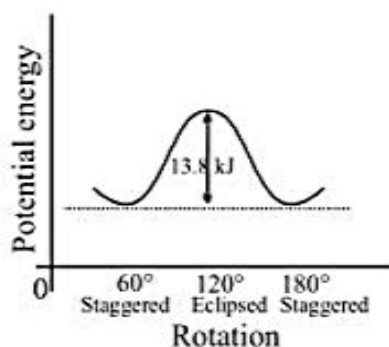
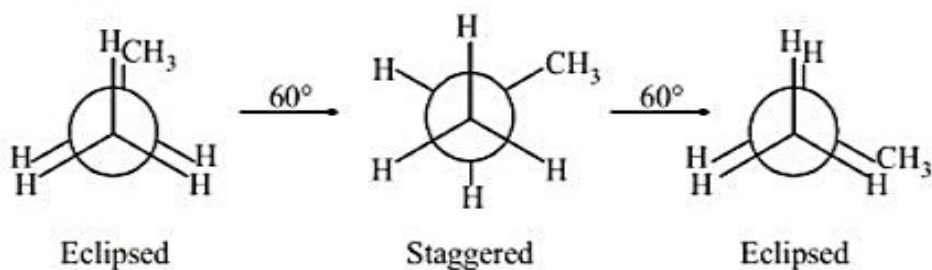


Vander Waal repulsion : Repulsion between atoms or group of atoms.

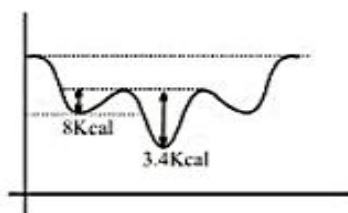
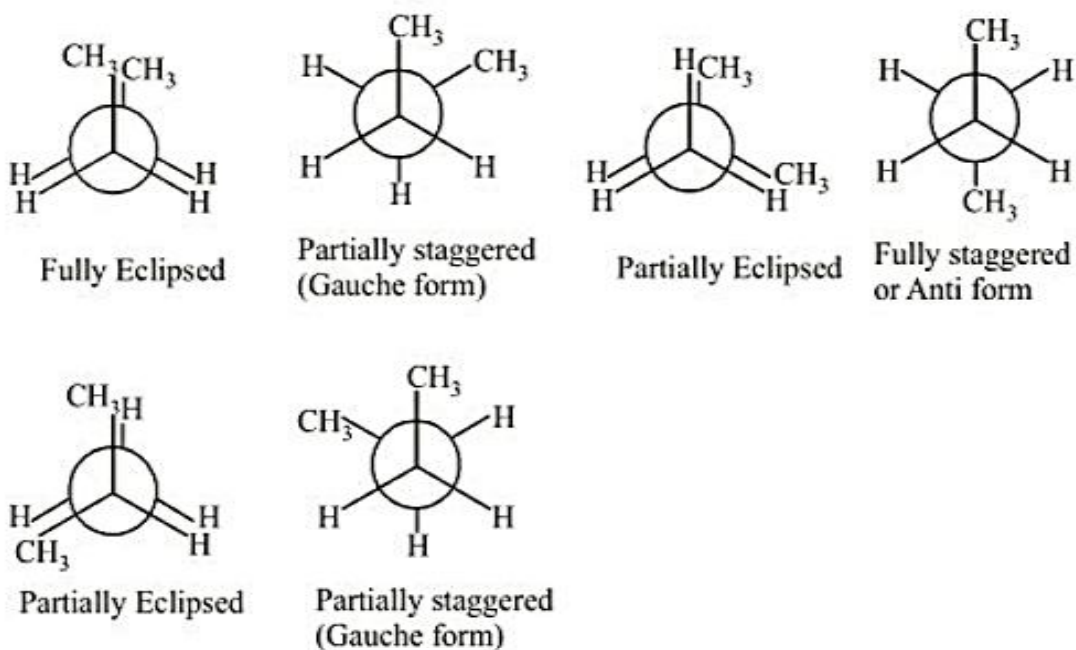
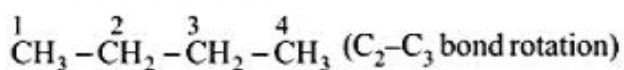
Torsional strain : Bond pair-bond pair repulsion in eclipsed form.

