

① STEREOCHEMISTRY

Terminology

Stereochemistry: structure in three dimensions

Stereoisomerism: different spatial arrangement of atoms or groups

Stereoisomers: Isomers have the same sequence of covalent bonds but differ in the relative disposition of atoms in space.

Enantiomers: mirror images

Diastereomers: Not mirror images

Racemic modification: mixture of equal parts

Resolution: separation of a racemic modification

Meso structures: molecules with internal mirror planes.

Chiral center: Carbon with 4 different groups attached.

Chirality: The property of non-superimposability

(2)

Configuration: the fixed relative spatial arrangement of atoms in a molecule.

Conformations: Rotations around single bond producing different arrangements.

Geometrical isomerism: Restricted rotation around double bond.

Optical isomerism: mirror image isomers rotating plane polarised light in opposite directions.

Plane of symmetry: mirror plane cutting the molecule into 2 equal parts.

Center of symmetry: A line passing through the center of a molecule meets identical parts.

Alternating axis of symmetry: Rotation followed by reflection produces original molecule.

(3)

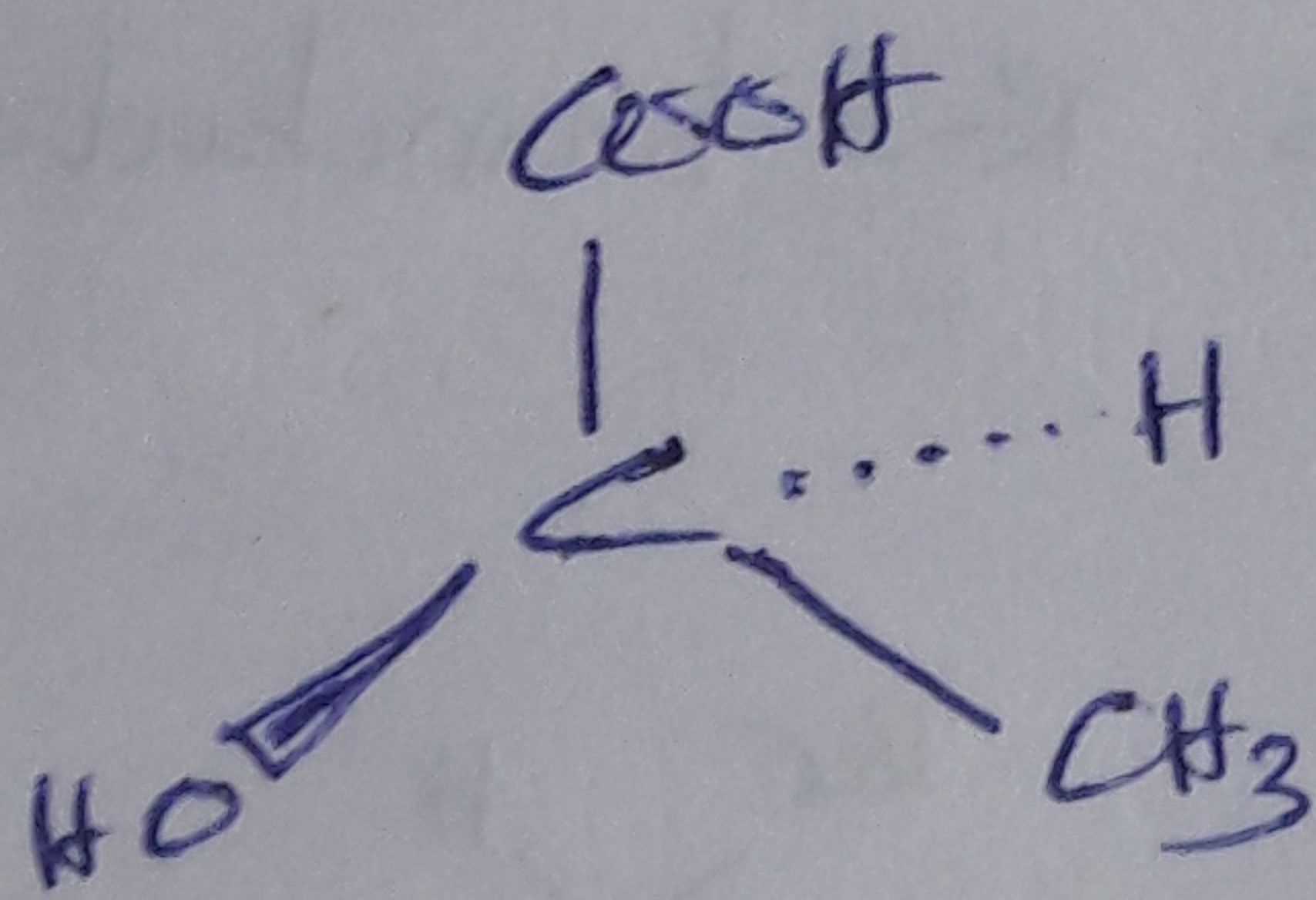
Optical activity and chirality:

