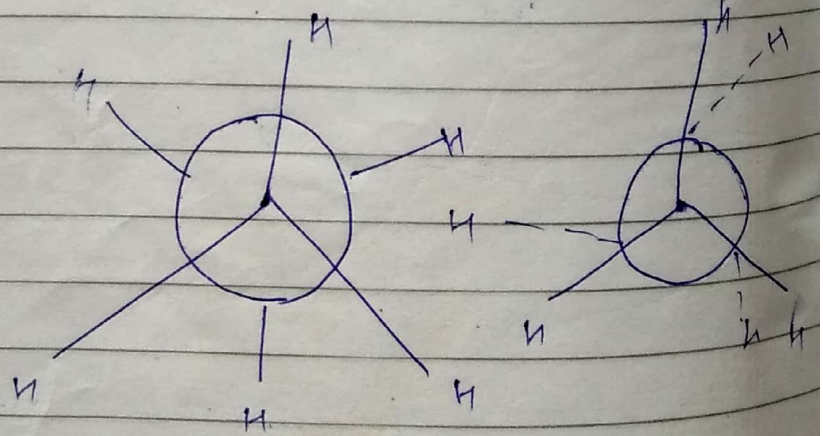
18/4/19

DATE : / 20
PAGE No

Conformation of Ethane:

Alkanes are characterised by σ bonds or single covalent bonds. These bonds permits free rotation about the inter nuclear axis of a σ bond (C-C bond). Therefore it is possible for such a compound to have different relative arrangement of their atom in space which can convert into one another. Such arrangements of atoms which can be change into one another by rotation around single bonds are known as conformations. The isomers having different conformation are called conformers therefore, Alkanes can have infinite no. of conformations.

Conformation of Ethane:



Staggered form eclipsed form

DATE: / 20
PAGE No

Ethane molecules has c–c and each carbon atom with attched to three hydrogen atoms. If one c atom is allow to rotate about c–c bond, while the other carbon atom remains stationary, an infinite no. of arrangements of the hydrogen of one carbon w.r.t those of the others can be obtained.

These ~~element~~ arrangements called conformation have same bond angles and bond length.

Out of the infinite no. of possible conf. of ethane, ~~two~~ represents the extreams
In the must conf., the H's are as far apart as possible. It is called Staggered conf.

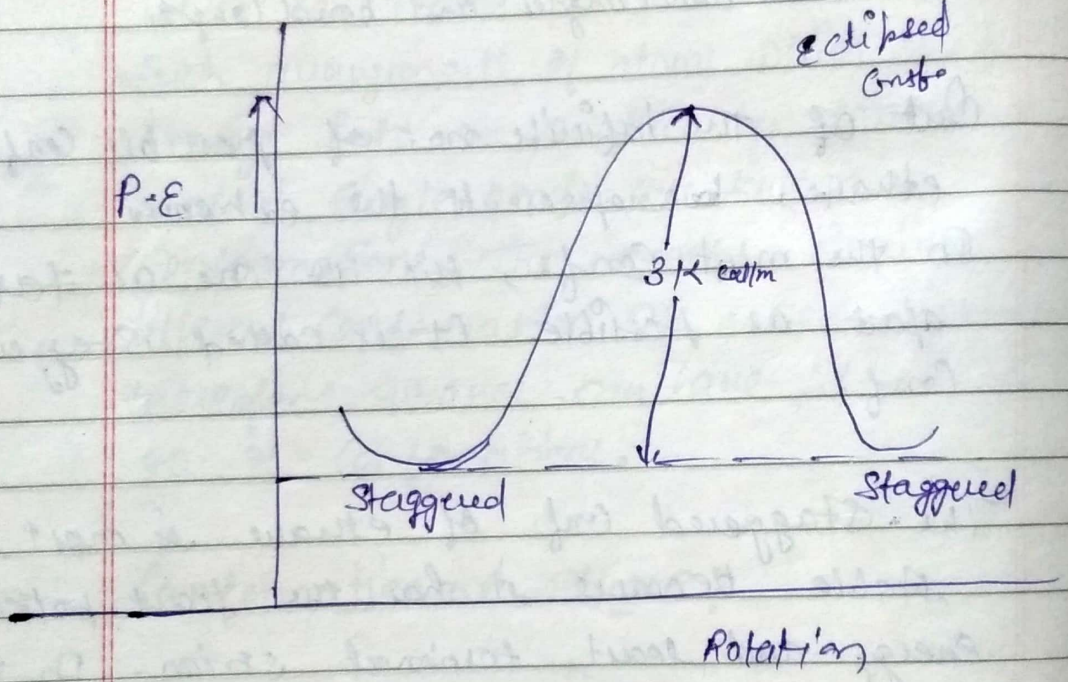
The Staggered conf. of ethane is most stable because it has the least potential energy and least torsional strian. In the

Second conf., the H are crowed togetuer and almost ellipsed eath other. It is called eclipsed conf.

eclipsed conf has the height Energy and thus has Lowest ~~and~~ Stability.

DATE : / 20
PAGE No

The various Conf. of ethane do not differ much in energy. the energy difference b/w the two extreme Conf. i.e staggered and Eclipsed Conf. is ~~Eng~~ ε 3 Kcal/mole.
and it constitutes the energy barier about the Carbon C — C bond.



V. Imp.

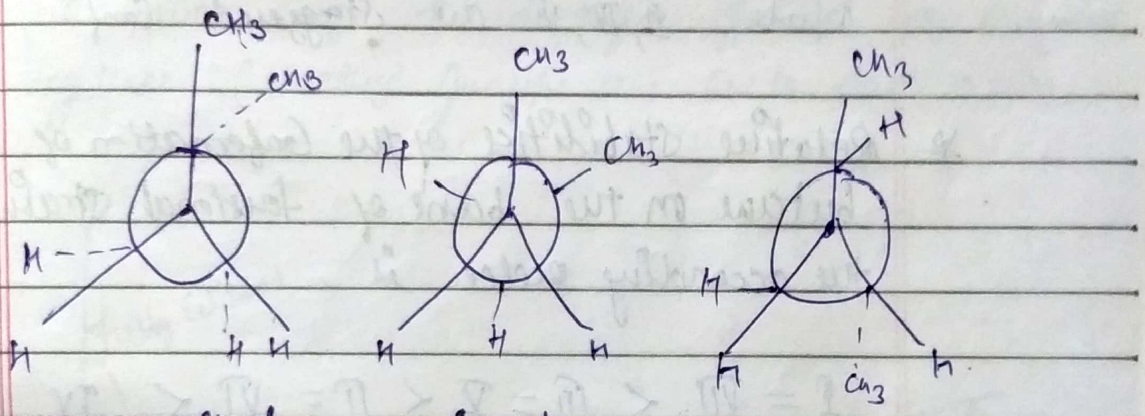
* Conf. of n-butane :

$CH_3 - CH_2 - CH_2 - CH_3$

n-butane is an alkane derived from ethane in which one of the hydrogen atom on each carbon is substituded by an CH_3 group