Potential energy curve : $E_{\text{ec}} - E_{\text{st}} = 3 \text{ Kcal / mole}$ or 12.5 kJ / mole



Conformation in propane :

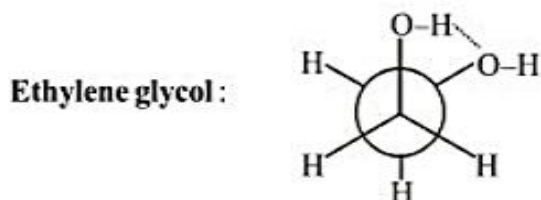
$$E_{ec} - E_{st} = 13.8 \text{ kJ/mole}$$

Conformation in n-butane :

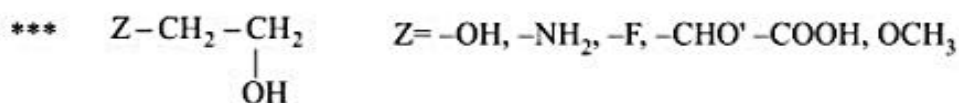
Stability order : Anti form > Gauche > Partial eclipse > fully eclipsed

- Exercise :**
- (i) n-pentane (about C_2-C_3)
 - (ii) 3-methyl pentane (about C_2-C_3)

Some important example :

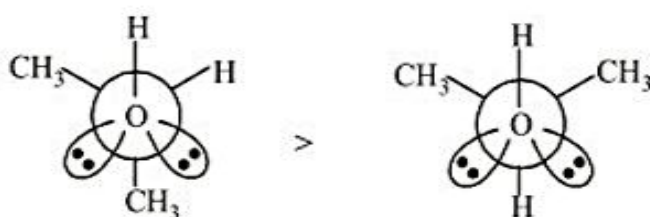
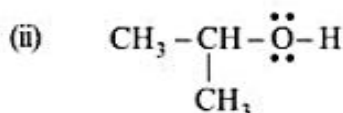
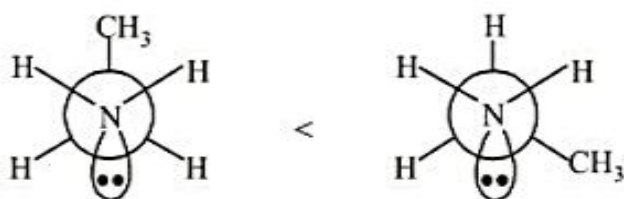
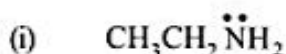


Gauche form is most stable due to intramolecular H-bonding.



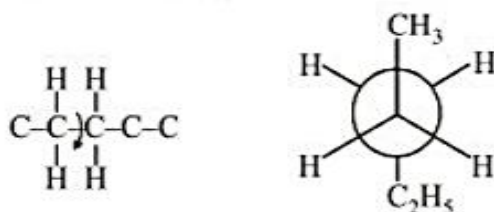
Gauche in all cases due to H-bonding.

Gauche effect : In a lone pair containing compound bulkier group should be placed in Gauche (60°) from l.p. As l.p. has minimum steric repulsion.

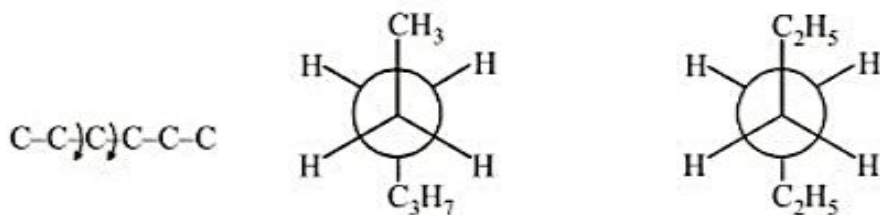


Draw most stable conformation of following compound.

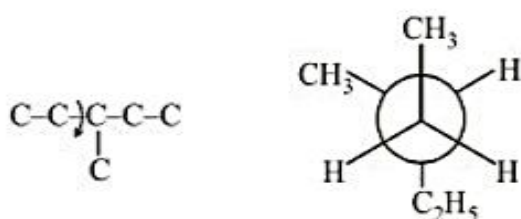
- (i) n-pentane (C_2-C_3) bond rotation.