- chirality
- enantiomers
- Racemates
- Resolution
- Specific rotation $[\alpha] = \frac{\alpha}{lc}$

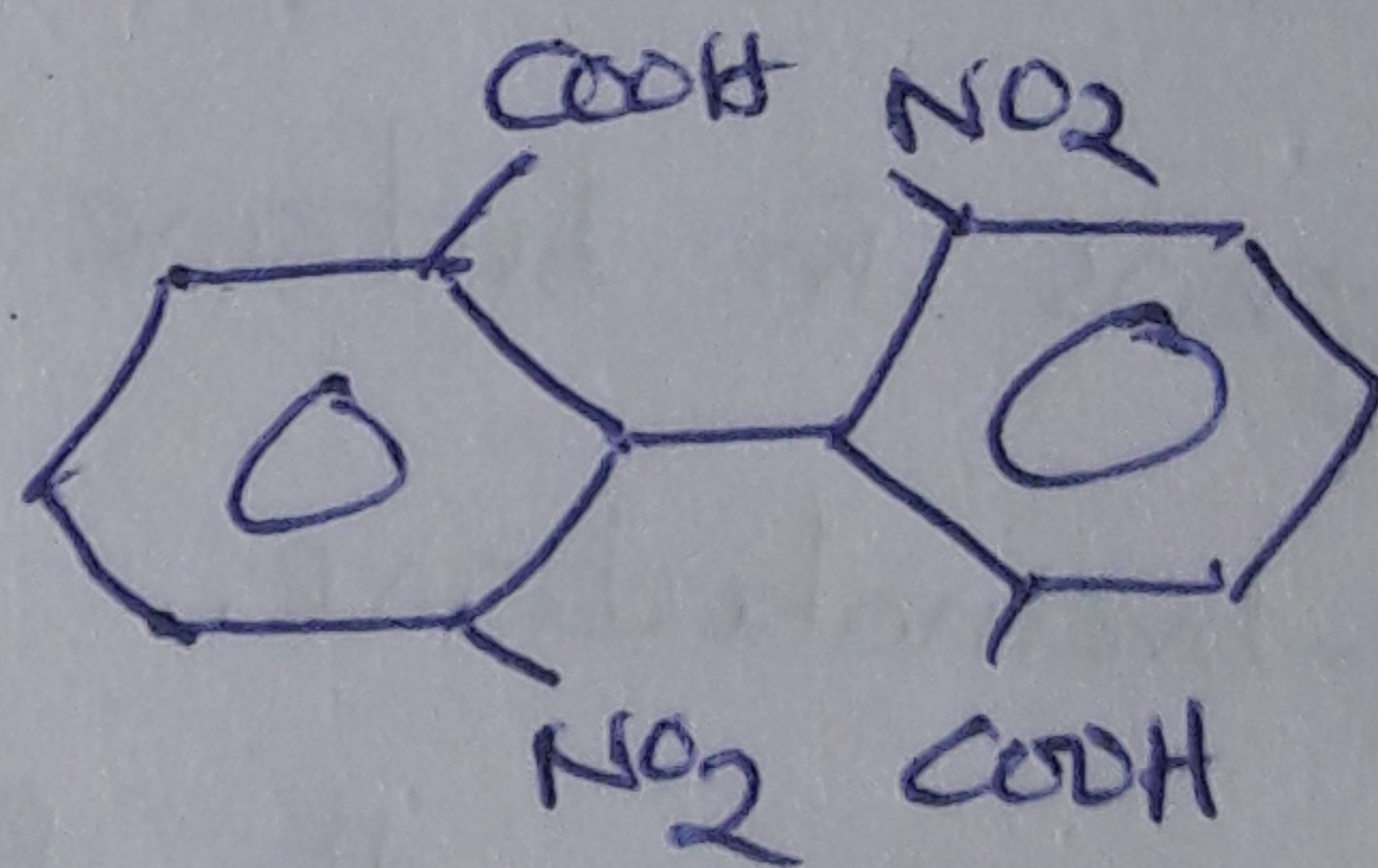
classification of molecules as asymmetric or dissymmetric

