

Stereochemistry

Same atomic connectivity but different arrangement of their atoms in space are known as stereoisomers.

Arises due to diff in structures.
eg in coordination compounds.

Structural

Isomers

Conformational

Due to rotation of molecule about single bond, different spatial arrangements of atoms/molecule arises. These spatial orientation of molecule which differs in dihedral angle and are easily interconvertible.

— Have low energy barriers
4.2 to 46 kJ/mol.

— Not isoable
eg 6 forms of butane

Stereochemical

Exhibited by ~~isomers~~ isomers having same molecular formula but diff configurations as C forms covalent bond which are directional.

— Configuration is the spatial arrangement of atoms & gps about double bond or ring.

— Isoable as difference in energy
84 kJ/mol.

eg geometrical

Stereoisomers

Enantiomers

Molecule with non-superimposable mirror images.

eg 2 hands

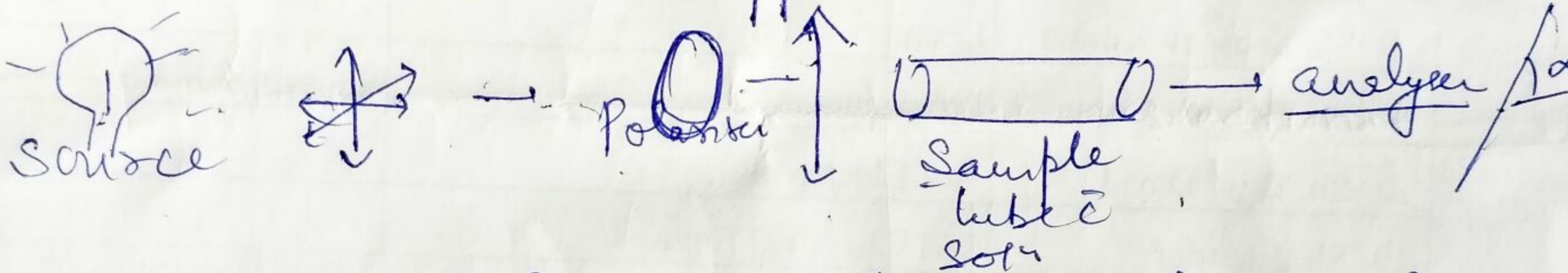
Diastereomers

do not have non-superimposable mirror images.

Chirality: Molecule is chiral if it is not superposed on its mirror reflection, eg tetrahedral C linked to four diff gps.

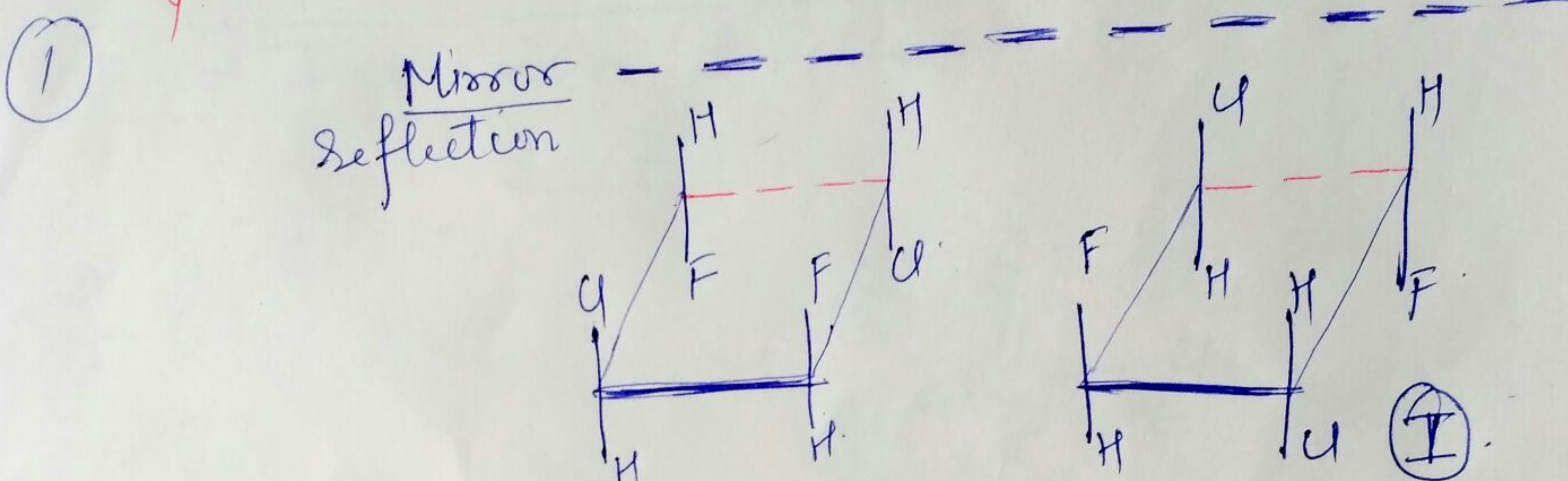
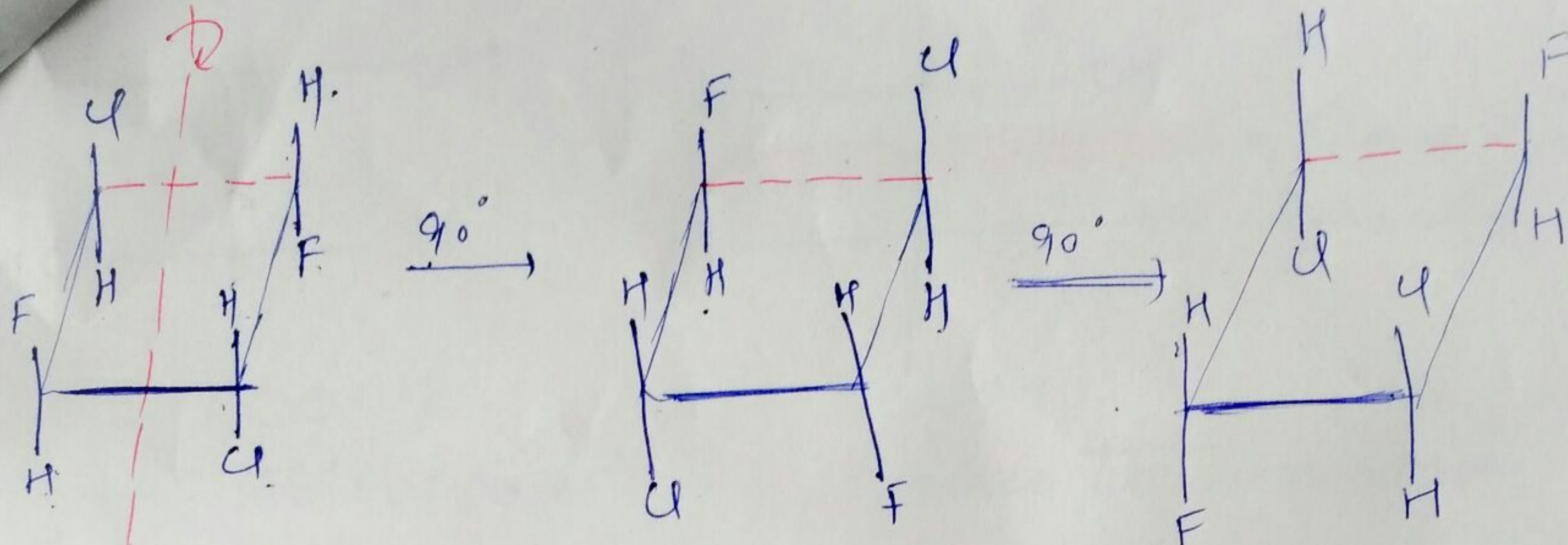
— Shoe, gloves

Optical activity: → when light is passed via a tube containing NICOL Prism (polarizer) the light becomes plane polarized. & when this is passed through the solⁿ of optically active molecule, the plane of polarised light is rotated either to the left or to the right. eg Carbon bonded to different substituents.



Instrument is Polarimeter (Consist of above) optical activity changes with λ of light. The yellow light from sodium lamp is used for experimental. optically inactive substance is placed in path of light beam. The light passes via sample and analyzer is turned to establish a dark field. this setting of analyzer defines 0 optical rotation. Now sample is placed. ~~At~~ The no. of degrees (α) that analyzer must be turned to re establish dark field corresponds to optical activity:

- If rotation of the lens in analyzer is to right (clockwise) — Dextrorotatory (+)
- If rotation is to the left — Levorotatory (-)



The multiplicity of the alternate axis is given by the extent of the rotation in first step

$$\frac{360^\circ}{180} = 2$$

Thus the molecule ① has two fold alternating axis of symmetry.

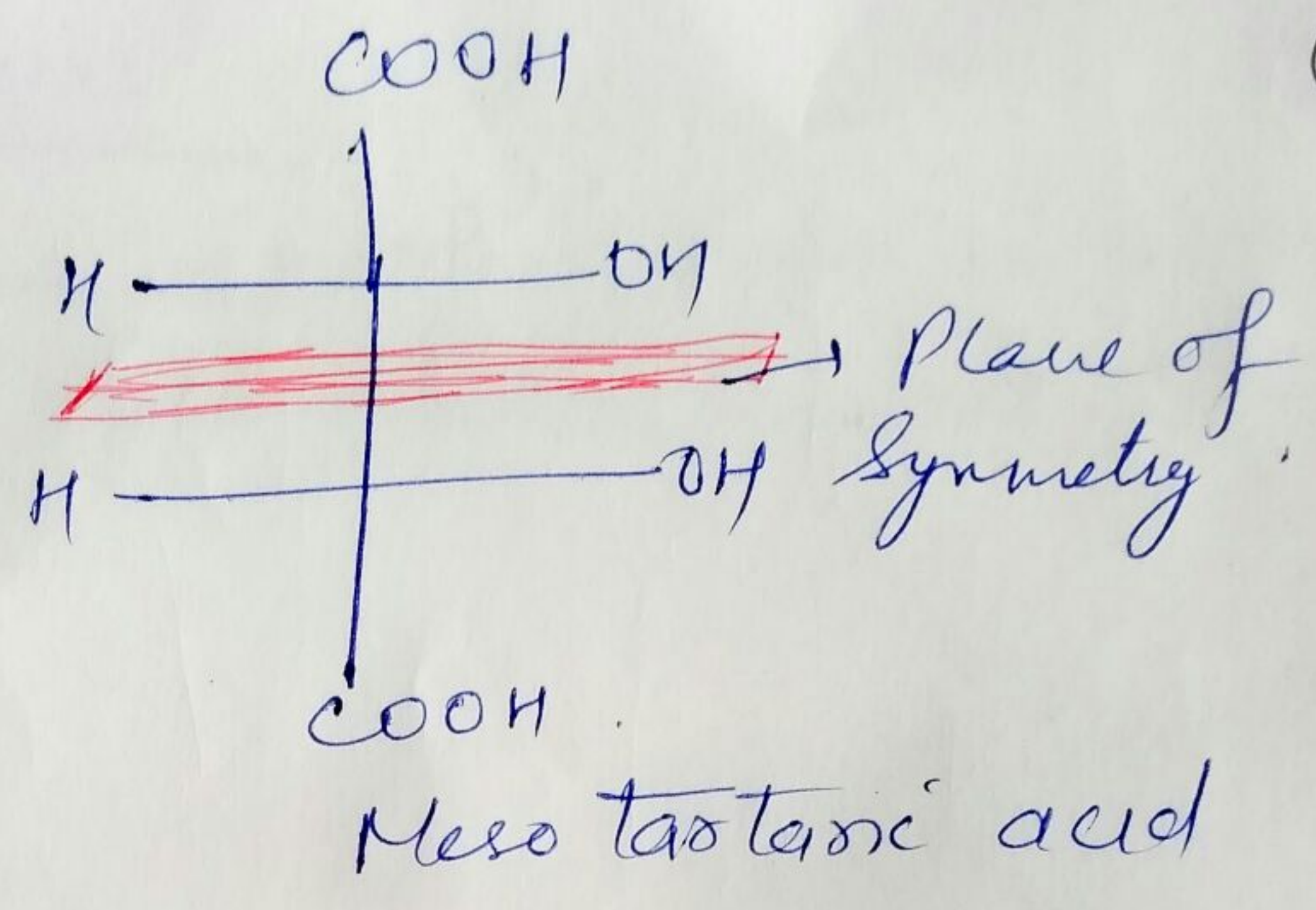
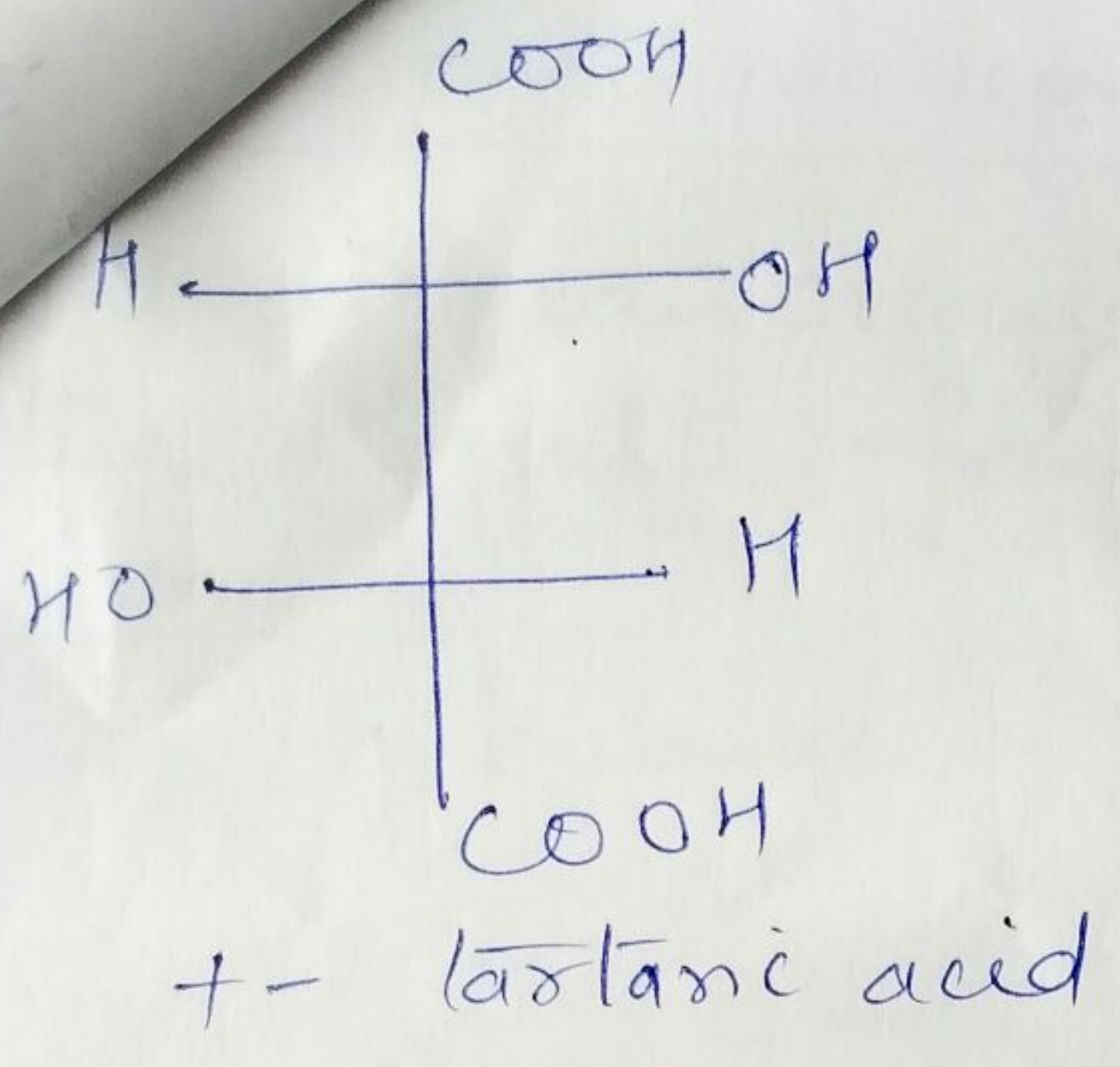
So molecule without S_n axis are dissymmetric and they are optically active.