DATE : / 20
PAGE No

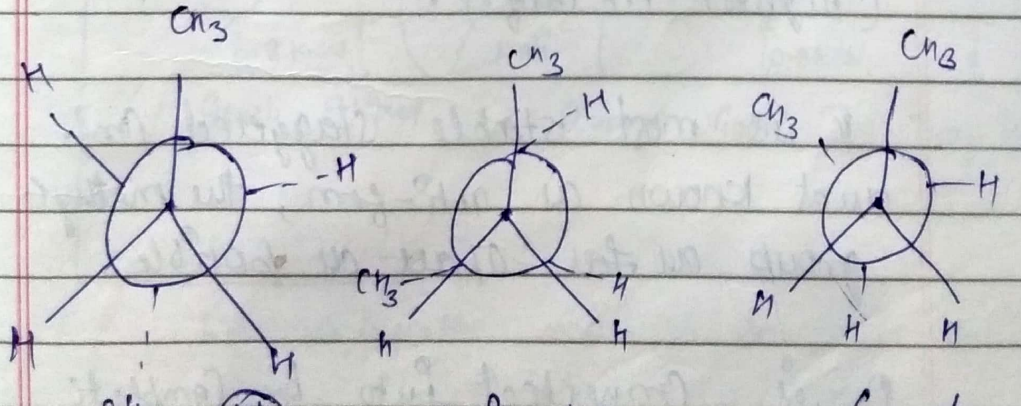
As in the case of ethane, Staggered Conf. have lower potential Energies and hence are more stable than eclipsed conf. n-butane more than one Staggered and Eclipsed conf. due the presence of methyl groups. In case of normal butane the central (C_2-C_3) bond gives various Conf. as shown in figure



fully eclipsed
I
(0°)

Gauch
II
(60°)

Eclipsed form
III
(120°)

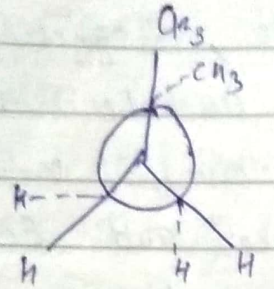


anti-Staggered form
(most stable form)
(180°)

Eclipsed form
(V)

Gauch
(VI)

DATE : / 20
PAGE No



VII

fully eclipsed

The conf. I, III, V, VII are eclipsed conf. while II, IV, VI are staggered conf.

* Relative stabilities of the conformation of butane on the basis of torsional strain, the according order is

I = VII < III = V < II = VI < IV

Conf. I and VII, are identical and are most strained eclipsed conf. (Highest P.E conf.).

V is most stable staggered conf. and known as anti-form, the methyle group are far apart as possible.

I is converted into by complete rotation of 360°.

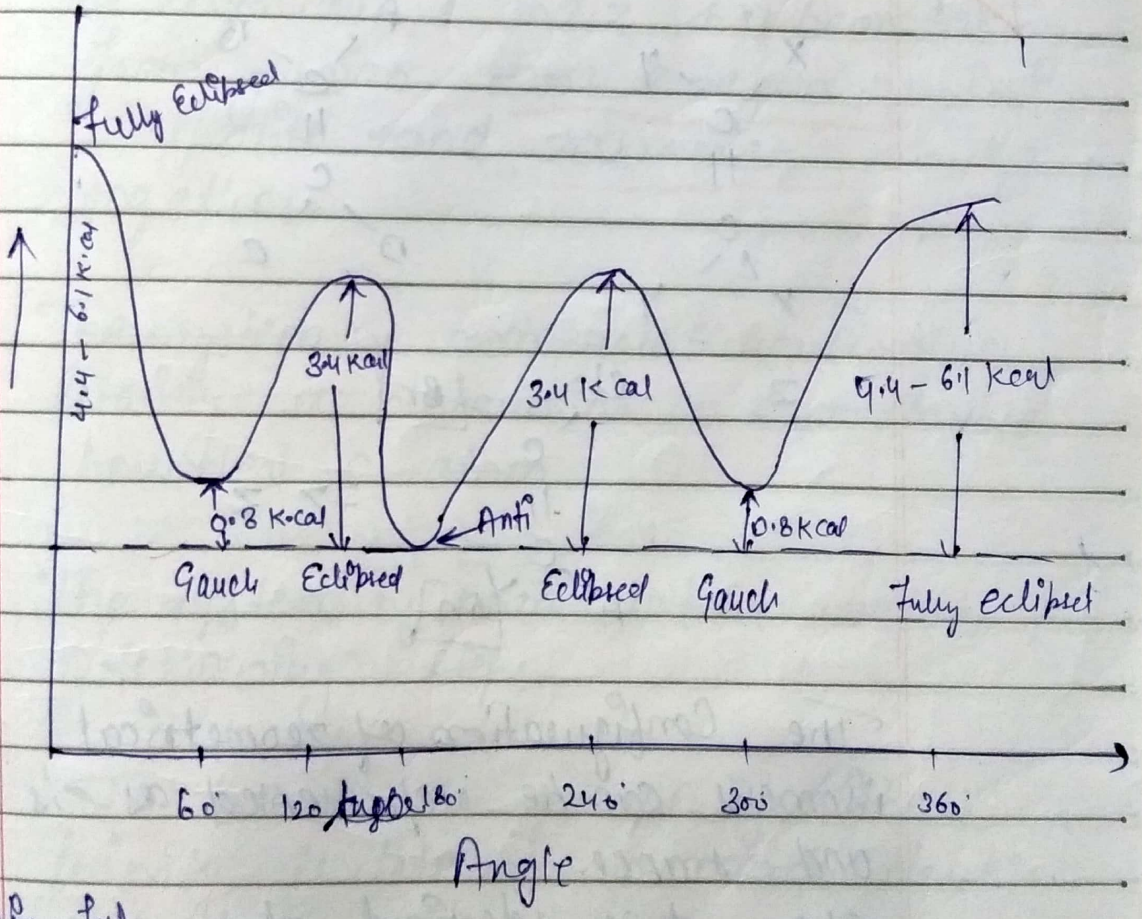
DATE: / 20
PAGE No

I $\xrightarrow{60^\circ}$ II $\xrightarrow{60^\circ}$ III $\xrightarrow{60^\circ}$ IV $\xrightarrow{60^\circ}$ V $\xrightarrow{60^\circ}$ VI $\xrightarrow{60^\circ}$ VII

Fully Eclipsed — Gauch — Eclipsed — anti — Eclipsed — Gauch — Fully Eclipsed

The anti conf. (IV) it has been found is more stable (by 0.8 kcal/mole) then the Gauch (II and VI).

Both are free of torsional strain. But in a Gauch Conf. the methyl groups are crowded together (methyl groups are 60° to each other)



Pu Pul

DATE : / 20
PAGE No

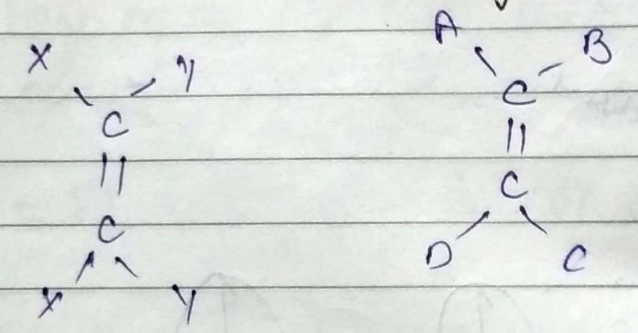
Imp.