An asymmetric molecule lacks a simple axis of symmetry and is optically active.

A dissymmetric molecule may or may not possess asymmetry and is optically active. It usually lacks an alternating axis of symmetry.



Lactic acid
asymmetric compound

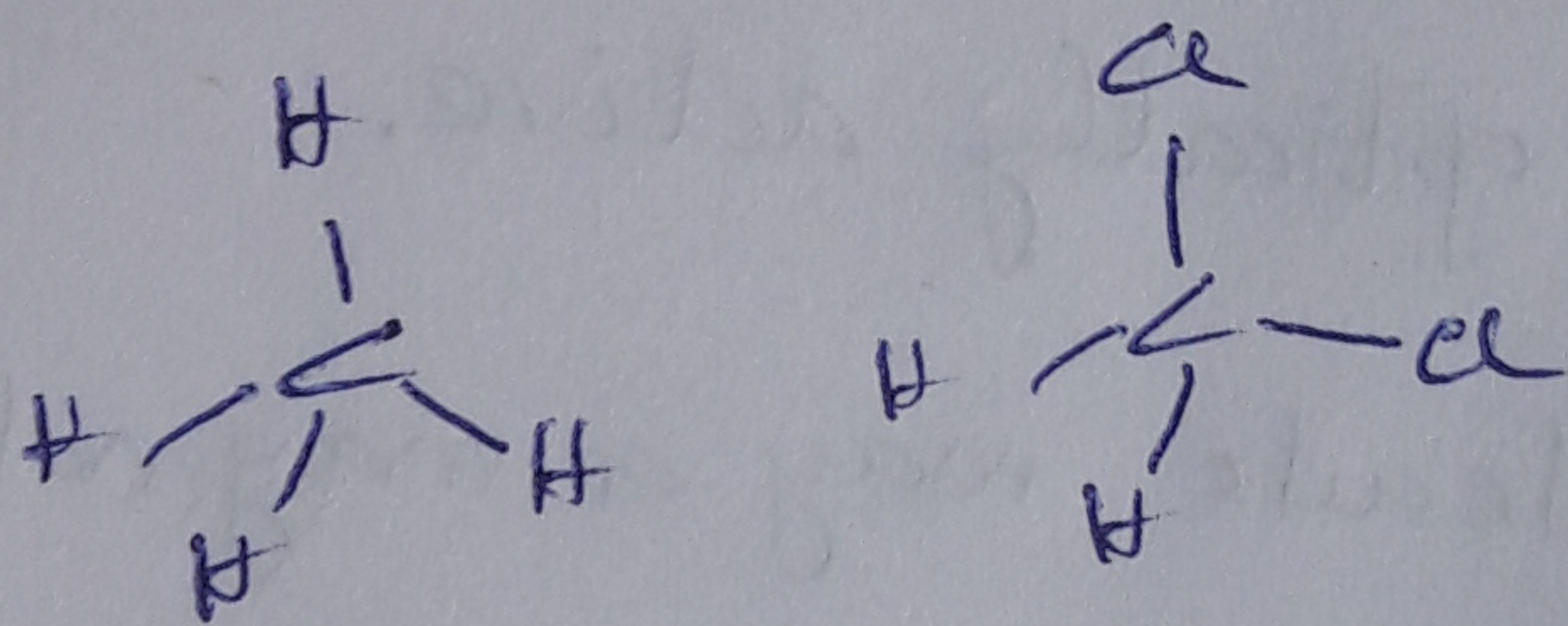


Dissymmetric compound.