Plane of symmetry is equal to S_1
 Centre of " " " " S_2

Diastereomers:- stereoisomers that are not mirror images of each other.

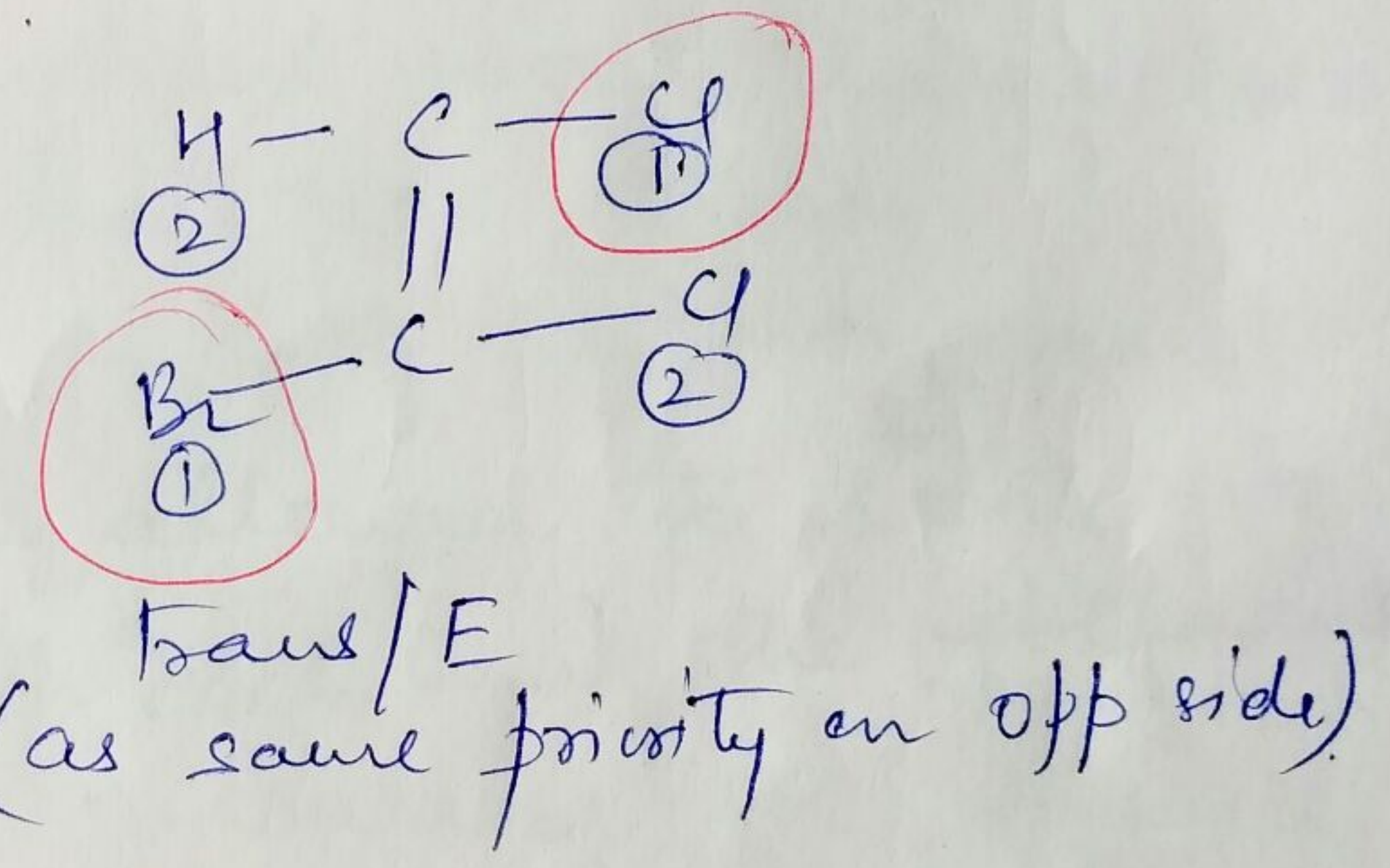
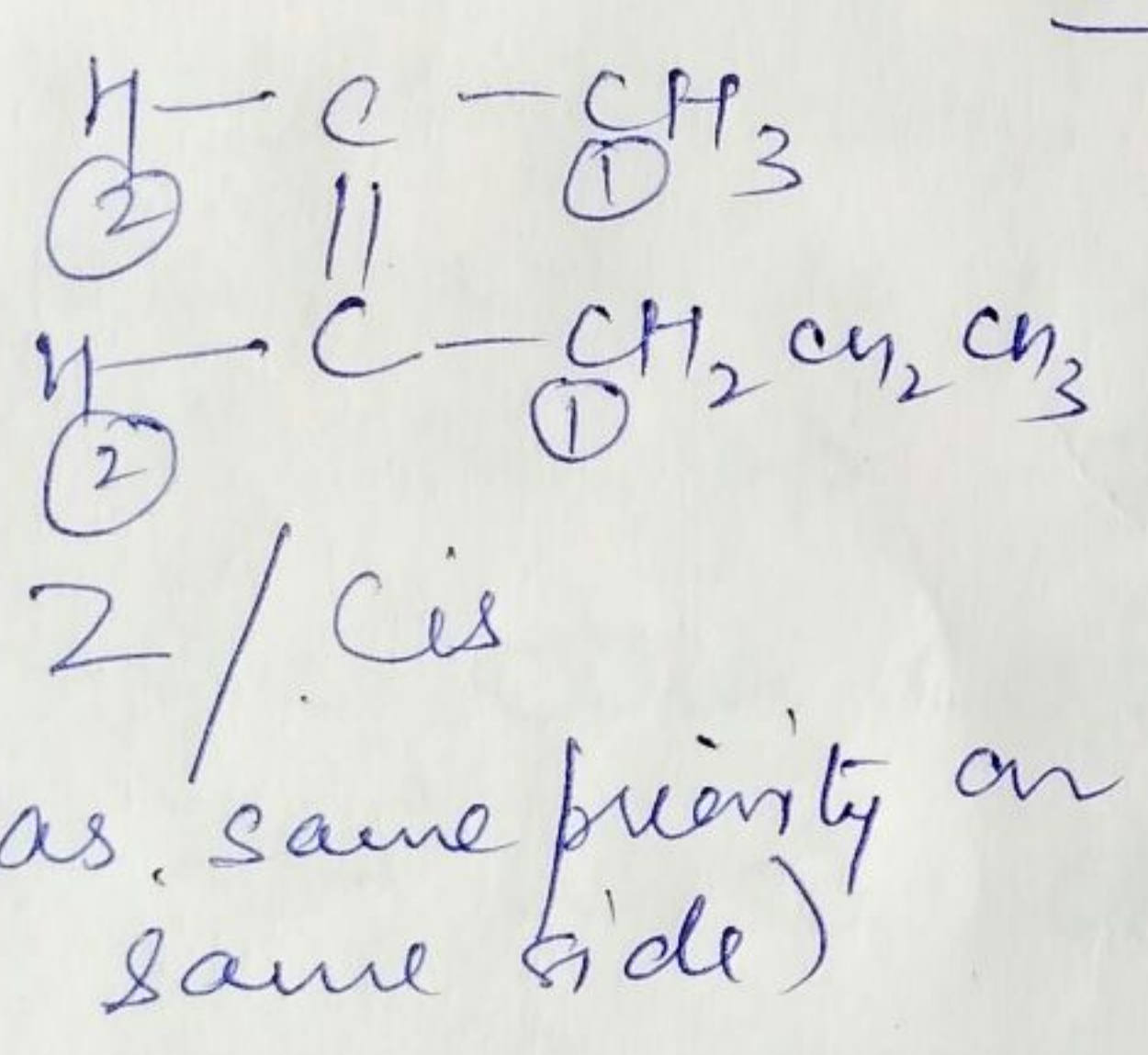
- they have diff. Physical & Chemical properties.
- they have diff amount of free energy.