* E-Z nomenclature:

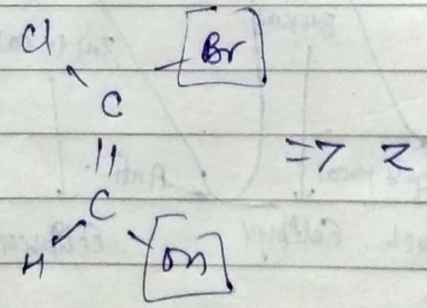
Compound which do not rotate the plane polarised are known as optically inactive

Some examples of optically active compounds

* E-Z System of Configuration:



Z



=> Z

The Configuration of geometrical isomers can be represented as cis and trance.

when two identical atoms or groups are on the same side of the double bound the isomer is called cis (same side)

DATE: / 20
PAGE No

and if they are on the opposite side, it is called trans (trans is opposite side). When atom or group attached to double bounded C atom are different cis trans can not be apply. A new system of nomenclature of geometrical isomers (E and Z) has been introduced to name such stereomers.

This system is based on Priority system developed by

The symbol E and Z has been taking from german word entagen naming opposite and zasammen naming together.

~~The system of nomenclature involves priority is determine on each double bounded C atom.~~

The system of nomenclature involves the following steps.

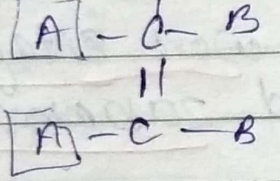
(1) The atoms or groups of higher priority is determine on each double bounded C atom.

DATE : / 20
PAGE No

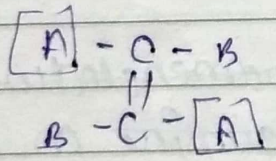
(Q) If the atom or groups of higher priority (A) represented by A) on each carbon atom are on the same side of the double bond, the isomers are assign the conf Z.

On the other hand if the atoms or groups higher priority on each C atom are opposite sides of double bond, the isomers is assign the conf. E.

Example



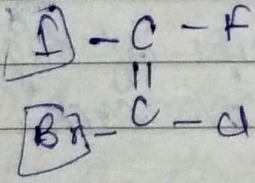
Z isomer



E - isomers

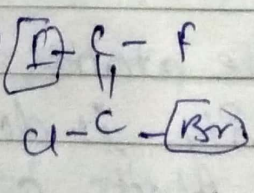
Where A and B represents the atoms and the group of higher priority and lower priority respectively.

(1)



Z isomers

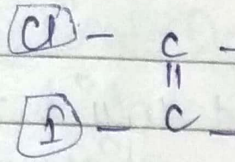
(2)



E - Isomers.

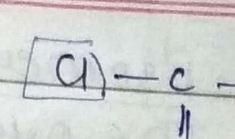
DATE: / 20
PAGE No

(3)



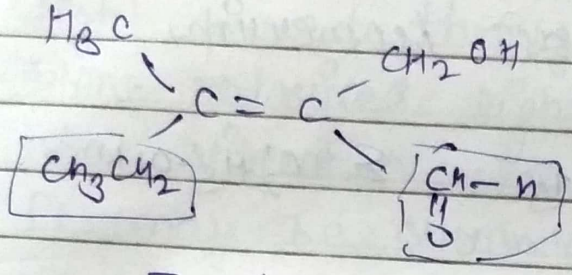
Z isomer

(4)



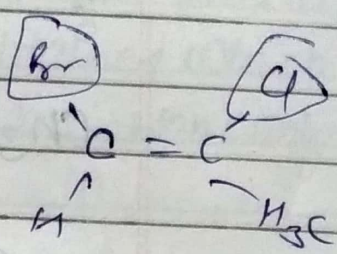
E - isomer

(5)



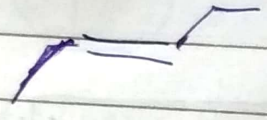
Z - isomer

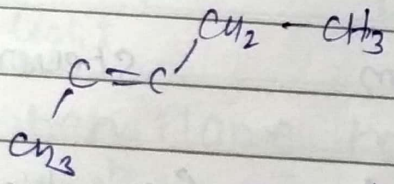
(6)



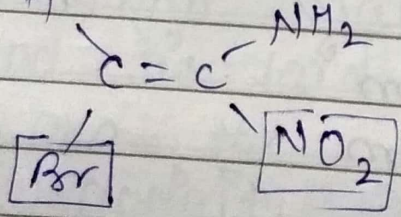
Z isomer

(7)





E - isomer



Z - isomer.

DATE : / 20
PAGE No

* Isomerism?

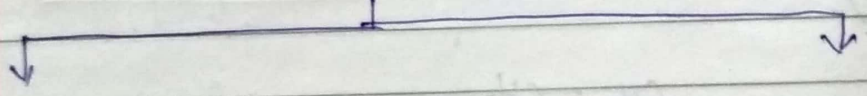
The organic compound which have same m.f but have different properties are known as isomers of each other and the phenomina is known as isomerism

CH_3-O-CH_3 & C_2H_5-OH

Same m.f
diff-properties

Types of Isomerism

Isomerism



Structural isomerism | Stereoisomers

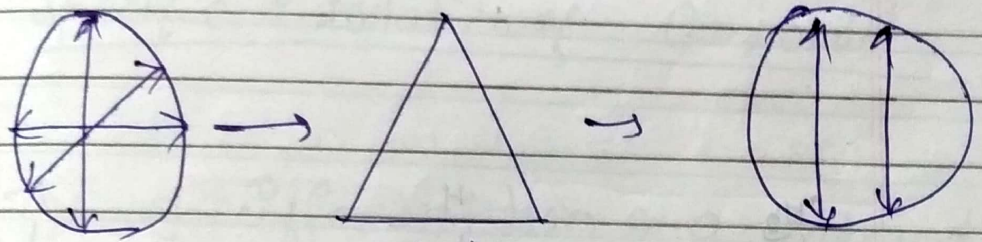
1) Chain isomerism
2) Position
3) Functional
4) metamerism
5) tautomerism

1) Geometrical Isomerism
(ii) optical isomerism

DATE: / 20
PAGE No

* Optical Isomerism:

Ordinary light consist of vibrations in all possible direction. When ordinary light passed through a nicol prism, plane polarised light is obtained which has vibrations are in one plane only. It may be shown as.



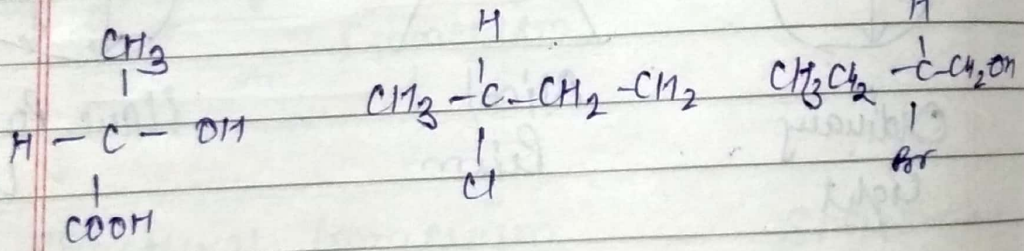
When plane polarised light through the sol^{n} of a temp if the plane polarised light rotate it towards left or right side then the compound is said to be optically active and the properties is optically activity and the phenominon is known as optical isomerism

DATE : / 20
PAGE No

The compound which do not rotate the plane of polarised light are known as optically inactive

*

Compound which do not rotate the plane polarised light are known as optically inactive.