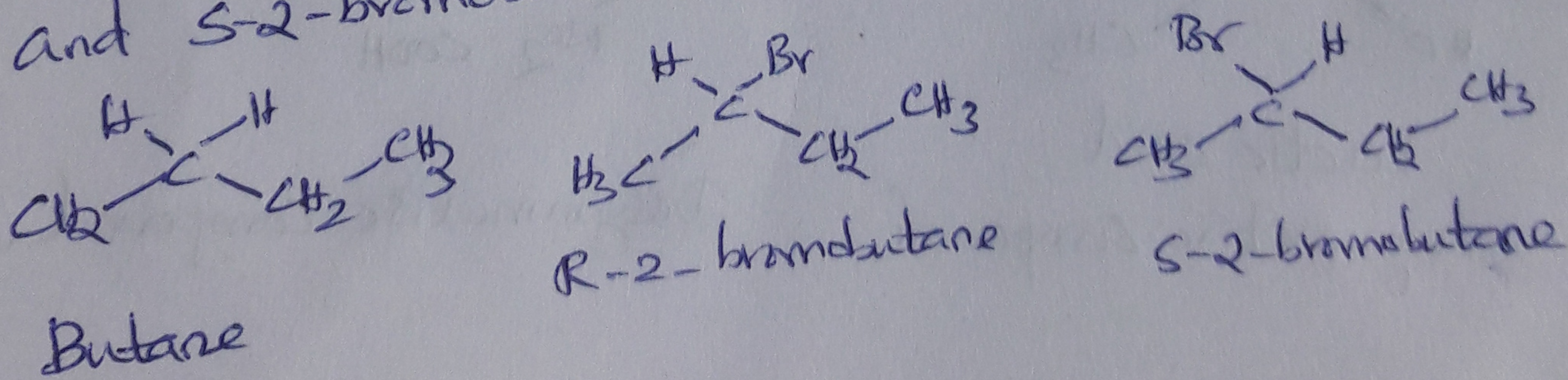
④

Topicity: is the stereochemical relationship between substituents and the structure to which they are attached. Depending on the relationship such groups can be homotopic, enantiotopic and diastereotopic.

Homotopic: homotopic groups in a chemical compound are equivalent groups. The molecule remains the same even if its atoms are interchanged. For example, the four hydrogen atoms of methane are homotopic with one another. Also the two hydrogens or the two chlorines in dichloromethane.