for eg. +- tartaric acid & meso tartaric acid

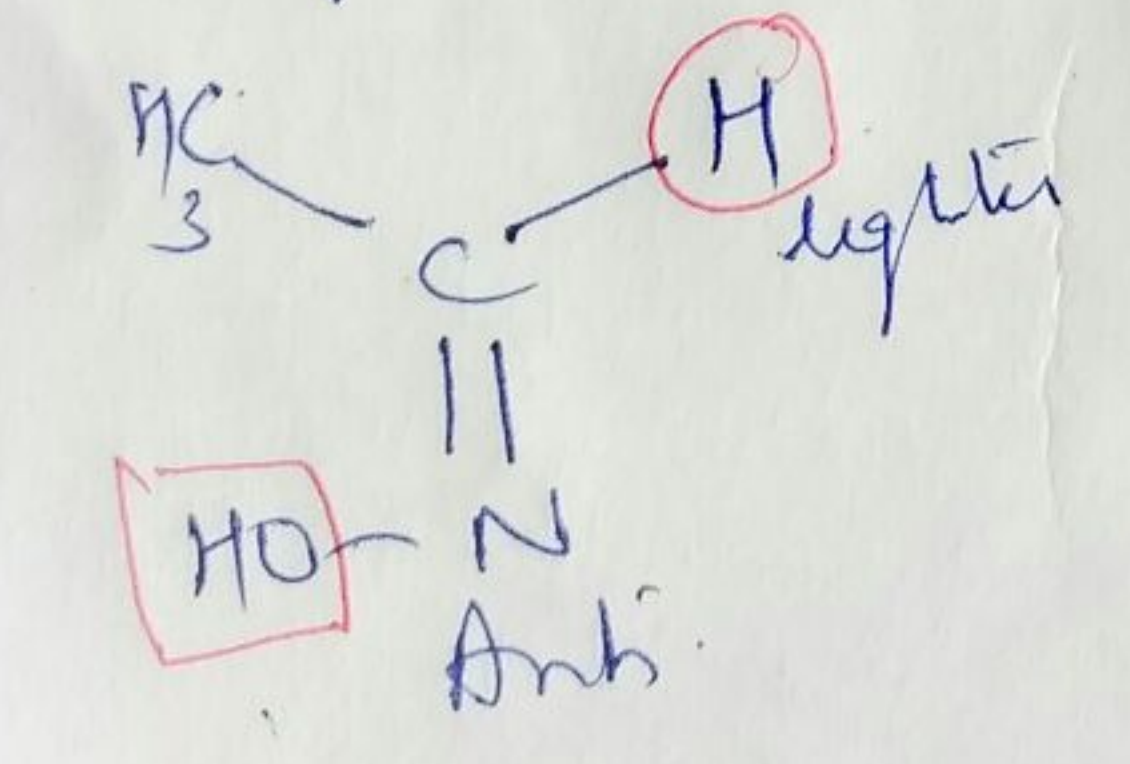
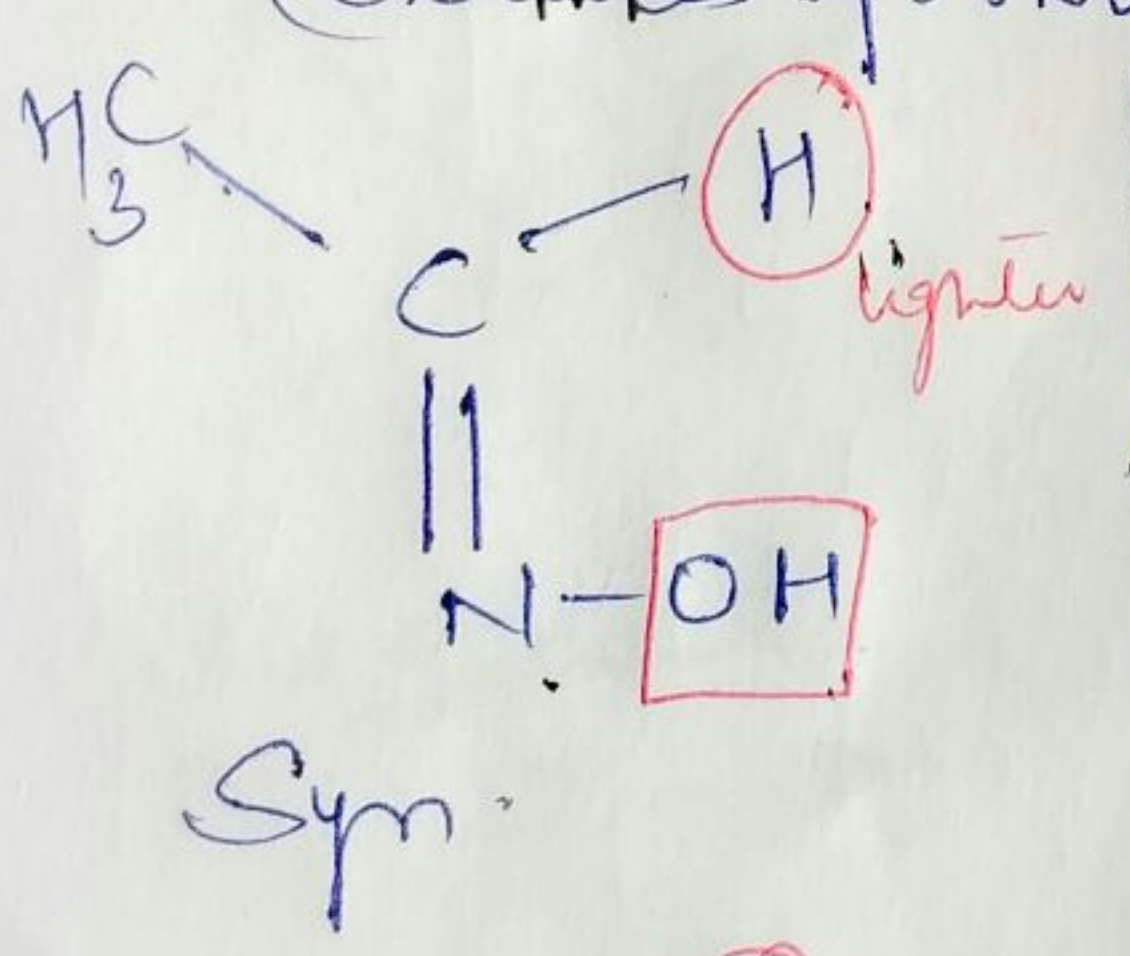


Optical Isomerism Practice

E/Z



Isomerism in oximes (C=N-OH)
(oximes formed by aldehydes or ketones exhibit syn anti isomerism)



Ketones exhibit syn anti isomerism

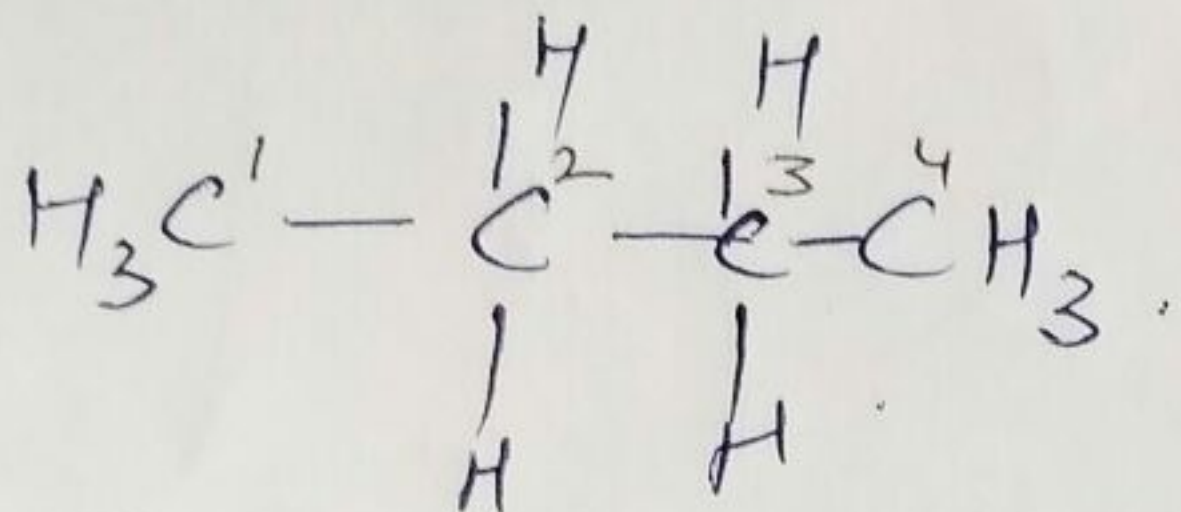
Syn → if the gp attached to N is on ~~lighter~~ side the side of lighter gp attached to C.

Anti → if opp side.

Conformational isomers

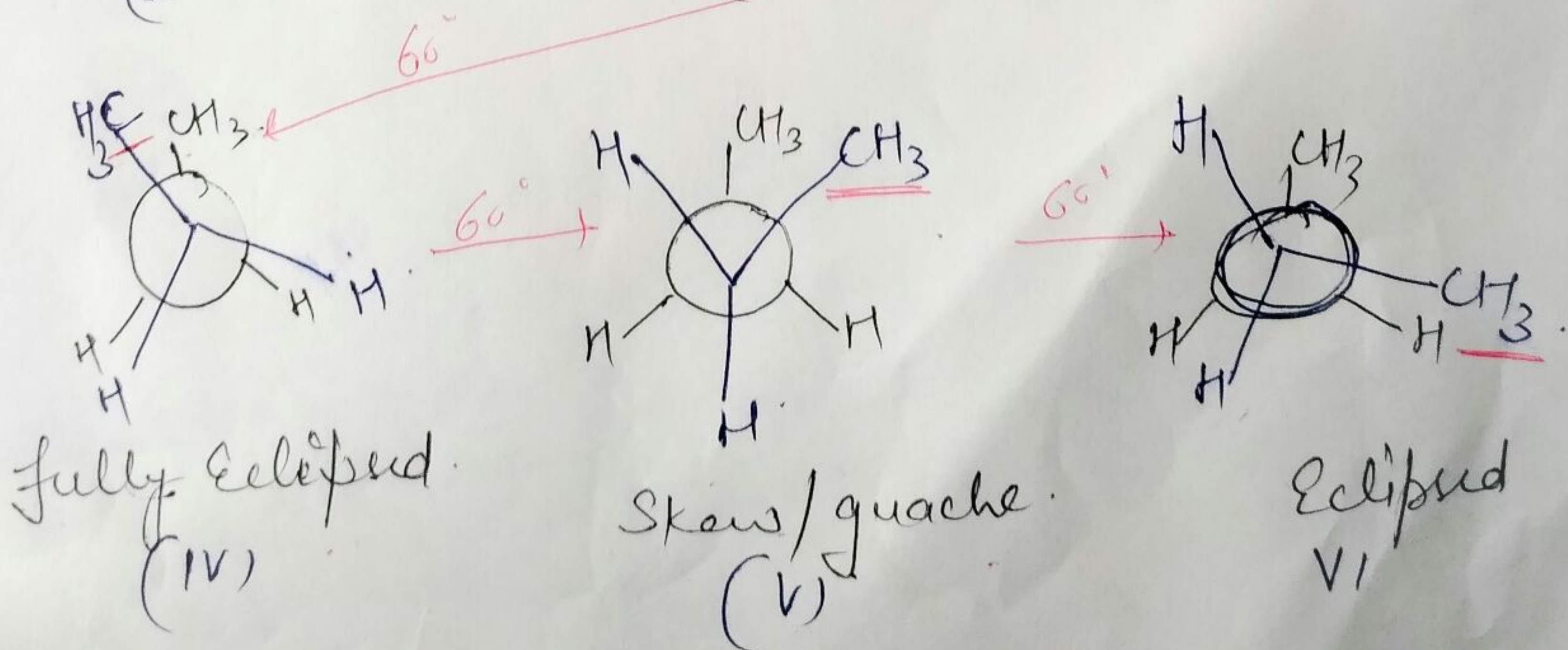
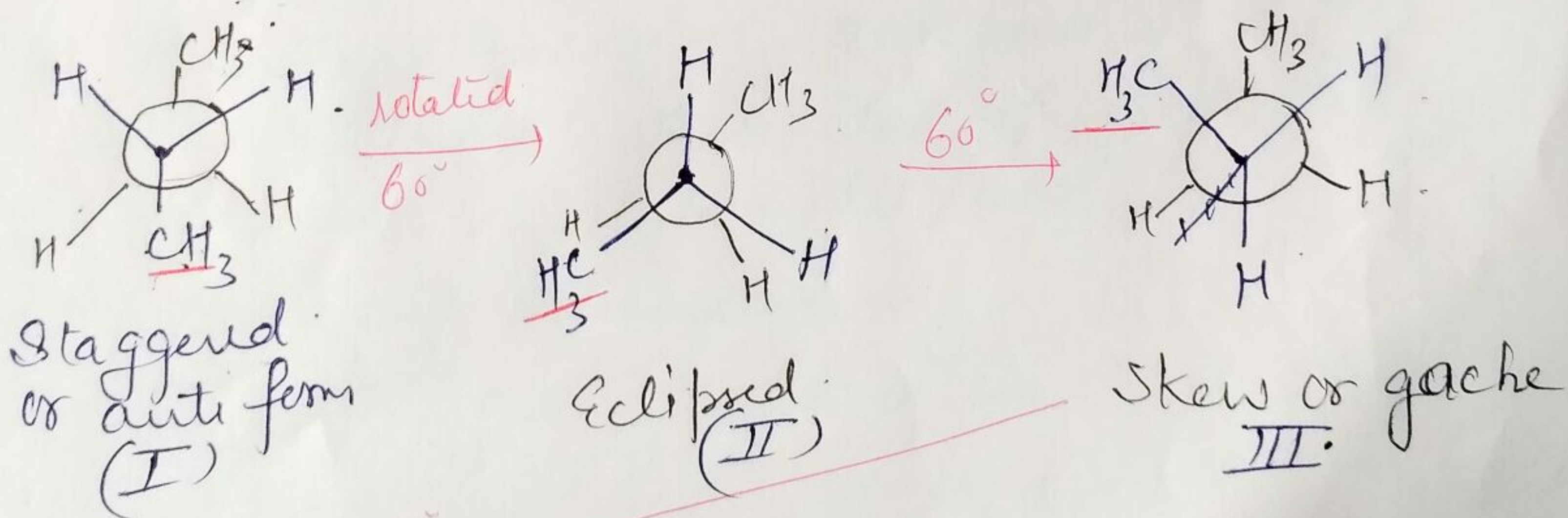
The different arrangement of groups in space that results from free rotation about C₂-C₃ bond.