Lactic acid 2-chloro Butane 2-bromo-1-butane

from the structure of above compound it is clear that they have asymmetric carbon atom. The C atom which is linked with four diff. atom of group is known as asymmetric carbon atom or stereogenic centre

DATE: / 20
PAGE No

The presence of Asymmetric carbon atom is essential for optical activity.

* The angle of optical rotation may be measured by the help of polarimeter

The angle of optical rotation observed when plane polarised light is passed through 10cm length of a solution containing 1 g/cm³ is known as specific rotation of Compound

The specific rotation of a Compound is Constant just like melting point, boiling point etc.

* optically active Compound are of two type.

(i) Dextro rotatory
(ii) Leavo rotatory

Dextro rotatory: They rotate Plane of polarised light towards Right side

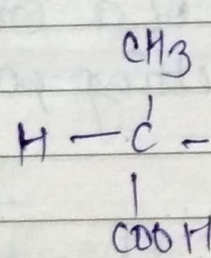
Leavo rotatory: They rotate the plane of polarised light towards Left side

DATE : / 20
PAGE No

* Diff. form of a compound which show different behaviour towards plane polarised light are known as optical isomers of each other and this phenominon is known as optical Isomerism.

Optical Isomers have same physical and chemical properties, but they show different behaviour towards plane polarised light.

* Optical Isomerism of Lactic Acid:



(Lactic Acid)

Lactic Acid exist in following two form.

(i) d-lactic Acid:
It rotates the plane polarised light towards Right side.

(ii) L-Lactic Acid: It rotates the planes of polarised light towards Left side.

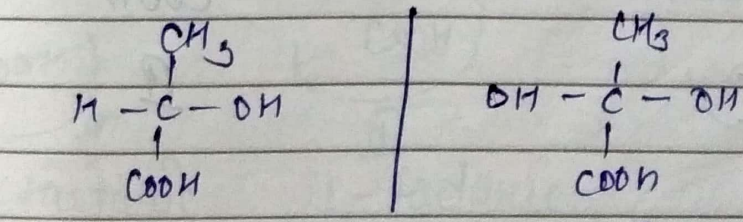
DATE: / 20
PAGE No

Therefore d-lactic Acid and L-lactic acid are optical isomers of each other.

It is found that optical rotation of d-lactic acid and L-lactic acid is equal quantity of d-lactic acid L-lactic acid will not rotate the plane of polarised light such mix is known as d-L mixture or resmic mixture.

It is found that d-form and L-form of a compound that d-form and L form of a compound differ. in arrangement on atoms on groups in space. In such a way that d-form is mirror image of L-form. but they do not super impose each other.

The structure d and L-lactic acid may be shown as



d-Lactic acid L-lactic acid

DATE : / 20
PAGE No

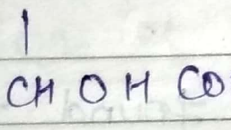
2.M

* The mirror Image isomers which do not Superimpose each other also known as enantiomers and enantiomorphs.

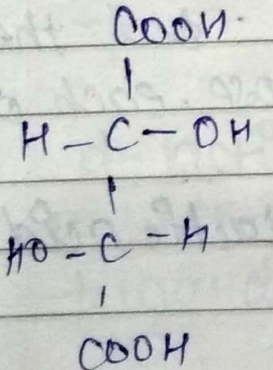
Note: No. of optical Isomers is given by 2^n. Here n is the no. of Asymmetric Carbon

* Optical Isomers of Tartaric acid:

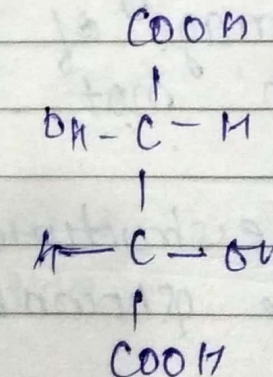
Tatric acid is



It Contains two asymmetric carbon atom therefore 4 ($2^n = 2^2 = 4$) 4 optical isomers must be Possible for tatric acid.

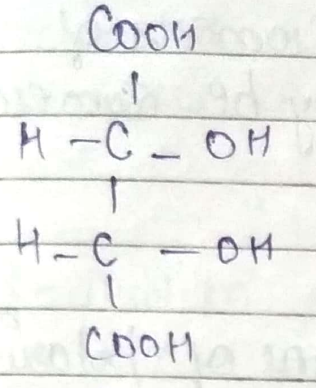


I

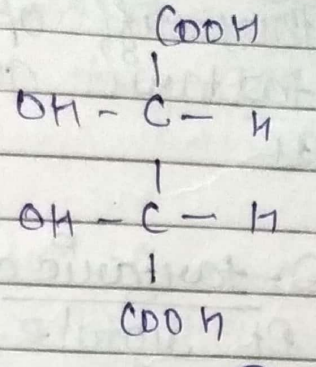


II

DATE: / 20
PAGE No



III

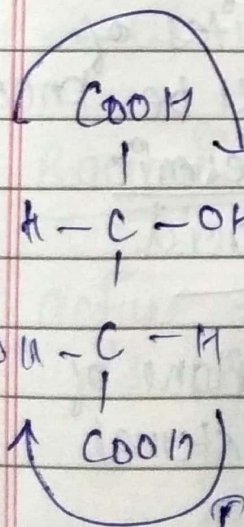


IV

Structure III and IV are similar to each other. thus only 3 - tartaric acid are theoretically possible.

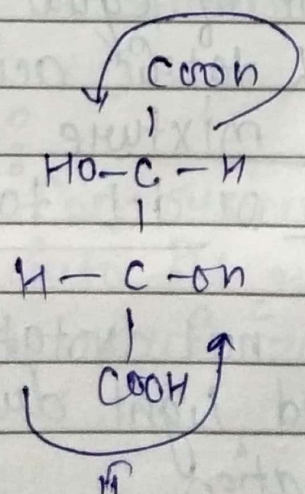
Practically also only 3 tartaric acid are known.

If the rotatitory power of structure is Consider from thus side of H or OH then rotating power of each structure may be shown as



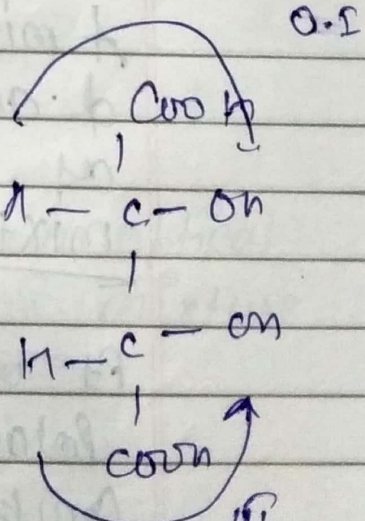
I

D - tartaric acid



II

L - tartaric acid



III

meso m - tartaric acid

O.I

O.N

DATE : / 20
PAGE No

Thus diff optical isomers of tartaric acid may be summarised as

(i) D-tartaric acid:
It rotate the plane of polarised light right side.

(ii) L-Tatric acid:
It rotates the plane of polarised light toward left side

(iii) M-Tatric acid: (meso form)

It does not rotates the plane of polarised light due to Internal Compensation
(angle of rotation zero)

A mixture of equal quantites of d and L tatric acid will be known as d-L mixture or racemic mixture of d-L tatric acid.