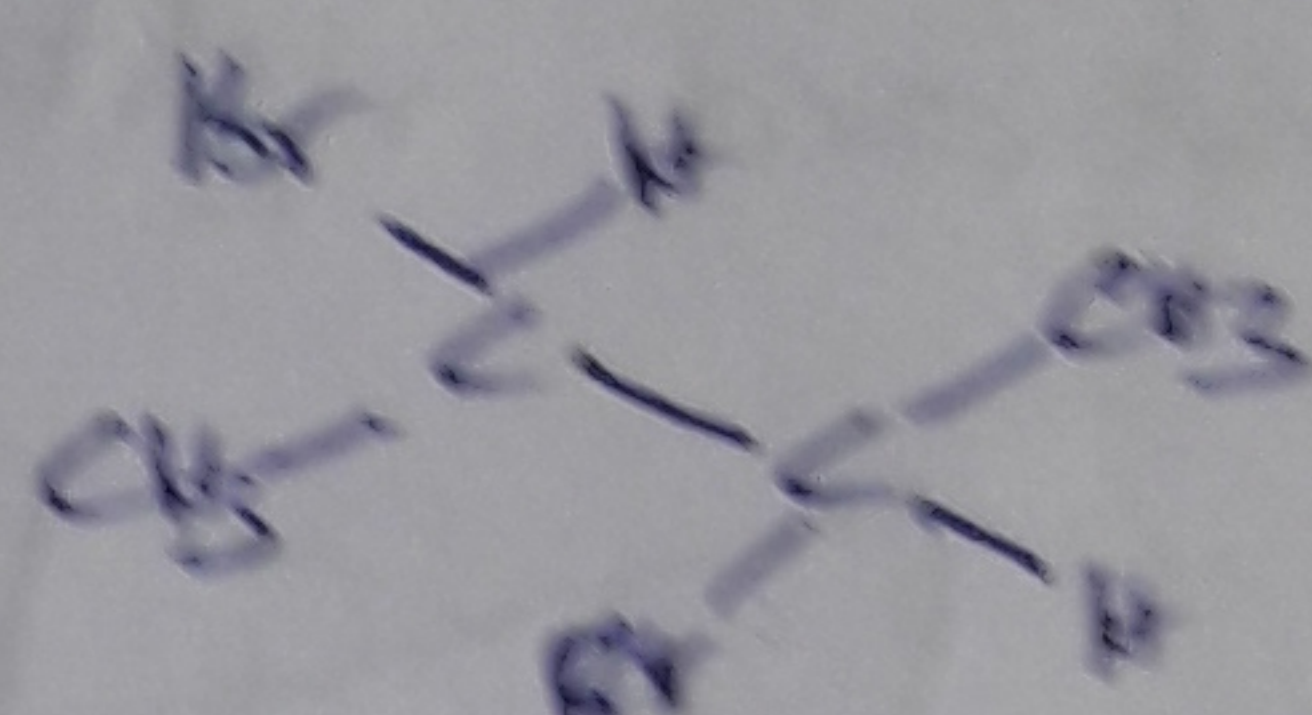
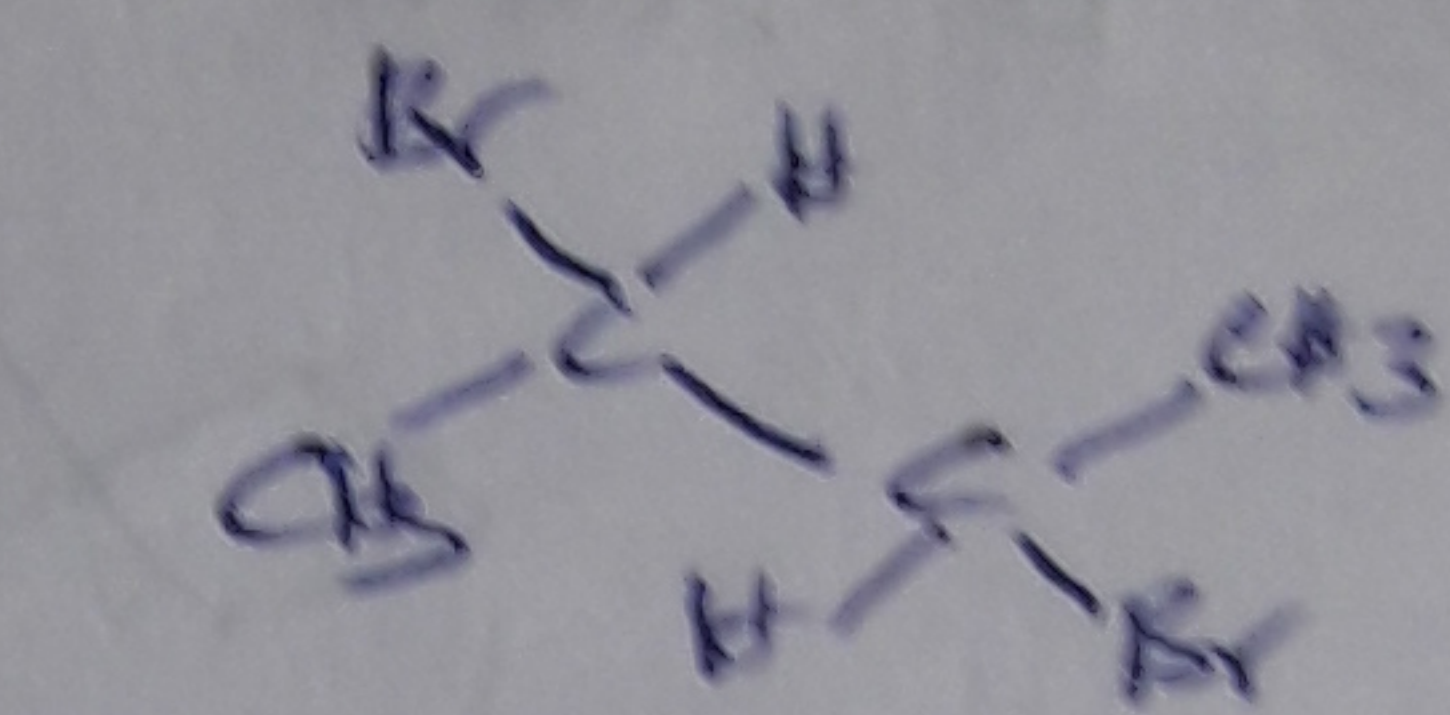