eg n butane

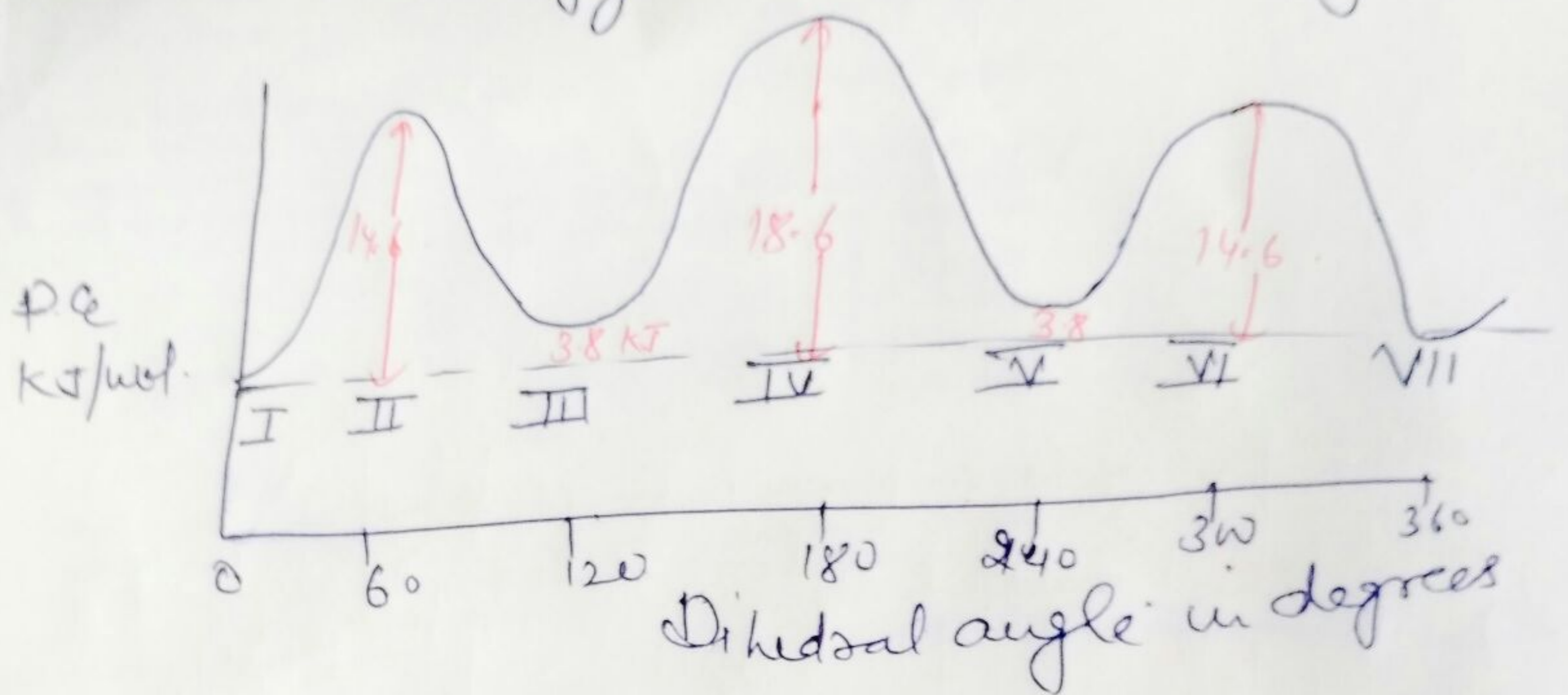


The bond b/w 2nd and 3rd C of butane is cylindrically symmetrical about the nuclear axis, which permits the free rotation.

If one gp CH₃-CH₂- is kept stationary and the other CH₃CH₂ gp is allowed to rotate via 360° in six steps (60° each time) the following six conformations of n-butane are obtained



energy changes (kJ/mol) taking place during rotation of C_2 or C_3 are shown as Potential energy Vs dihedral angle.



So,

- (i) The fully staggered form (I) is most stable.
- (ii) The skew or gauche forms (III, V) are slightly less stable than fully staggered (I). Energy diff b/w them is 3.8 kJ.
- (iii) Potential energy of eclipsed II and VI is 14.6 kJ/mole while that of ~~fully~~ fully eclipsed (IV) is 18.6 kJ/mole.
- (iv) They are stereoisomers.
- (v) III and V are conformational enantiomers.
- (vi) Staggered (I) and gauche (III/V) are conformational diastereomers.
- (vii) Stability order of isomers.



Fully staggered \rightarrow skew or gauche \rightarrow Eclipsed \rightarrow fully eclipsed.

Iso means equal, Mer means first

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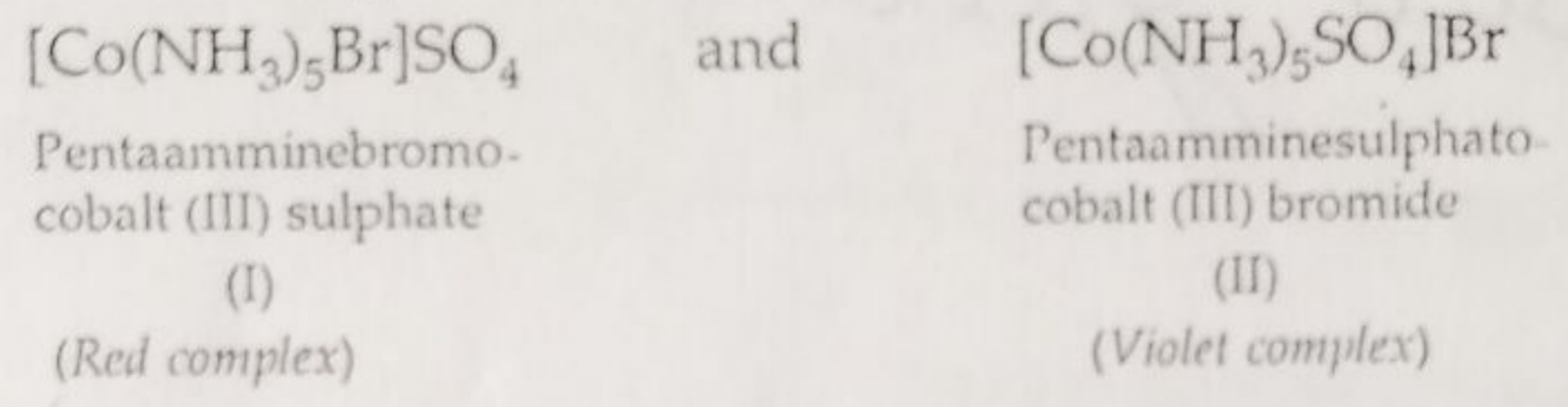
ISOMERISM IN COORDINATION COMPOUNDS

As in the case of organic compounds, the coordination compounds exhibit following two main types of isomerism :

(A) **Structural isomerism** arises due to the *difference in structures*. This type of isomerism can be further subdivided into following types :

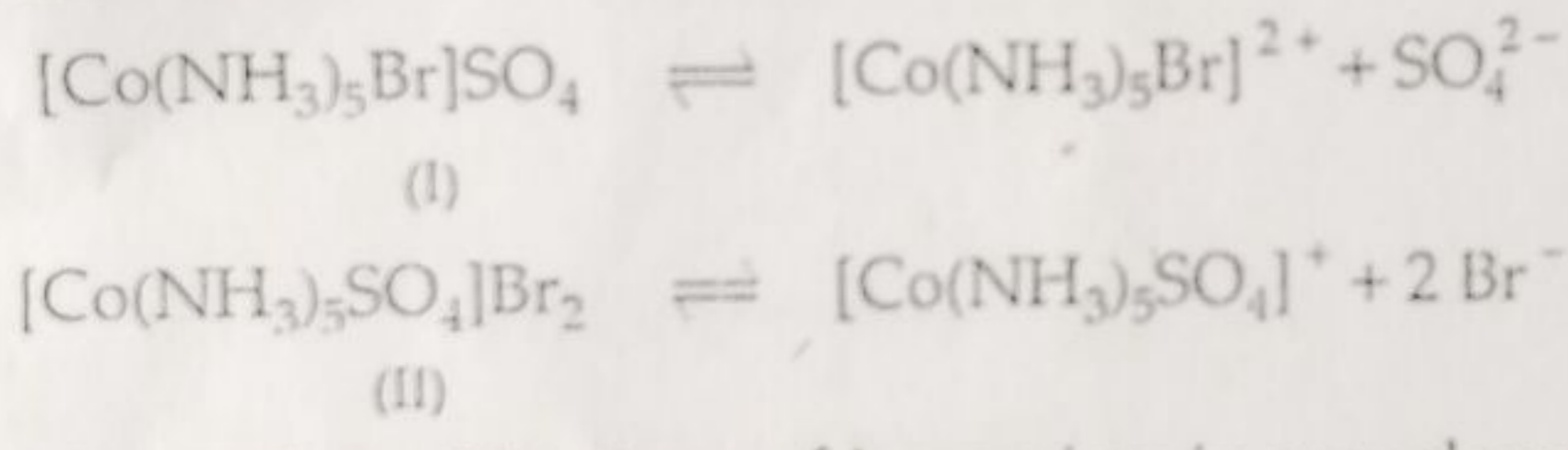
(1) **Ionization isomerism** : Complex compounds which have the same empirical formula, but give different ions in solution on ionization, are called **ionization isomers**. This type of isomerism is due to the difference in positions of ligands, because ligands in the coordination sphere do not ionize.

Example : The following two isomers :

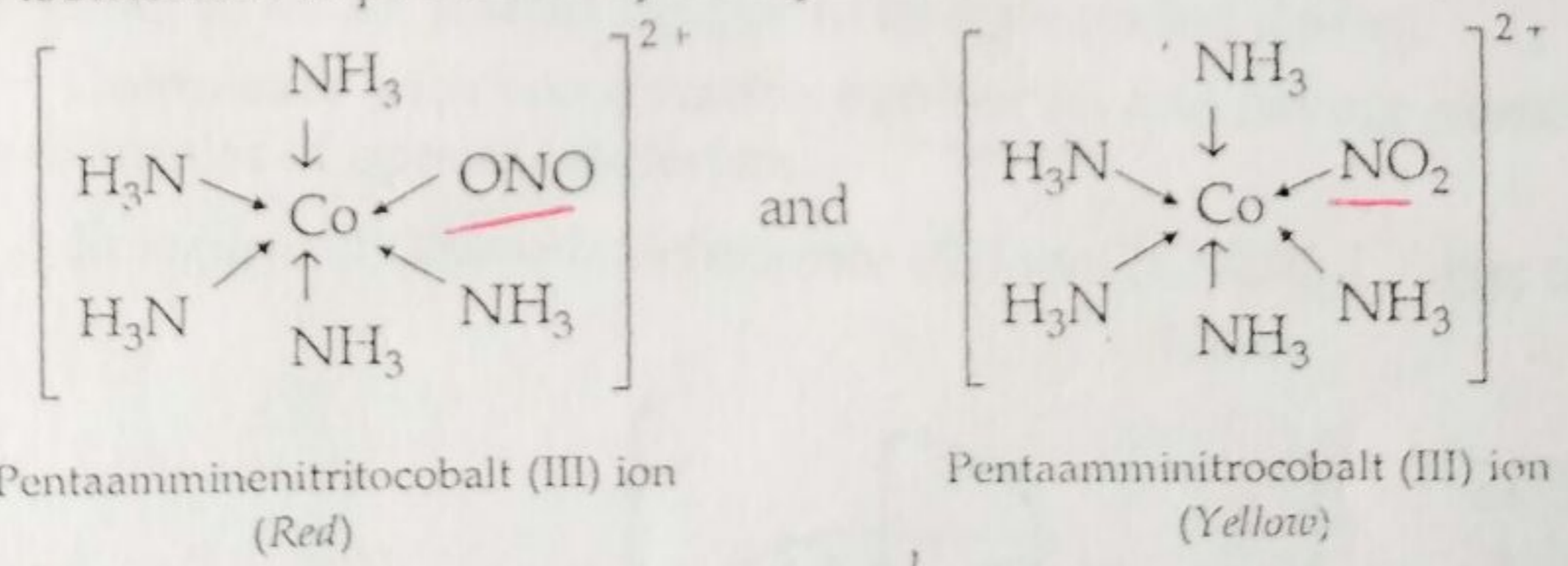


This is exchange of ions in coordination sphere of metal ion and ions outside it

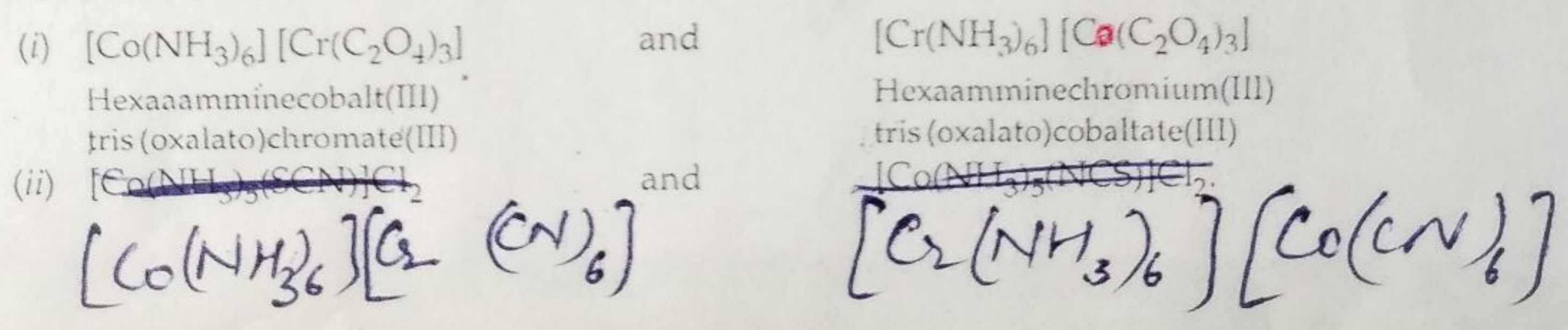
Compound (I) gives the test for **sulphate ions** (i.e., a white precipitate of BaSO_4 with BaCl_2 solution); while (II) gives test for **bromide ions** (i.e., a light yellow precipitate of AgBr with AgNO_3 solution) and *not* for sulphate ions, when dissolved in water. Thus, in (I), the sulphate ion is *outside* the coordination sphere; while in (II), the bromide ion is *outside* the coordination sphere. The modes of ionization of these two isomers are :