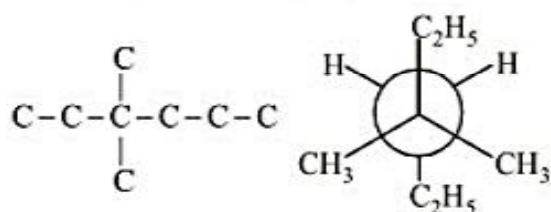
- (ii) n-hexane (C_2-C_3) rotation
(C_5-C_6) rotation



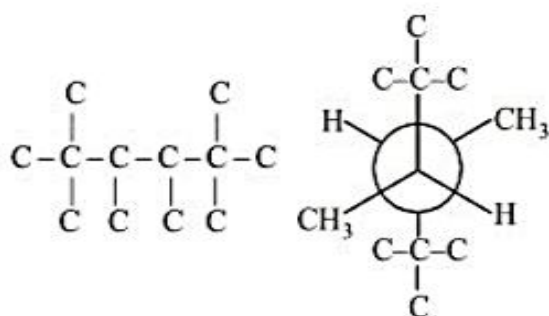
(iii) 3-methyl pentane (C_2-C_3)



(iv) 3,3-dimethyl hexane (C_3-C_4):

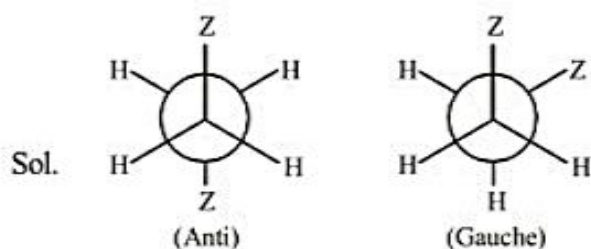


(v) 2,2,3,4,5,5-hexamethyl hexane (C_3-C_4):



Q. Write stable conformer for $\text{Z}-\text{CH}_2-\text{CH}_2-\text{Z}$ in Newman's projection. If $\mu_{\text{solution}} = 1.0 \text{ D}$ and mole fraction of anti form = 0.82, find μ_{Gauche} [JEE 2005]

Ans. $\mu_{\text{Gauche}} = 5.55 \text{ D}$



Mole fraction of anti form = 0.82

Mole fraction of Gauche form = 0.18

$$\begin{aligned}\mu_{\text{obs.}} &= 1 \\ 1 &= \mu_{\text{(anti)}} \times 0.82 + \mu_{\text{(Gauze)}} \times 0.18 \\ \mu_{\text{(anti)}} &= 0 \\ \therefore 1 &= \mu_{\text{(Gauze)}} \times 0.18 \\ \mu_{\text{Gauze}} &= \frac{1}{0.18} = 5.55 \text{ D}\end{aligned}$$

Conformation in cyclo alkane :

Baeyer's strain theory : According to Baeyer's strain theory, the amount of the strain is directly proportional to the angle through which a valency bond has deviated from its normal position. i.e.

$$\text{Amount of deviation } d = \frac{1}{2} (109^\circ 28' - \text{Valency angle})$$

$$\text{in cyclopropane } d = \frac{1}{2} (109^\circ 28' - 60^\circ) = 24^\circ 44'$$

$$\text{in cyclobutane } d = \frac{1}{2} (109^\circ 28' - 90^\circ) = 9^\circ 44'$$

$$\text{in cyclopentane } d = \frac{1}{2} (109^\circ 28' - 108^\circ) = 0^\circ 44'$$

$$\text{in cyclohexane } d = \frac{1}{2} (109^\circ 28' - 120^\circ) = -5^\circ 16'$$

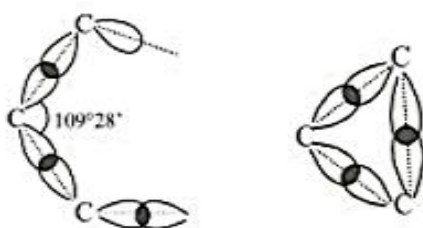
Heat of combustion :

Cyclohexane > Cyclopentane > Cyclobutane > cyclopropane

Heat of combustion per $-\text{CH}_2-$

Cyclopropane > Cyclobutane > Cyclopentane > Cyclohexane

Orbital picture of angle strain :



In cyclopropane however, the C–C–C bond angle cannot be $109^\circ 28'$ but instead must be 60° . As a result the C-atom cannot be located to permit their sp^3 orbitals to point toward each other. there is less overlap and the bond is weaker than the usual C–C bond.

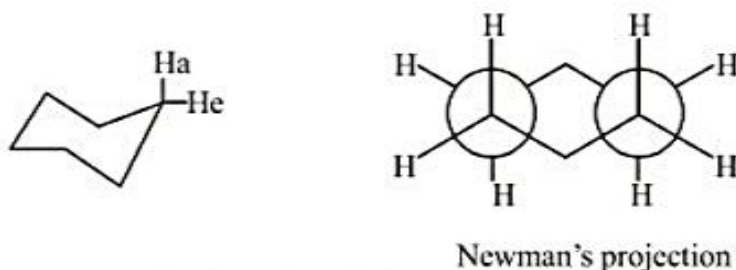
Conformation of cyclohexane : Cyclohexane exist in different form, such on chair form, boat form twist boat form, half chair form.