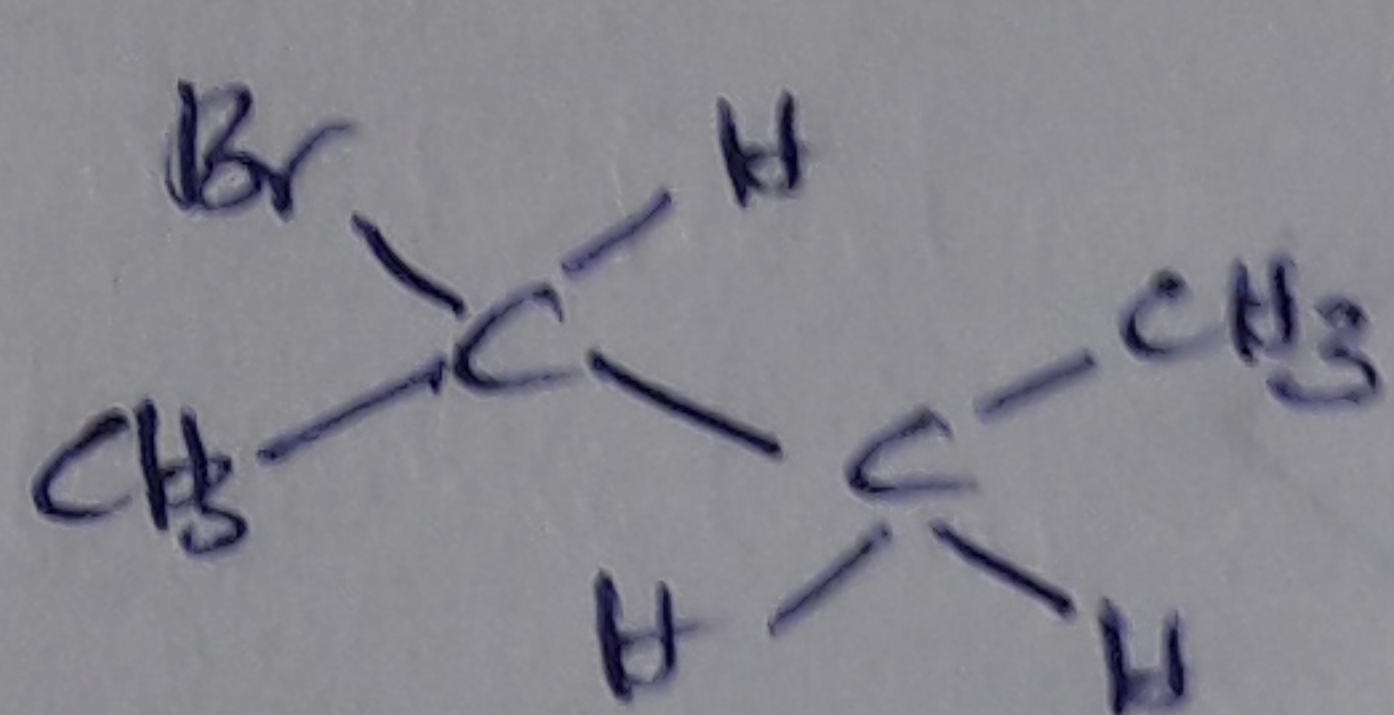