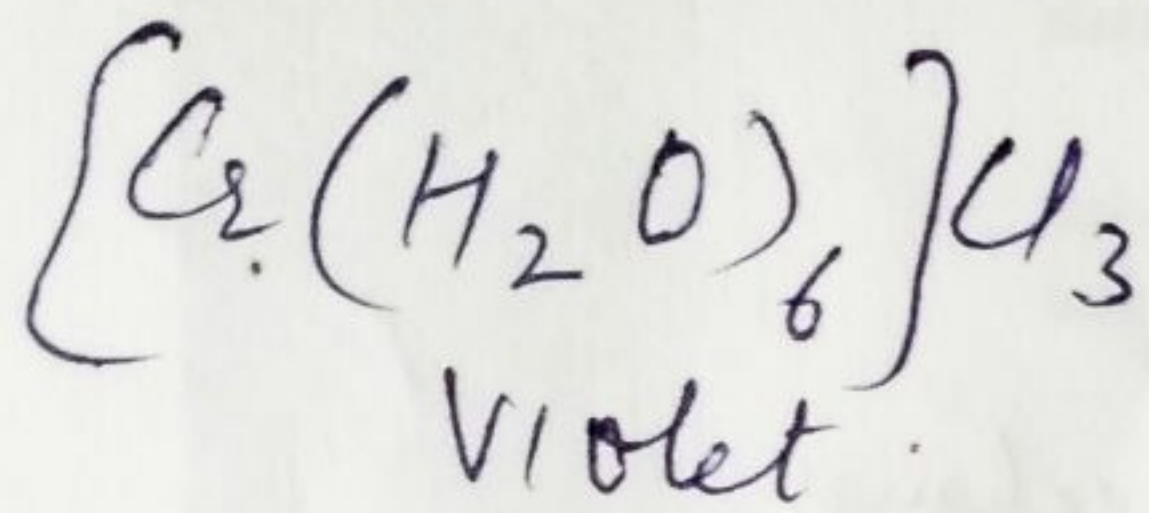
(2) **Linkage isomerism** : This type of isomerism in complexes is found due to the presence of certain ligands having two or more different atoms so that they can coordinate with the central metal ion through either of the atoms. For example, NO_2^- ion can ligand either through its nitrogen atom or oxygen atom. This gives rise to two different isomers, which differ in the metal atom-ligand atom linkage. Other ligands which can give rise to linkage isomerism are SCN^- and $\text{S}_2\text{O}_3^{2-}$ ions. An example of linkage isomerism is provided by two pentaamminenitrocobalt (III) ion.



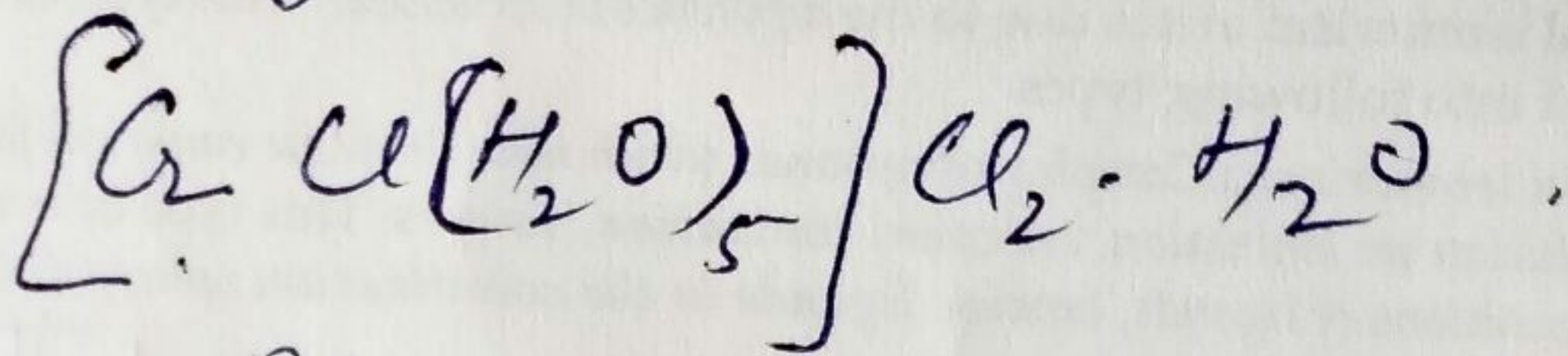
(3) **Coordination isomerism** is a type of isomerism exhibited by complex compounds in which both cation and anion are complexes and the ligands can exchange between the cation and anion. Example of coordination isomers are :



(4) Hydrate Isomerism: Compds which have same composition but differ in the no. of water molecules present as ligands (i.e. in coordination sphere) and as molecules of hydration.



Violet.

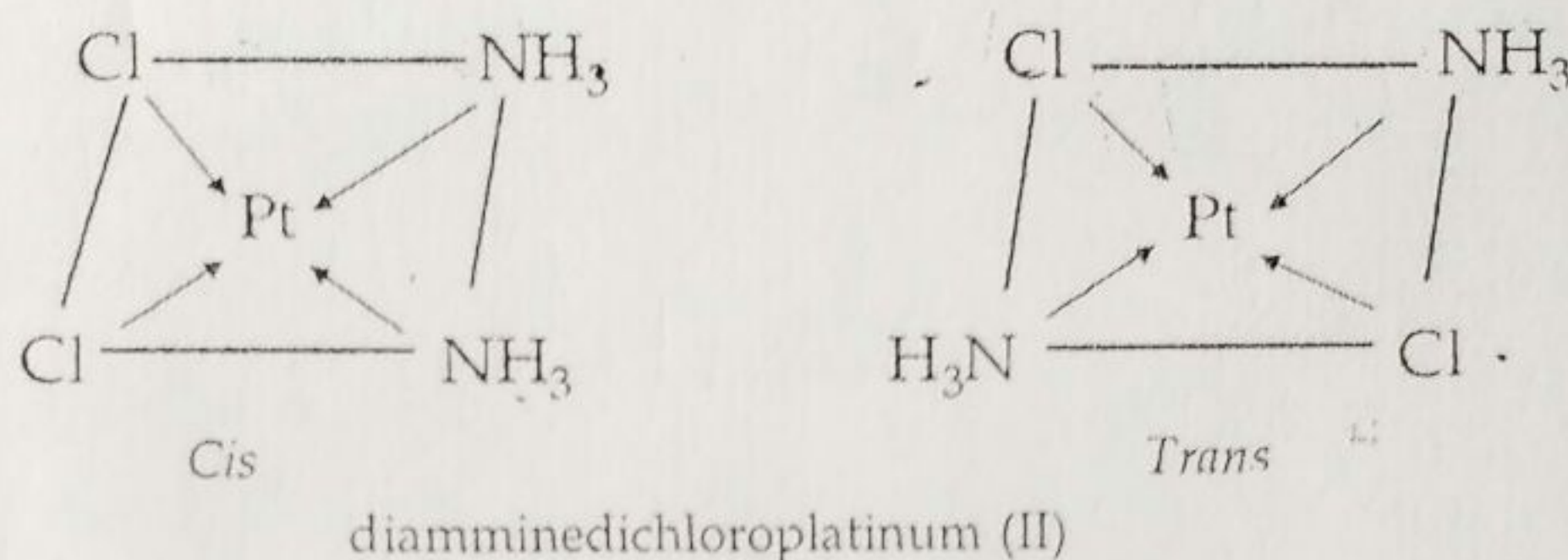


Blue green.

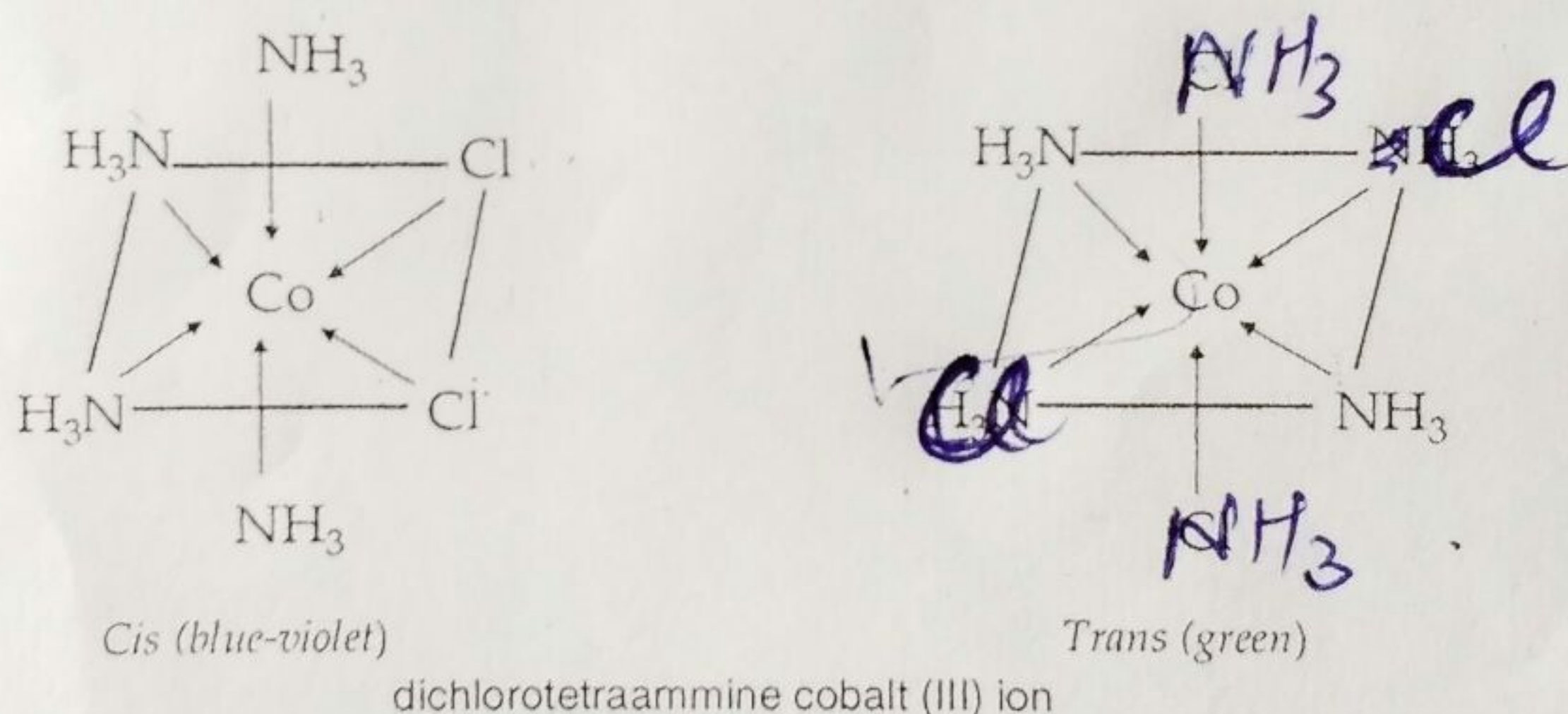
(B) Stereoisomerism (or space isomerism) in coordination compounds is due to difference in arrangement of ligands in space around a given metal atom or ion. It is of following two types :

(1) Geometrical (or cis-trans) isomerism : This type of isomerism occurs in disubstituted complexes with coordination number four and six having square planar and octahedral arrangement respectively. It does not occur in tetrahedral complexes, because the relative positions of the ligands attached to the central metal atom or ion is same wrt each other. When similar groups are adjacent to each other, it is called cis isomer; whereas when similar groups are opposite to each other, it is called trans isomer.

Examples : (i) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ complex, with square planar arrangement, exists in two geometrical isomeric forms :



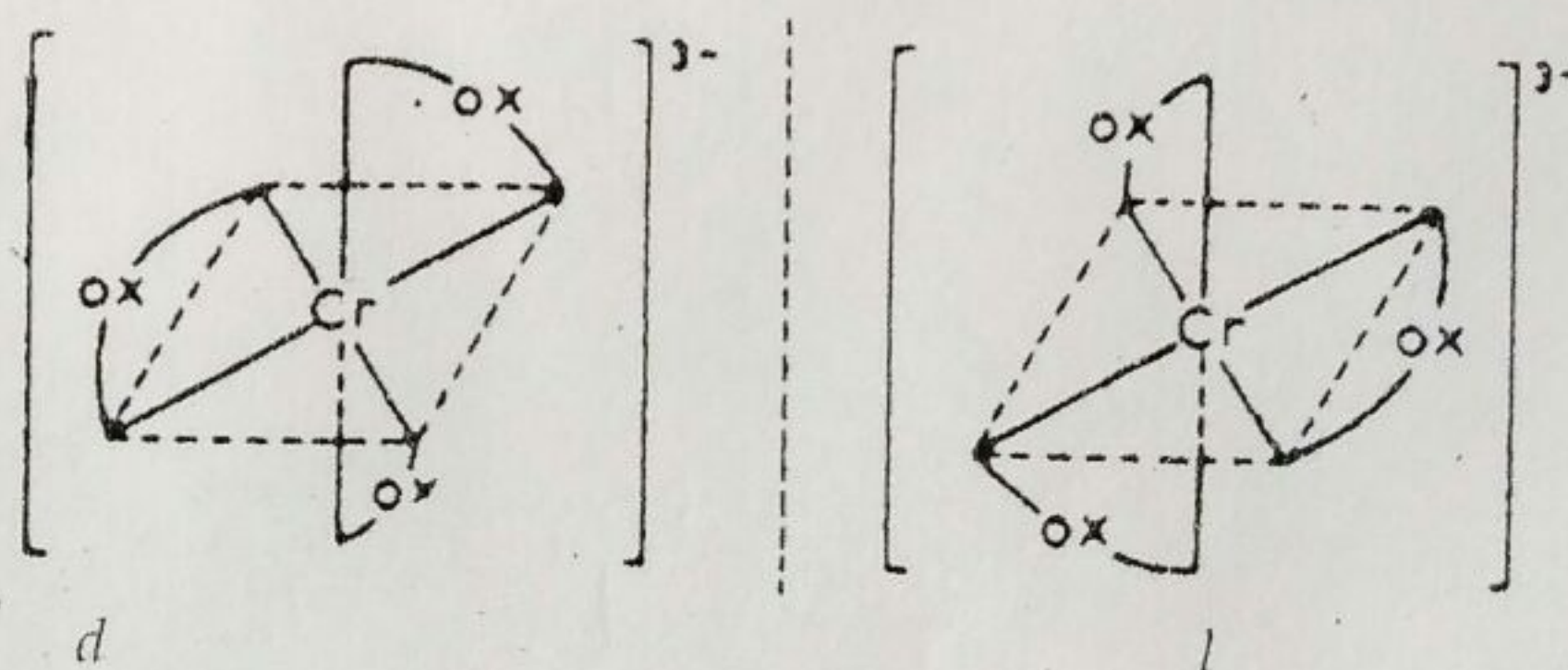
(ii) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ complex, ion, with octahedral arrangement, exists in two geometrical isomeric forms :



(2) Optical isomerism : is due to lack of symmetry in the complex. Optical isomers are just mirror images of one another and they cannot be superimposed. Optical isomers rotate the plane of polarized light either to its left (called levo) or to its right (called dextro).