Stability order : Chair form > boat form

Boat conformation :

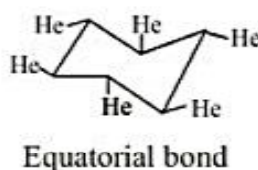
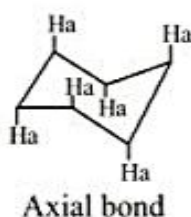


due to interaction between the flag pole hydrogen, boat conformation is unstable.

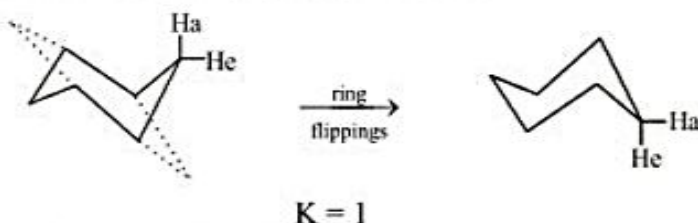
Chair form of cyclohexane :

There are two type of hydrogen in cyclohexane:

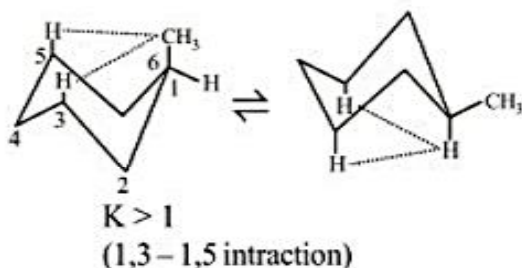
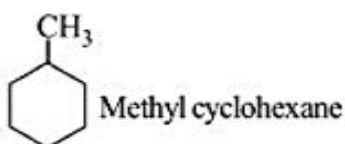
- (i) Axial hydrogen (Ha)
- (ii) Equatorial hydrogen (He)



In cyclohexane all carbon maintain tetrahedral geometry so that cyclohexane is most stable cycloalkane. At room temperature one chair form flips to another chair form during flipping axial bonds converts to equatorial & equatorial bonds converts to axial.

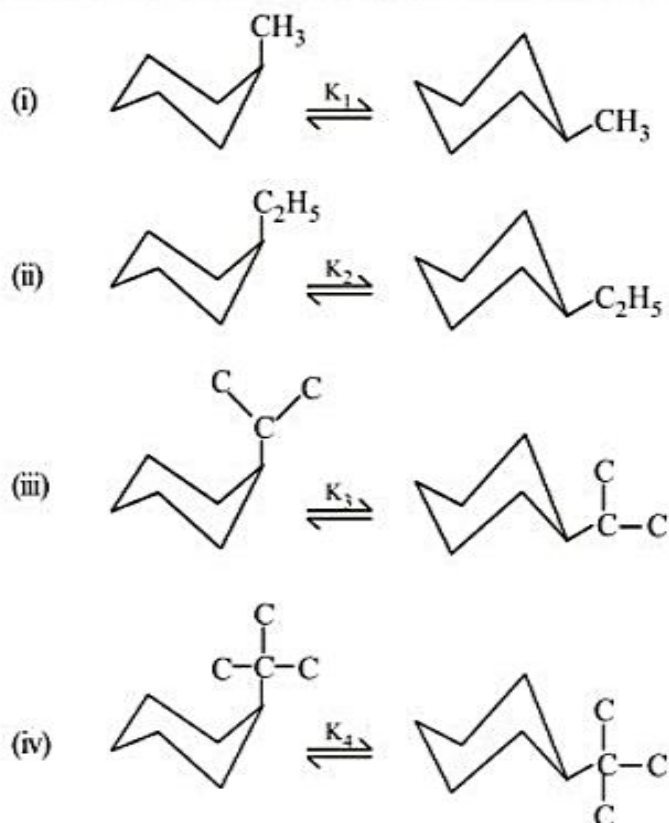


Both chair form are equally stable.

Conformation of mono substituted cyclohexane :

When methyl group is add axial position than their will be more 1,3 – 1,5 intraction so that this conformation will be least stable. By ring flipping methyl group occupied equatorial position so that new reverse chair form will be more stable.

Write the orders of equilibrium constant for following equilibrium.



order $K_1 < K_2 < K_3 < K_4$

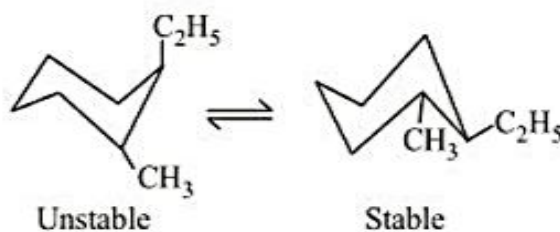
As the size of alkyl group increases 1,3-1,5-interaction also increases, so that bulky alkyl group preferably occupied equatorial position.