Enantiotopic: If replacement of one or other group (~~replaces~~) produces a chiral compound, the groups are called enantiotopic. For example replacement of the hydrogens in butane produces R-2-bromobutane and S-2-bromobutane.



(5)

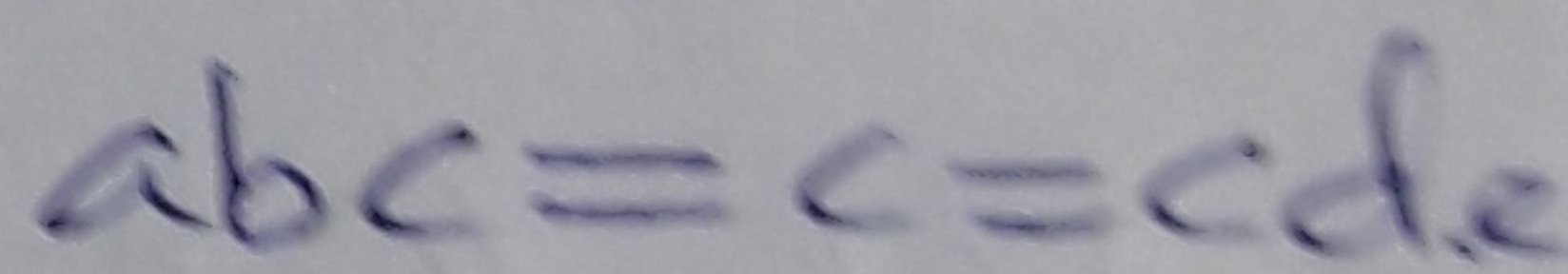
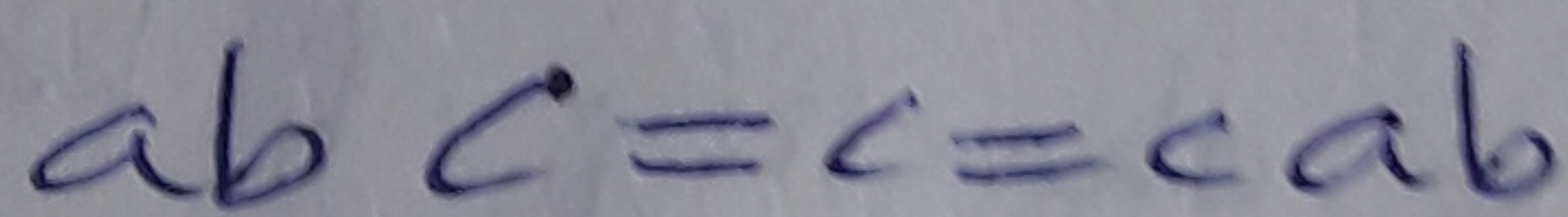
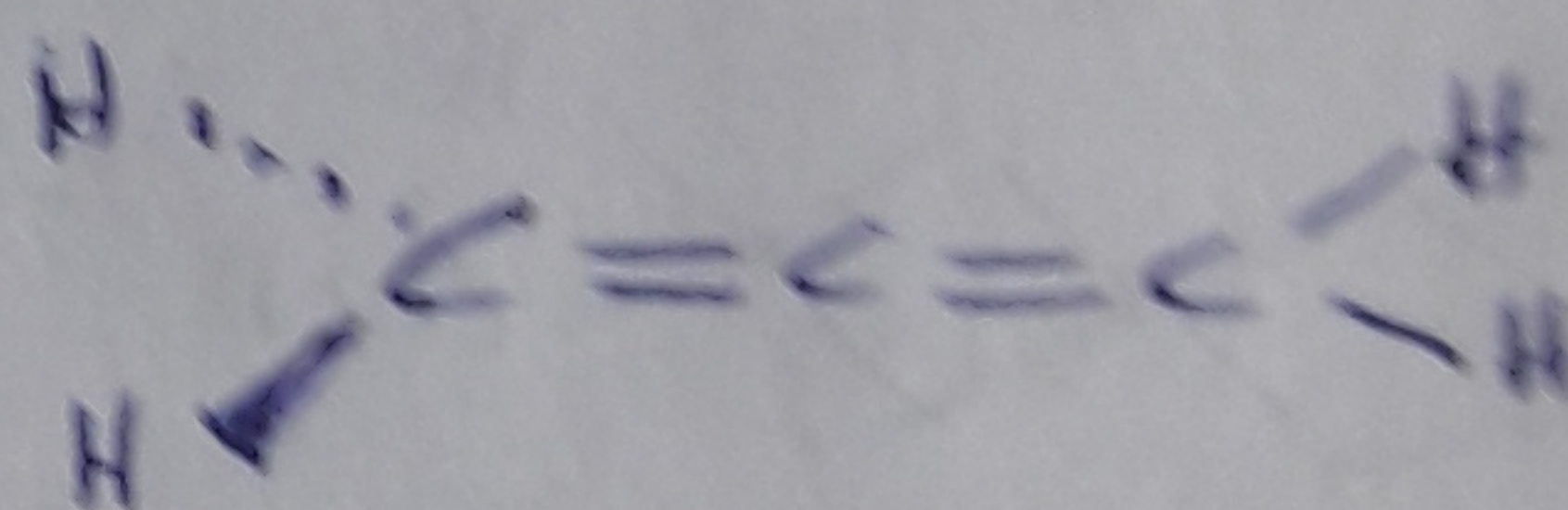
Diastereotopic: If 2 groups replaced in a comp. and produce diastereomers, the atoms or groups are called diastereotopic. For example 5-2-bromobutane has 2 hydrogens if replaced produce 2 diastereomers.