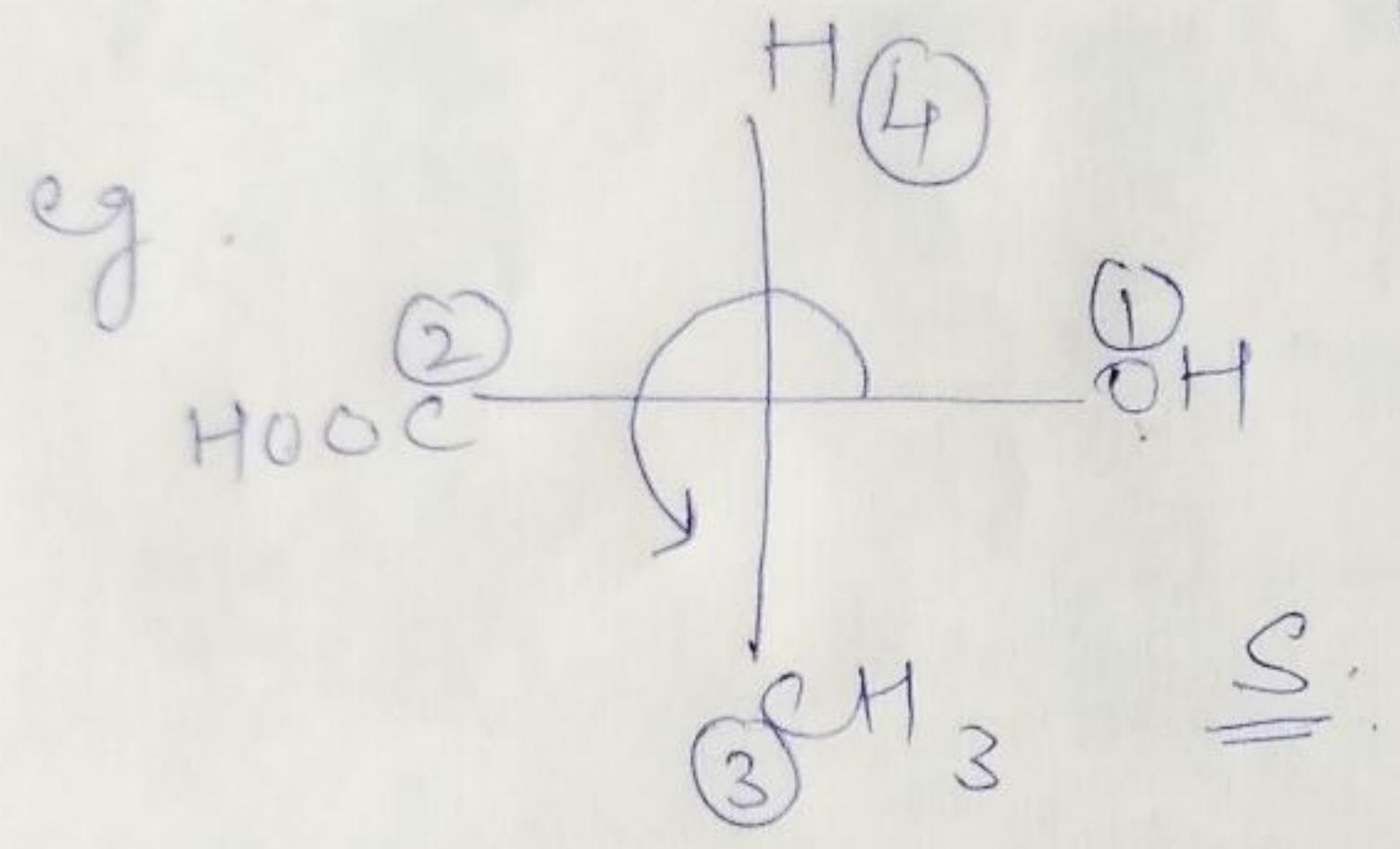
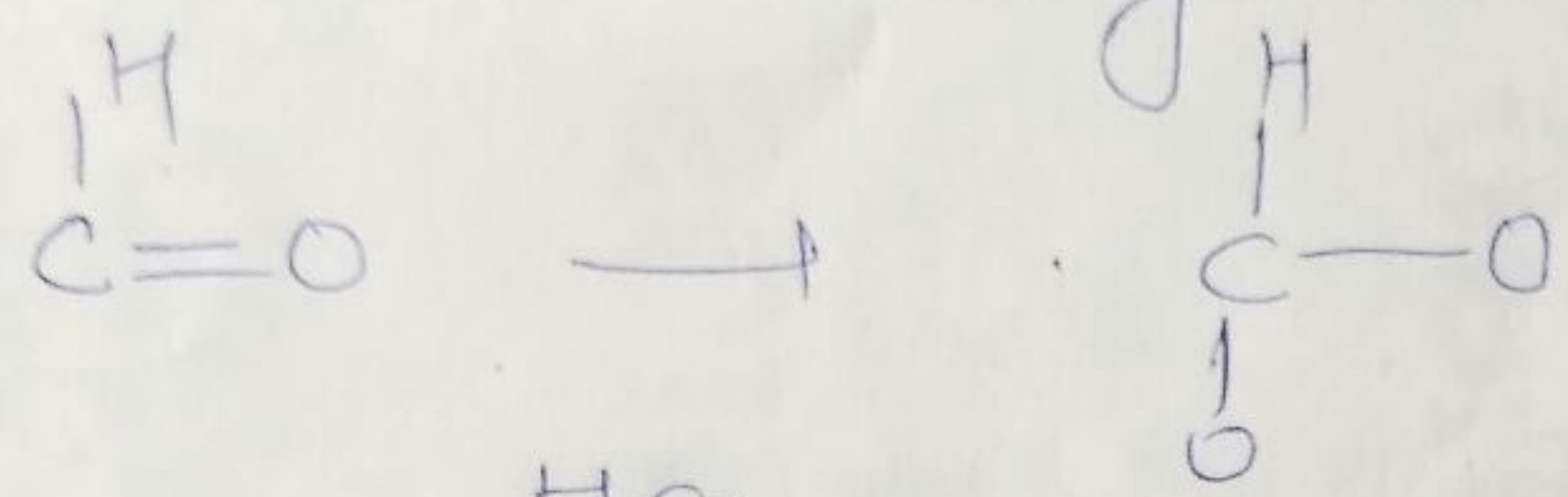
Complexes with coordination number six and having bidentate and hexadentate ligands provide examples of optical isomerism.

Examples : (i) Trioxalatochromate (III) ion, $[\text{Cr}(\text{OX})_3]^{3-}$ has two optical isomers are :



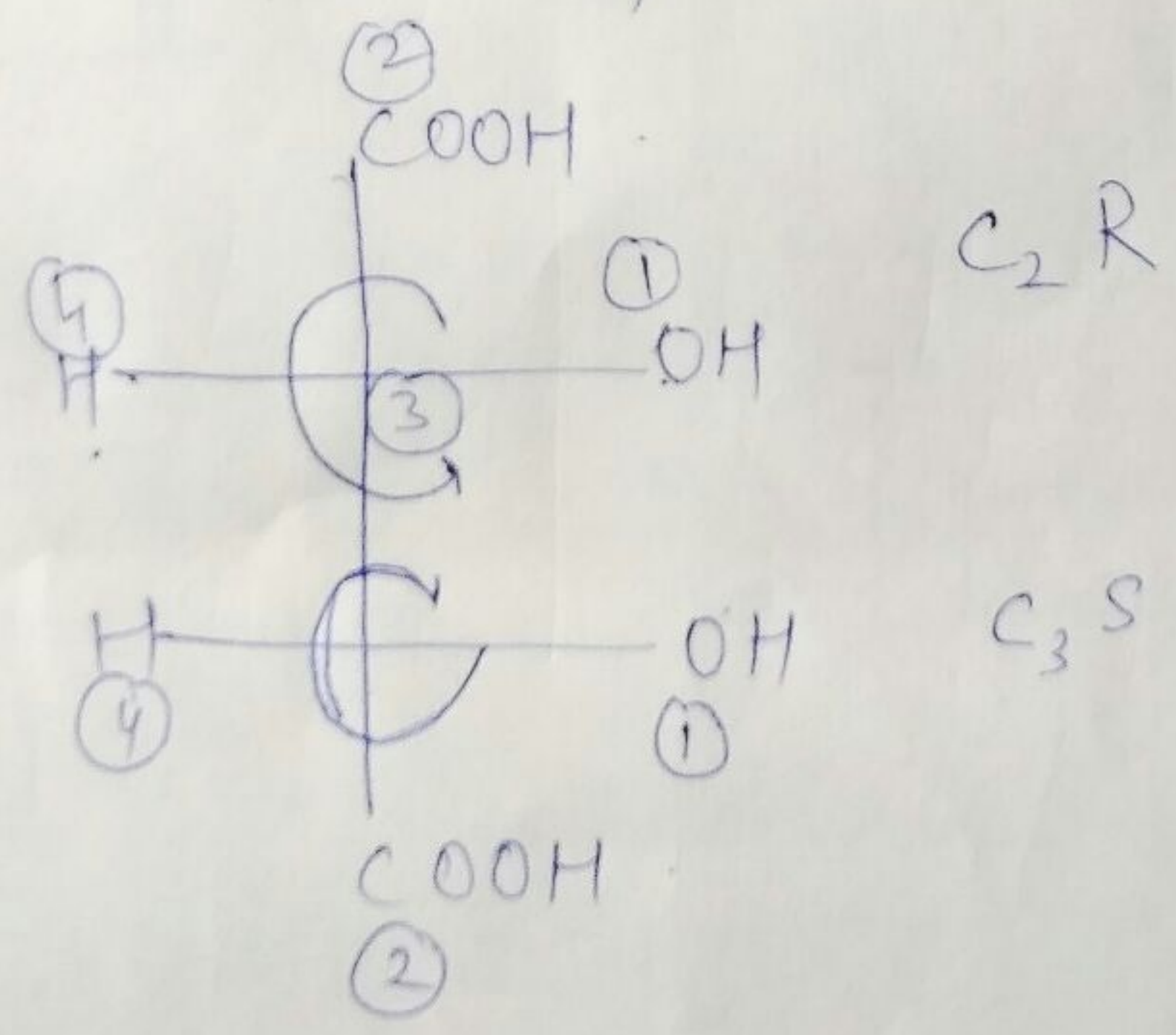
and S configuration is applicable to Chiral centre
is based on CIP Nomenclature (Cahn
Ingold & Prelog).

- #1 here numbering is done acc to higher atomic no. get higher priority.
- #2 double bond is regarded as 2 single bonds.