It will not rotate the plane of Polarised Light due to external Compensation

DATE: / 20
PAGE No

d and L - tartaric acid are mirror image isomers therefore they are enantiomers (SN)

d- and m or L and m form are not mirror image of each other, they are known as distereomers (SN)

The optical isomers which are not mirror image each other distereiomers

for Ex: d and m, L and m form

Note:
The seperation of resmic mixture is known as resolution.

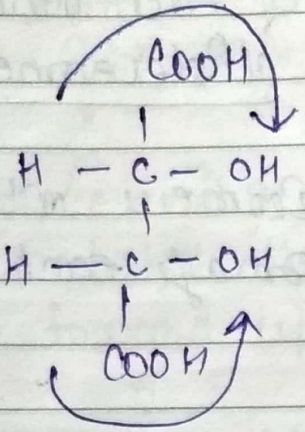
Note: d and L forms are also knowns as +ve and -ve form.

¥ Racimization:
Conversion of an optical active form into its resmic mixture is known as Racimization.

DATE : / 20
PAGE No

* Cause of optical activity:

certain forms of some compounds containing asymmetric carbon are not always optically active.



m-tartaric acid

Presently the following two Cond^{n} are considered necessary for the presence of optical activity in a molecule

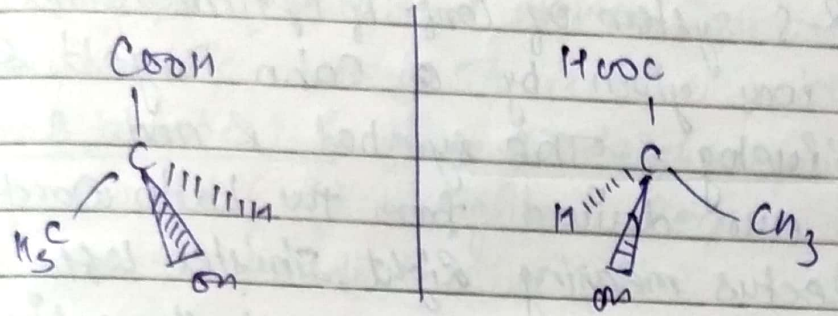
(i) molecular dissymmetry or Asymmetry
(ii) Non super imposability.

* Differenciate b/w Enentiomers and diasteriomers:

* Enentiomers: also known as optical isomer is one of the two stereoisomers that are mirror image of each other

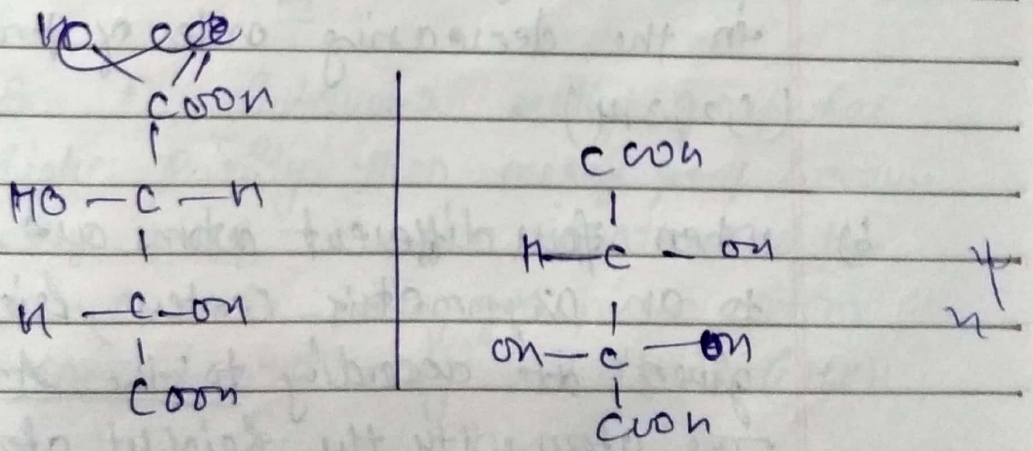
DATE: / 20
PAGE No

that are not super imposable. Such as one left and Right hand are the same Expect for being reversed along one axis.



* Diastereomers:

Diastereomers are a type of a stereoisomer Diastereomerism occurs when two or more stereoisomers of a Compound having different Configuration at one or more equivalent stereocenters and are not mirror image of each other.



DATE : / 20
PAGE No

26/04/19

* R-S System of Configuration:

R = Rectus ⇒ Right
S = Sinistel ⇒ Left

R-S system of conf. of optical isomers was given by Cahn Ingold & Prelog. The symbol R and S are derived from the Latin word Rectus meaning Right, Sinistel left.

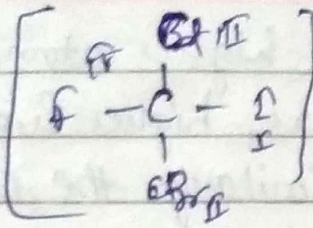
The conf. of an optically active comp. is based on atached to a asymmetric The Nature of the group is determine by the Priority of the groups which depends upon the following Rule.

(a) four diff. atoms or groups attached to a asymmetric centre are arange in the decreasing order of priority. (1, 2, 3, 4)

b) When four different atoms are attached to an asymmetric centers, Priority is given according to the A. Number The atom with the heighest atomic No. is given the heighest Priority. Therefore, in Bromochloro fluro Iodomethane

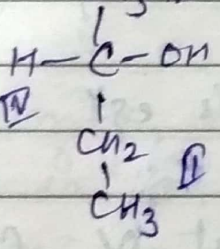
A. No. | A. mas | next atom | double or triple bond

DATE: / 20
PAGE No



c) If isotopes of the same element are attached to an asymmetric center, The isotopes coity Higher mass number is given the heigher priority.
for Ex: D (H^2) is given heigher Priority as compared to H (H^1)

d) If two atoms attached to an asymmetric center are the same, The priority is determined by the atomic Number of next atom away from asymmetric centre

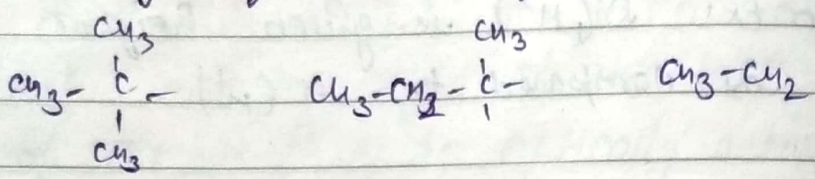


for Ex In Butanol-2 methyl group has higher priority then methyl group because in ethyl group C atom is attached to C, C, H, C in methy group C atom is attached to only H atoms (C, H, H, H)

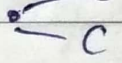
DATE : / 20
PAGE No

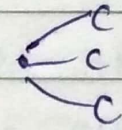
d) Since C atom has higher atomic no. than H, ethyl gp has higher priority over methyl group. Similarly the priority of tertiary Butyl, isopropyl and ethyl group is in the order

tertiary butyl > isopropyl > ethyl



e) An atom attached with a double or triple bond is equivalent to two or three such atoms

for Ex =C is eq^{n} 

≡C is eq^{n} 

for example : out of CHO and CH_2OH groups, CHO gp ($-\overset{H}{C}=O$) has higher priority than CH_2OH ($-\overset{H}{\underset{H}{C}}-OH$)

* On the basis of these rules some common rules are given the following priority sequence in the decreasing order.