Draw most stable chair conformation of following compound.

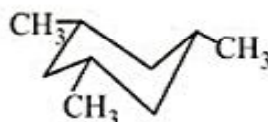
(a) 1,2-dimethyl cyclohexane



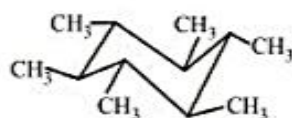
(b) 1-ethyl-2-methyl cyclohexane



(c) 1,3,5-trimethyl cyclohexane



(d) 1,2,3,4,5,6-hexa methyl cyclohexane



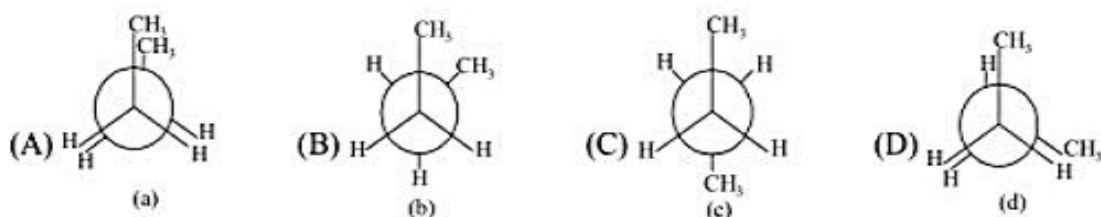
(e) 1-ethyl-2,3-dimethyl cyclohexane



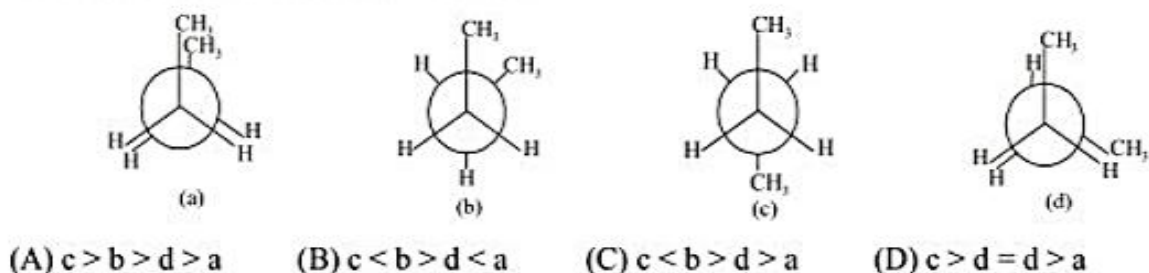
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MCQ

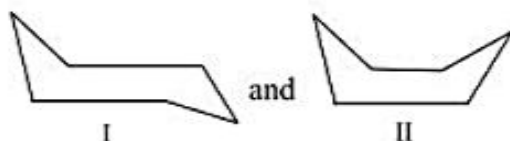
Q.1 Which form is more stable among all these arrangements



Q.2 Correct order of stability among the following



Q.3 Which form is more stable in the shown case-

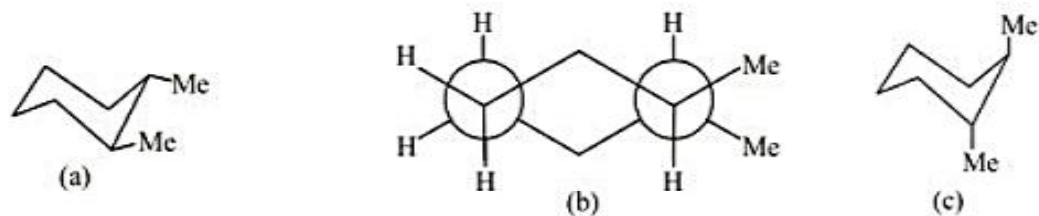


- (A) I (B) II (C) I = II (D) II > I

Q.4 Increasing order of stability among the three main conformation (i.e. eclipse, anti, gauche) of ethylene glycol is:

- (A) Eclipse, gauche, anti (B) Gauche, eclipse, anti
(C) Eclipse, anti, gauche (D) Anti, gauche, eclipse

Q.5 The correct stability order of the following species is



- (A) $c < a < b$ (B) $c = b < a$ (C) $c < a = b$ (D) $a = b = c$

ANSWERS

- Q.1 C Q.2 A Q.3 A Q.4 C Q.5 C