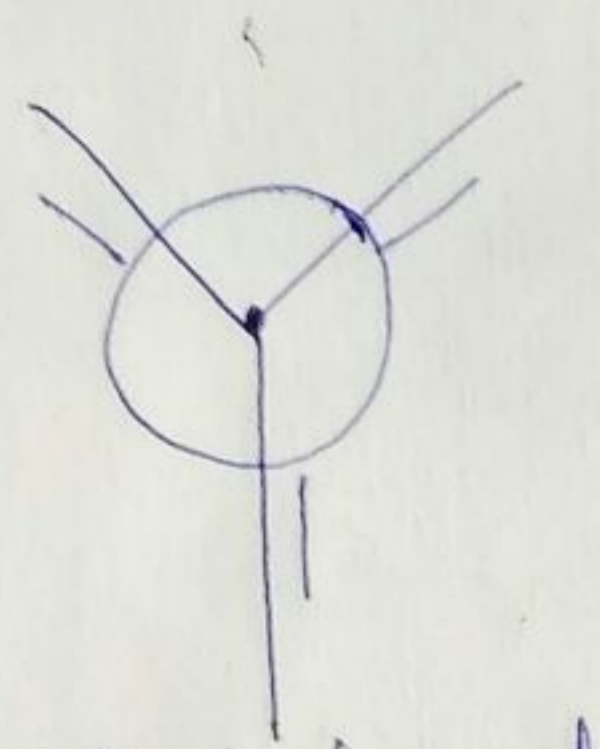
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(i) If lowest priority gp is on vertical position.	Eye moves clockwise	Eye moves anticlockwise
	R	S
(ii) If lowest priority gp is on horizontal position	S	R

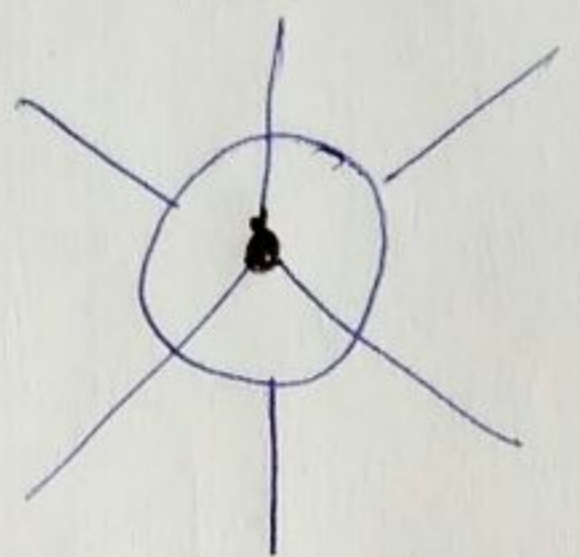


Conversion of Fischer into Newman & Vice Versa.

- 1) Viewing the C-C bond by head front is Newman form.
- 2) front C as point C & Back C in circle form.



Eclipsed

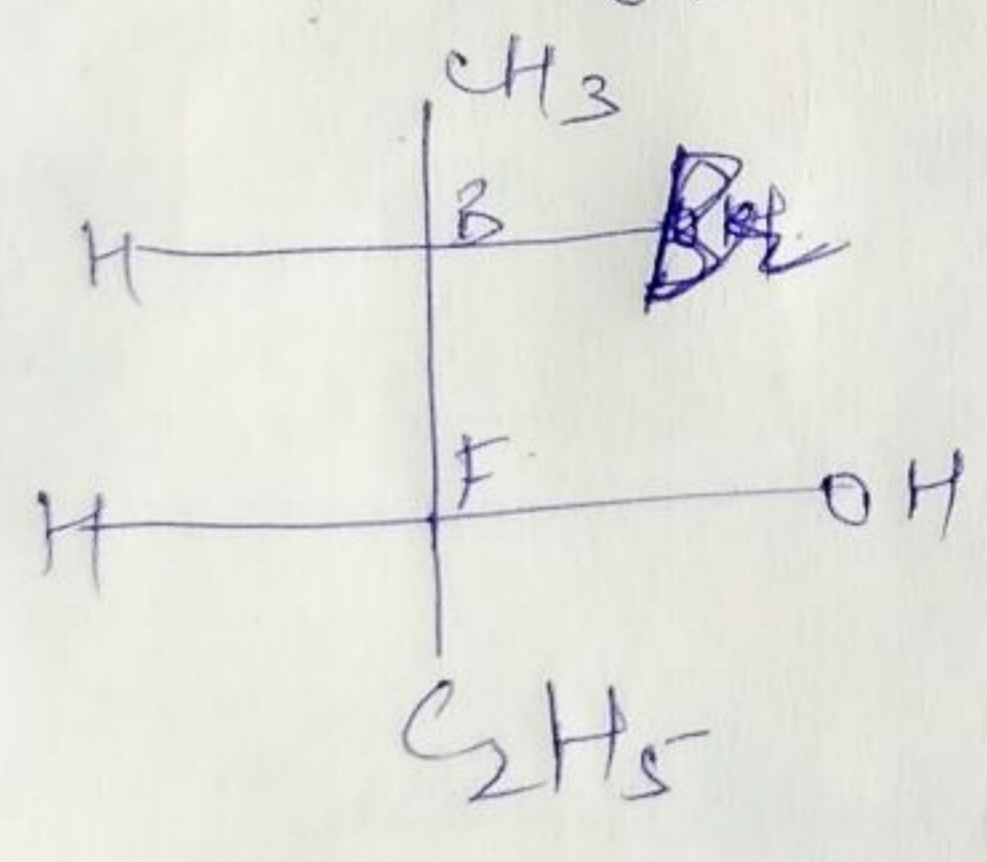


Staggered

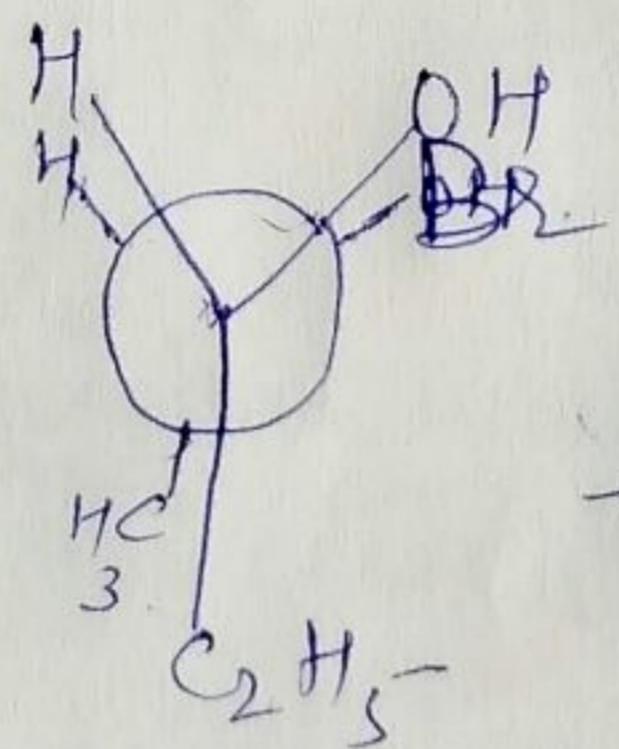
(Unstable due to torsional strain)

3) Groups on the same side becomes anti in the staggered form of Newman formula & vice-versa

4) Lower C is front C. Upper C - Back C.

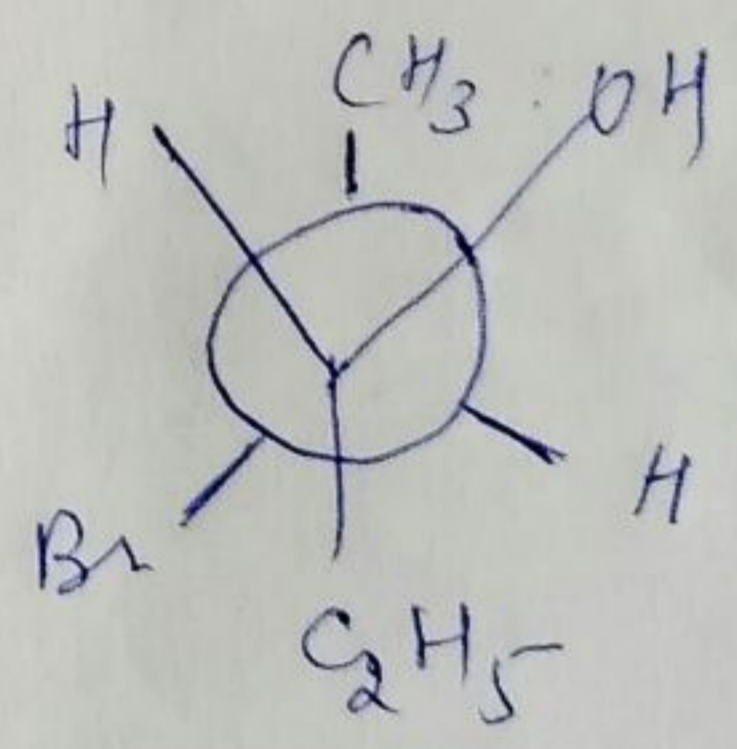


Fischer

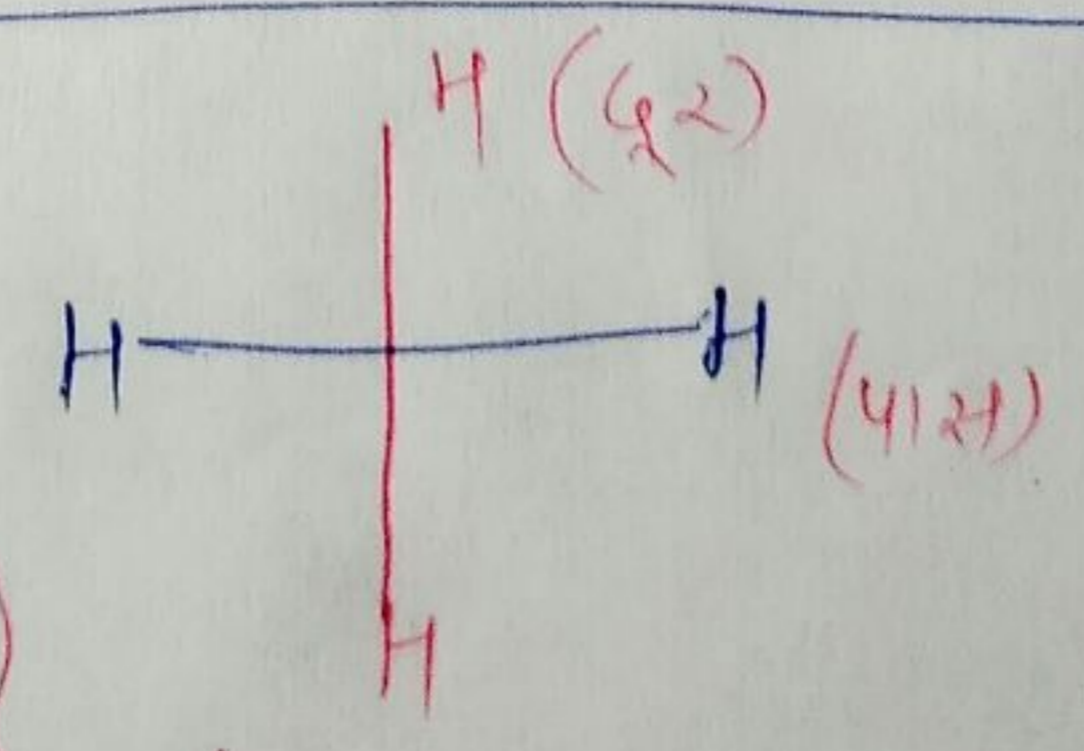
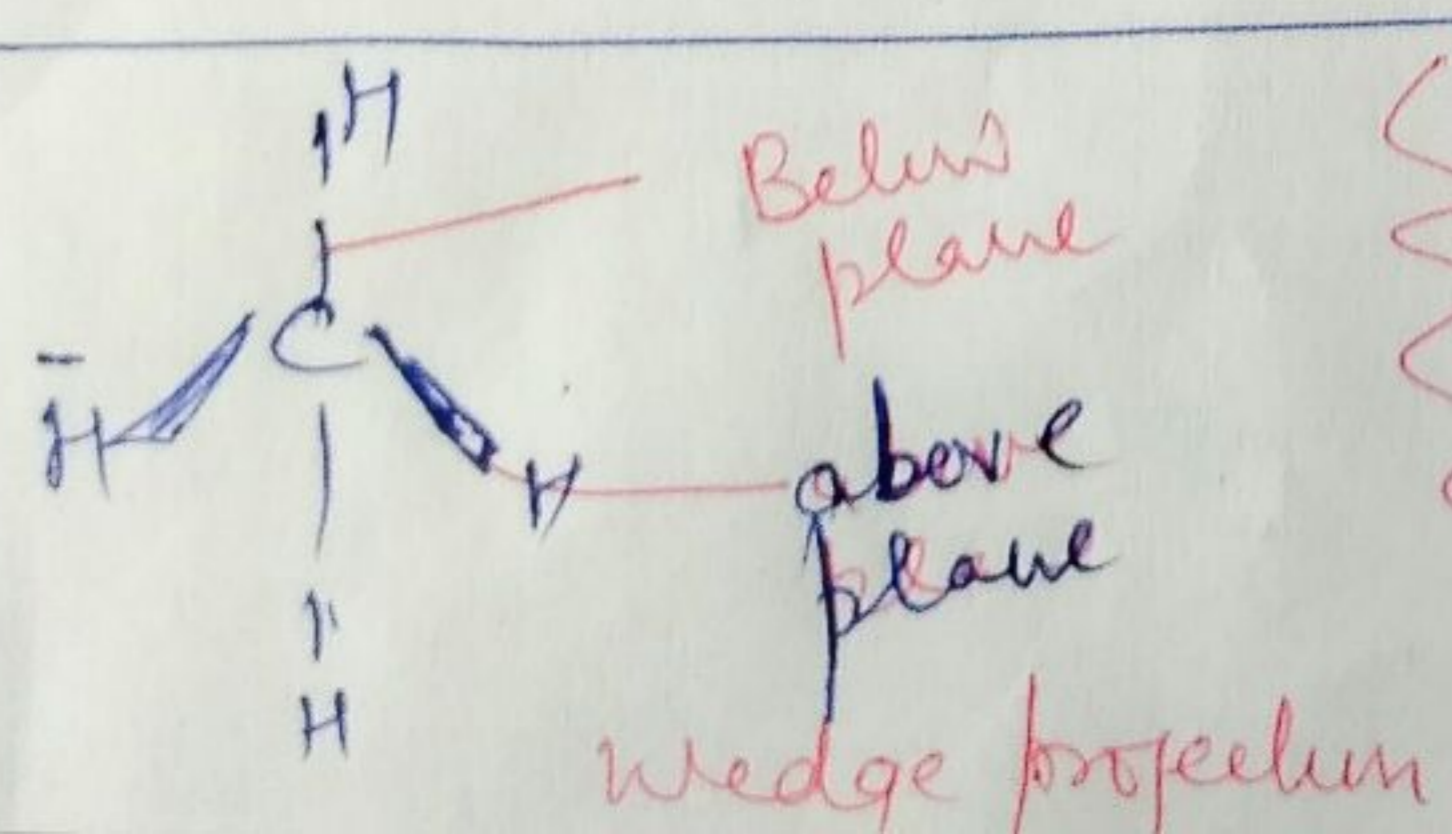