DATE: / 20
PAGE No

→ $-I > -Br > -Cl > -SO_3H > -F > -OCH_3 > -OH >$

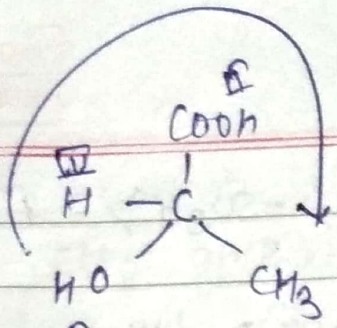
$-NO_2 > -NHCOCH_3 > -NHCH_3 > -NH_2 > -\overset{O}{\overset{\|}{C}}-Cl >$

$-\overset{O}{\overset{\|}{C}}-OH > -\overset{O}{\overset{\|}{C}}-NH_2 > -\overset{O}{\overset{\|}{C}}-H > -CH_2OH >$

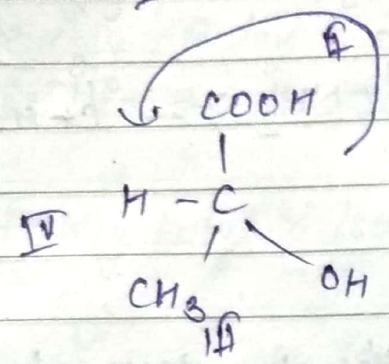
$-CH_3 > H$

After given priorities to four atoms or groups attached to an asymmetric centre, the molecule is now rotating so that the atom or group of lowest priority (IV) is directed away from the viewer. Now, the arrangement of remaining three atoms or groups is viewed in the decreasing order of their priority. In doing so, if the I moves in a clockwise direction the conf. is assigned R. (Rectus meaning Right) while if the I moves in anticlockwise dir, the conf. is assigned as S (Sinister meaning left)

DATE : / 20
PAGE No



R config.



S config.

Draw * R-S config. for the molecules Represented by planar formula (Fisher projection formula)

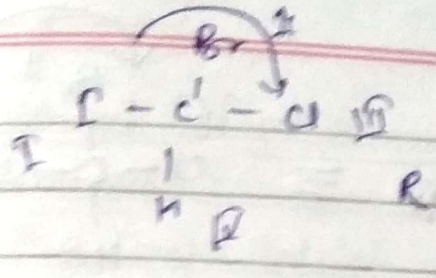
In such cases, Step first decides the priorities of the various atoms or groups remains the same, But the step second is different.

Here, four different cases may be Considered.

Case-1 When the atom or group of lowest priority is at the bottom

Simply rotate the I in order of decreasing priority and find the Config.

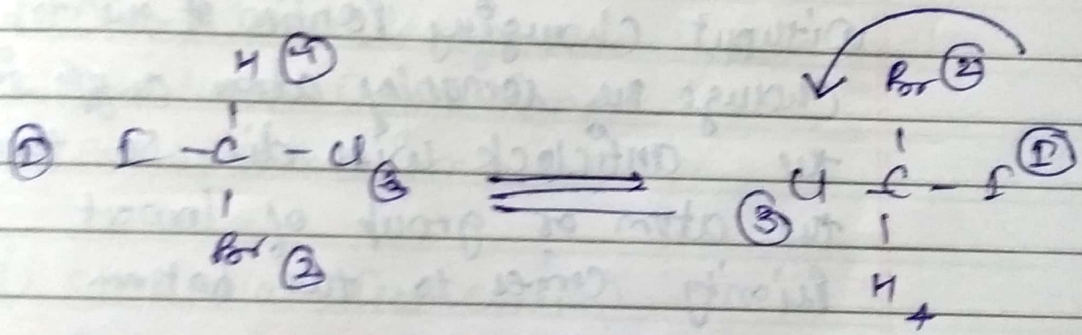
I gets rotate in c.w dir.



Case-2

When the atom or group of Lowest priority is at the top

Rotate the entire molecule through 180° so, as to Bring the atom or group of Lowest priority is at the Bottom.



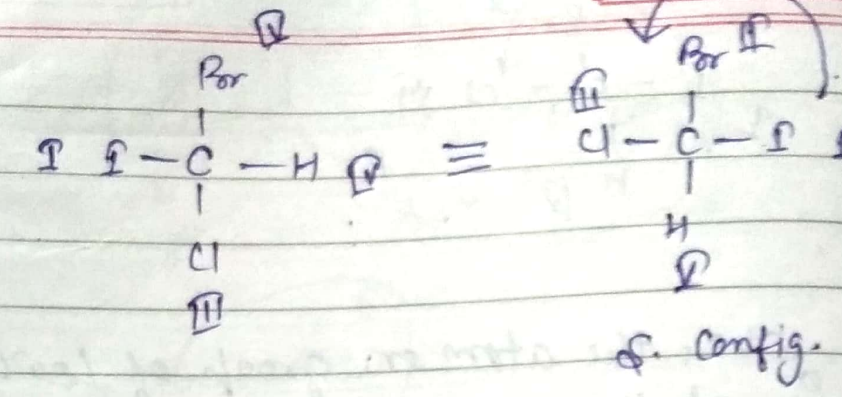
S Config.

Case-3

When the atom or gp of Lowest priority is at the Right hand side of horizontal line

Without changing the pos. of the top Change the position of other atoms or gp. in clock wise dir, so that the atom or group of Lowest priority Comes to the bottom

DATE : / 20
PAGE No

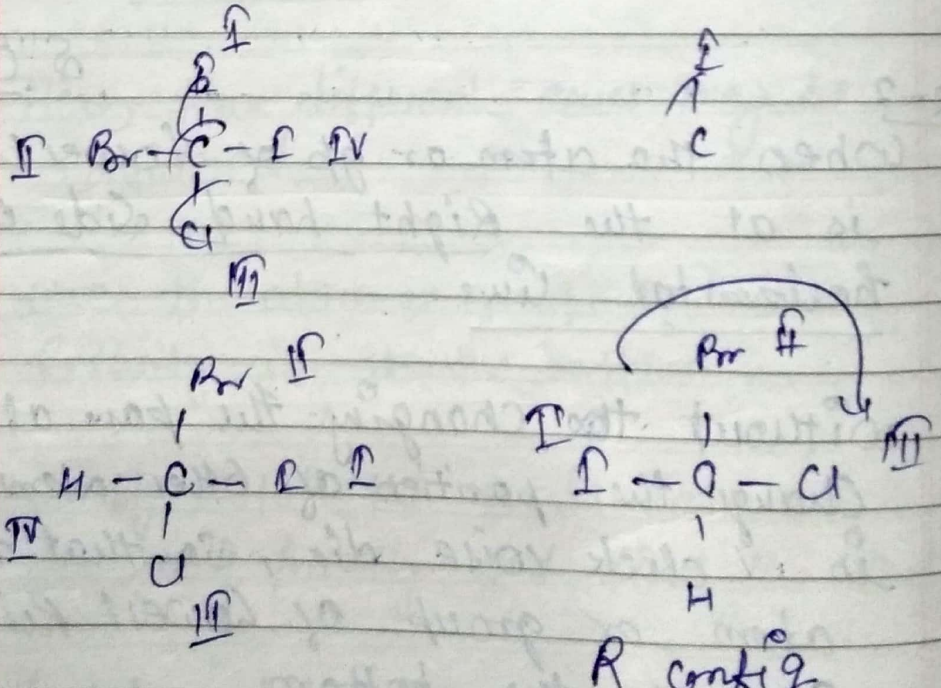


S. config.

Case - IV

The atom or group of lowest priority is at the left hand side of horizontal line:

Without changing position of the top change the remaining atom or gp in the anticlockwise dir. so that the atom or group of lowest priority comes to the bottom



R config.