Eclipsed

Rotate by 180°



(Newman)



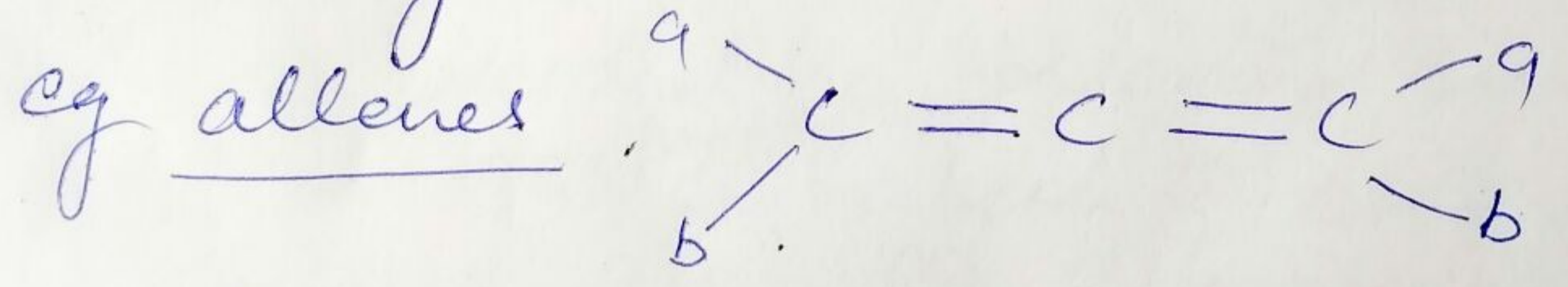
isomerism molecule which
Meso form have centre of sym/plane of sym.
 though having chiral C. are internally compensated
 form called Meso form eg Meso tartaric acid.

② The no. of optical isomers for chiral molecules

	No. of chiral C	Formula	No. of optical isomer
①	one	$2^1 + 1$	<u><u>$2 + 1 = 3$</u></u>
②	two or more unlike C.	2^n (configuration) 2^{n-1} (racemic)	
③	two or more like C eg (tartaric acid)	2^{n-1}	

④ Compds without chiral C atoms

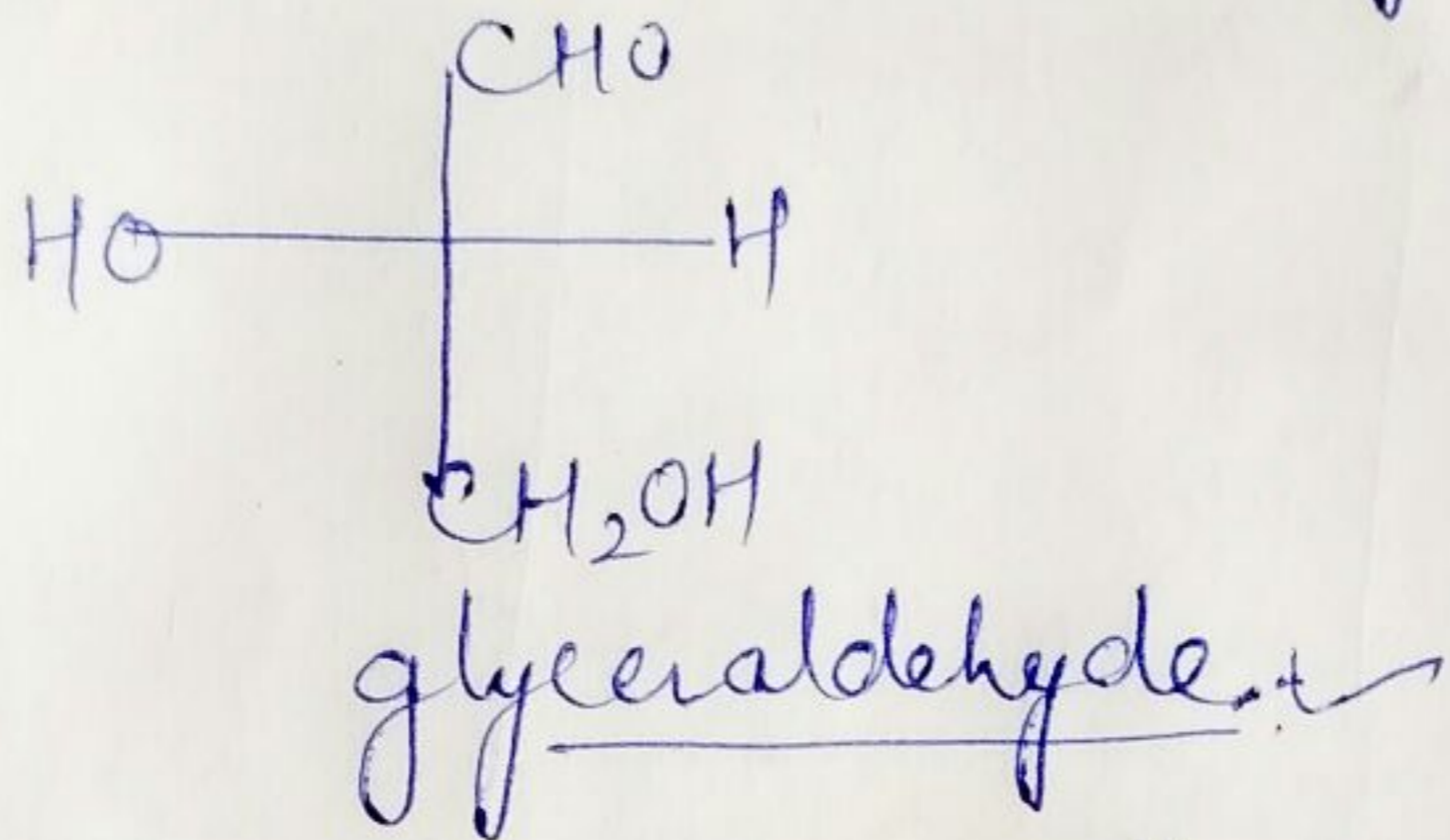
for showing optical activity, the presence of chiral C is not the necessary or sufficient condition. The chirality as a whole is the necessary condition.



Cumulenes having even no. of C atoms differently substituted at ends.

Actual Configuration: - Actual Configuration of the chiral molecules in space.

Relative configuration: - The configuration of a compound with reference to the arbitrary assigned configuration of the reference substance is known as its Relative configuration.

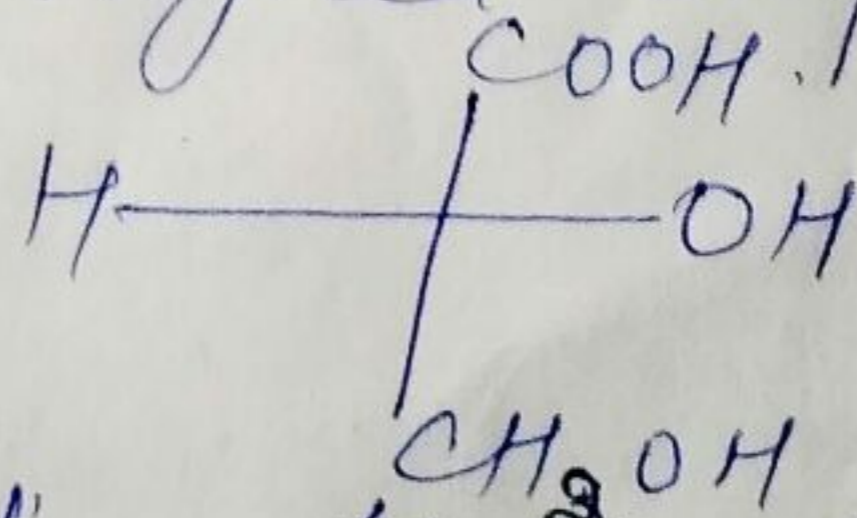


Enantiomers (having single chiral centre) differ only in their absolute configuration

but 2 diastereomers (having more than one chiral centre) differ in their relative configuration.

Absolute configuration is decided by experimental proof - Actual arrangement around an atom which is decided by priority rules.

Byevoet in 1951^{found that} the absolute configuration of dextrotartaric acid as determined by a special type of X Ray analysis of its Na-Rubidium salt was found to be the same as that on the arbitrarily assigned configuration of D(+) glyceraldehyde.

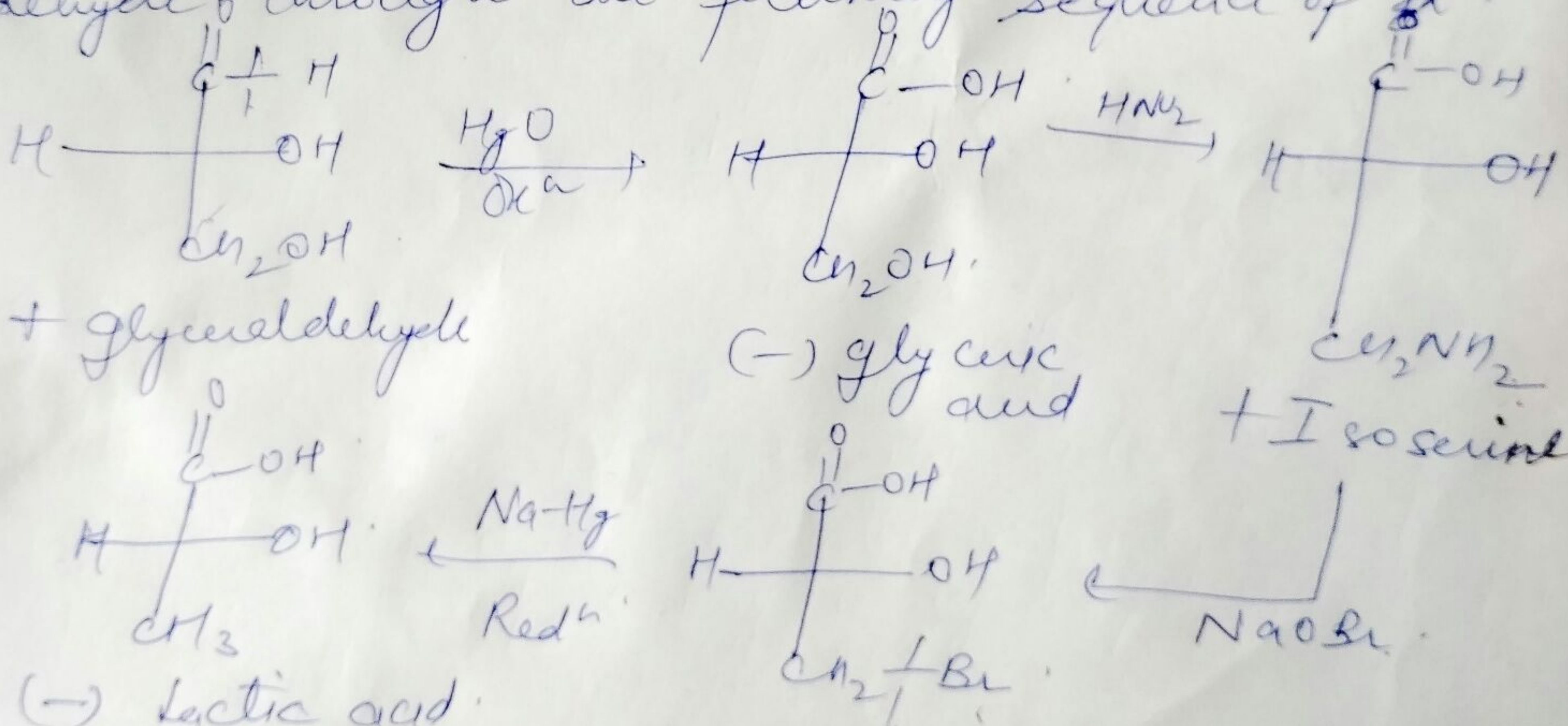


Hence all the configurations that have been assigned relative to (+) glyceraldehyde are, conveniently Absolute Configuration

relation of chiral molecules were related (14) each other through rxⁿ of known stereochemistry. Attempts were also made to relate all configurations back to a simple compound that have been chosen arbitrarily to be standard.

This standard compound was D-glyceraldehyde. The absolute configuration of any compound is now known once it had been correlated directly or indirectly with glyceraldehyde.

for eg the configuration of laevorotatory (-) lactic acid can be correlated to (+) glyceraldehyde through the following sequence of rxⁿ.



By chemical transformations showing how the configurations of laevorotatory (-) lactic acid had been related to dextrorotatory (+) glyceraldehyde. None of the transformations causes any change at asymmetric C atoms.