DATE : / 20
PAGE No

21/4/19

* Optical Isomerism of transition metal Compound :

The comp. which have same M.F but have different Properties are known as Isomers of each other and the phenominan is known as Isomerism

For Ex :

$$[Ni(NH_3)_2(NO_2)_2]Cl_2$$

&

$$[Ni(NH_3)Cl_2](NO_2)_2$$

Isomerism is of two type.

i) Structual Isomerism
ii) Stereoisomerism

i) Structual Isomerism :

This type of Isomerism arises due to the difference in structual formula of the Complex same M.F

2 Stereoisomerism :

This type of isomerism arises due to the difference in arrangement around

around the central metal in space.

DATE : / 20
PAGE No

(1) Structural Isomerism:
Following type of Structual Isomerism is found in complexes

i) Hydration Isomerism
This type of Isomerism arise due to the difference in position of water molecules in the complexes
For Ex:
$[Cr(H_2O)_6]Cl_3$ & $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

Hexa aquo chromium(III) chloride
Penta aquo chromium
Penta aqua mono chloro chromium(III) monochloride hydrate

2) Ionisation Isomerism:
This type of isomerism arrises due to the formation of different types of ions by complexes.
for ex:

$[Cr(NH_3)_5Br]SO_4$ & $[Cr(NH_3)_5SO_4]Br$

3) Linkage Isomerism:
It arrises due to the diff. in linking of ligand with complex ion with central metal.

DATE: / 20
PAGE No

for Ex:

$[Co(NH_3)_5(NO_2)]Cl_2$ & $[Co(NH_3)_5(ONO)]Cl_2$

4) Coordination isomerism:
It arises due to interchange the ligands b/w two complex ions
for Ex:

$[Co(NH_3)_4][Pt(Cl_4)]$ & $[Cu(Cl_4)][Pt(NH_3)_4]$

5] Ligand isomerism:
It arises due to isomerism in ligand
for Ex:

$[Cr(CH_2(NH_2)-CH_2-CH_2(NH_2))_3]Cl_3$ & $[Cr(CH_2(NH_2)-CH(NH_2)-CH_3)_3]Cl_3$

(2) Stereoisomerism or space isomerism:
This type of isomerism arises due to the diff. in arrangement of around the central atm in space.
It may be of two type.

DATE: / 20
PAGE No

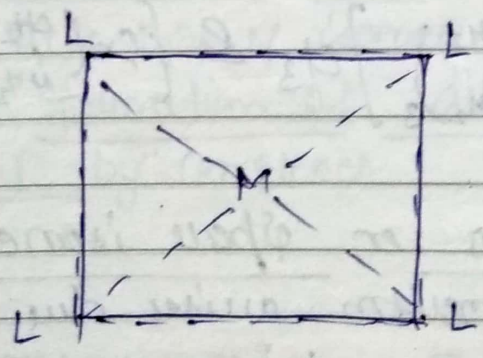
1) Geometrical Isomerism:

It arises due to diff. of arrang of ligands around the central metal in such a way that geometrical structure of complexes change in space.

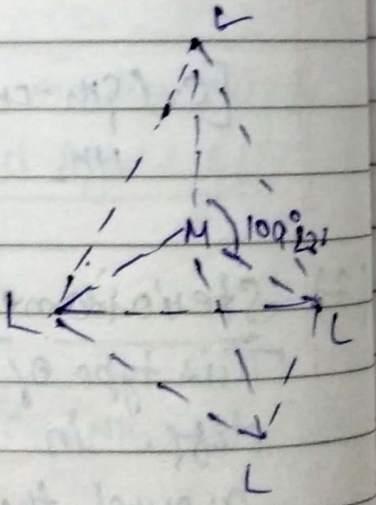
2) optical isomerism:

Diff. forms of a complex which show different behaviour towards plane polarised are known as optical isomerism of each other

In many coordination complexes, following shapes are possible



Square planar

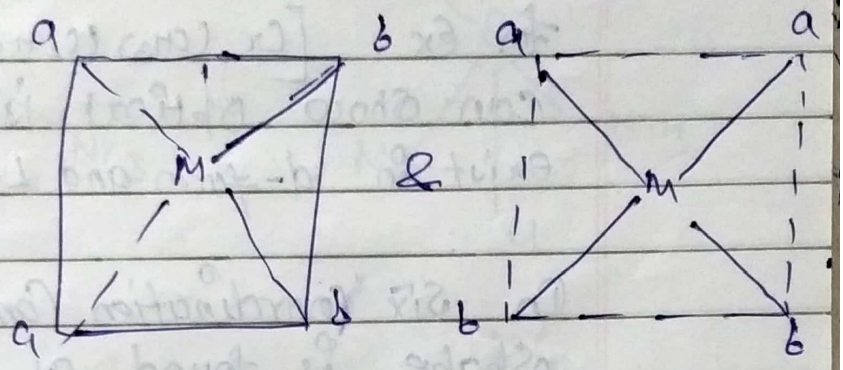


Tetrahedral

DATE : / 20
PAGE No

The complexes of type $[Ma_4]$ and $[Ma_3b]$ will not show any isomerism of the above ~~one~~ type of shape

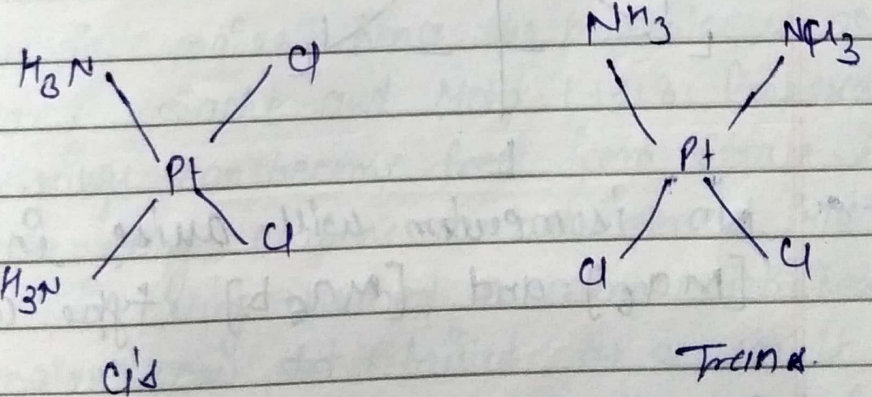
In complexes of type $[Ma_2b_2]$ Geometrical Isomer can exist in sq. planar shape as



cis trans

for Ex:

$[Pt(NH_3)_2Cl_2]^{2+}$ exist in cis and trans form as



cis Trans

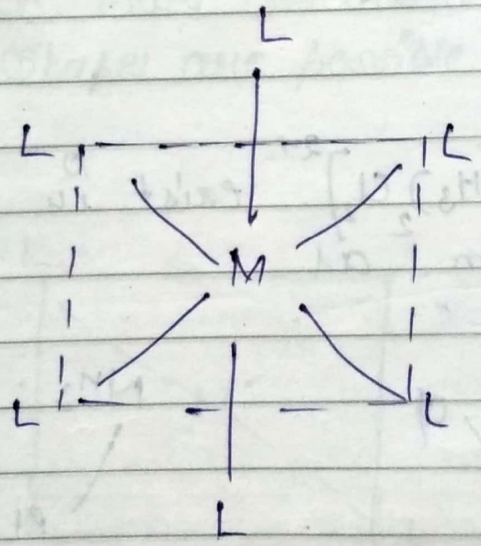
DATE : / 20
PAGE No

In tetrahedral shape geometrical isomerism does not arises in (Ma_2b_2) complexes (Ma_2b_2)

In tetrahedral complexes optical isomerism in [Mabcd] type complexes

for ex $[Cr(CH_3)(C_2H_5)(S)(C_6H_5COO^-)]^{2-}$ can show optical isomerism and will exist in d-form and L-form

In six coordination complexes octahedral shape is found as



No isomerism will arise in case of $[Ma_6]$ and $[Ma_5b]$ type complexes

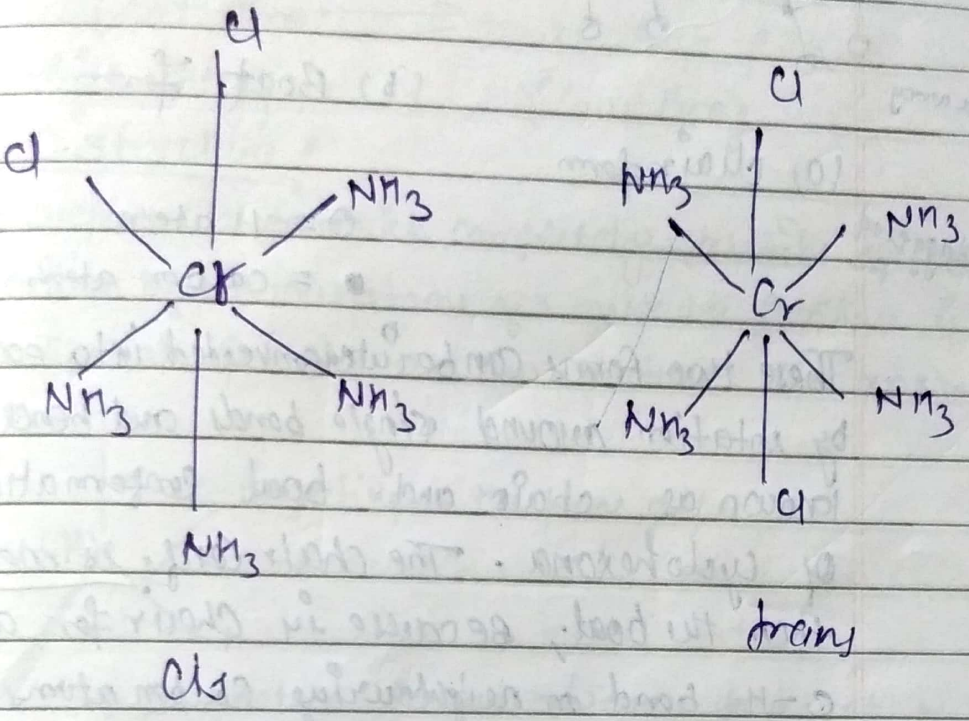
In complexes of the type $[Ma_4b_2]$, cis and trans geometrical isomerism will be possible

Representation of 3D structure

centre of symmetry

Conformation Sh
DATE: / Chair or
PAGE No Boat here

for Ex: In case of complexes $[Cr(NH_3)_4(Cl_2)]^{+1}$ Cis and trans isomers may be shown as



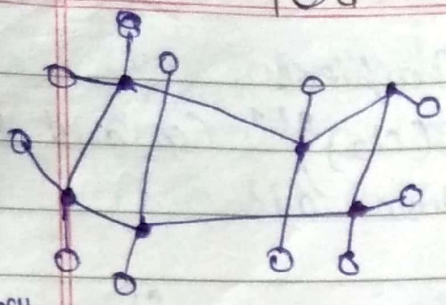
* Conformation of Cyclohexane:

Cyclohexane is not planer because if were a planar molecules 6 carbon atoms would have been line in a plane and hence c-c-c bond angle have 120°. but since the normal tetrahedral angle is 109°28'. hence the molecules is not planar. Sache and Mohr (1918 Proposed that such rings can become free from strain. if all the ring carbons are not forced into one plane. If ring assumed a normal tetrahedral of 109°28' are not Retained as a result, The strain with in the ring is released. Cyclohexane can exist in two non-planar conformation, both are strainless. There are called chair and boat form of cyclohexane

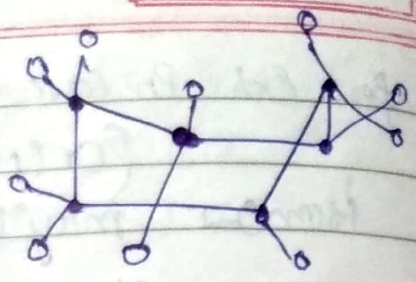
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DATE : / 20
PAGE No

Peri



(a) Chair form



(b) Boat form

staggered form

eclipse

H = far away

O = H atom
● = carbon atom

These two forms can be interconverted into each other by rotation around single bonds and hence are known as chair and boat conformations of cyclohexane. The chair conf. is more stable then the boat, because in chair for all the C–H bond on neighbouring carbon atoms are in staggered position there are in the eclipsed position in case of boat form.

The boat form is flexible and can be easily distorted into many shapes and in these the hydrogen eclipsing are reduced.

The chair form is rigid and when it is converted into boat form some angular deformation is required. The energy barrier for this transformation is about 37.7 to 46.0 KJ/mole

Twist boat form confin has 6.7 KJ/mole less energy then that of classical boat conf.

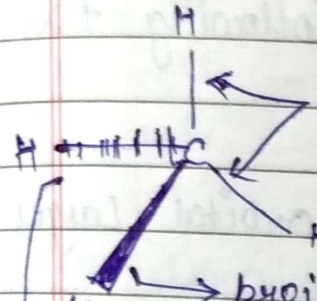
DATE: / 20
PAGE No

and the chair Conf. has 22.2 KJ/mole less energy then that of twist boat form

boat form ⇌ Twist boat form
(high Energy) (Low Energy)

* 3-D structure:

A representation which completely describe the actual position of various atoms of a molecule in space is called a spatial formula or 3-D structure. i-e 3D structure



projecting in the plane paper

→ projection towards observer infront of paper
→ projection away from observer behind plane of paper

(1) The 3D structure of organic Comp. can be represented on paper by using certain conventions

(2) by using solid and dashed wedge formula, 3D image of molecule from a 2D picture can be perseped

(3) the thick line or solid wedge indicates a bond lying above the plane of the paper and projecting towards the observer

4) A dashed wedge is used to represent a bond lying below the plane of paper and projection away from the observer

(5) wedges are used in such a way that the broadest is towards the observer. The bond lying in the plane of paper and by using a normal or an ordinary line