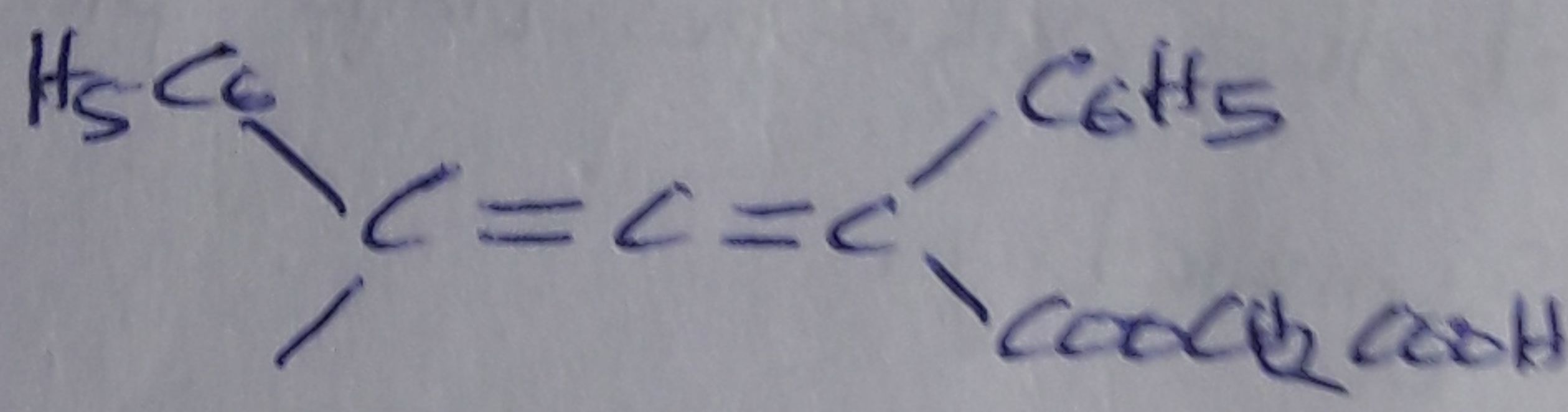
(2S, 3R)-2,3-dibromobutane (2S, 3S)-2,3-dibromobutane.

Dissymmetric molecules

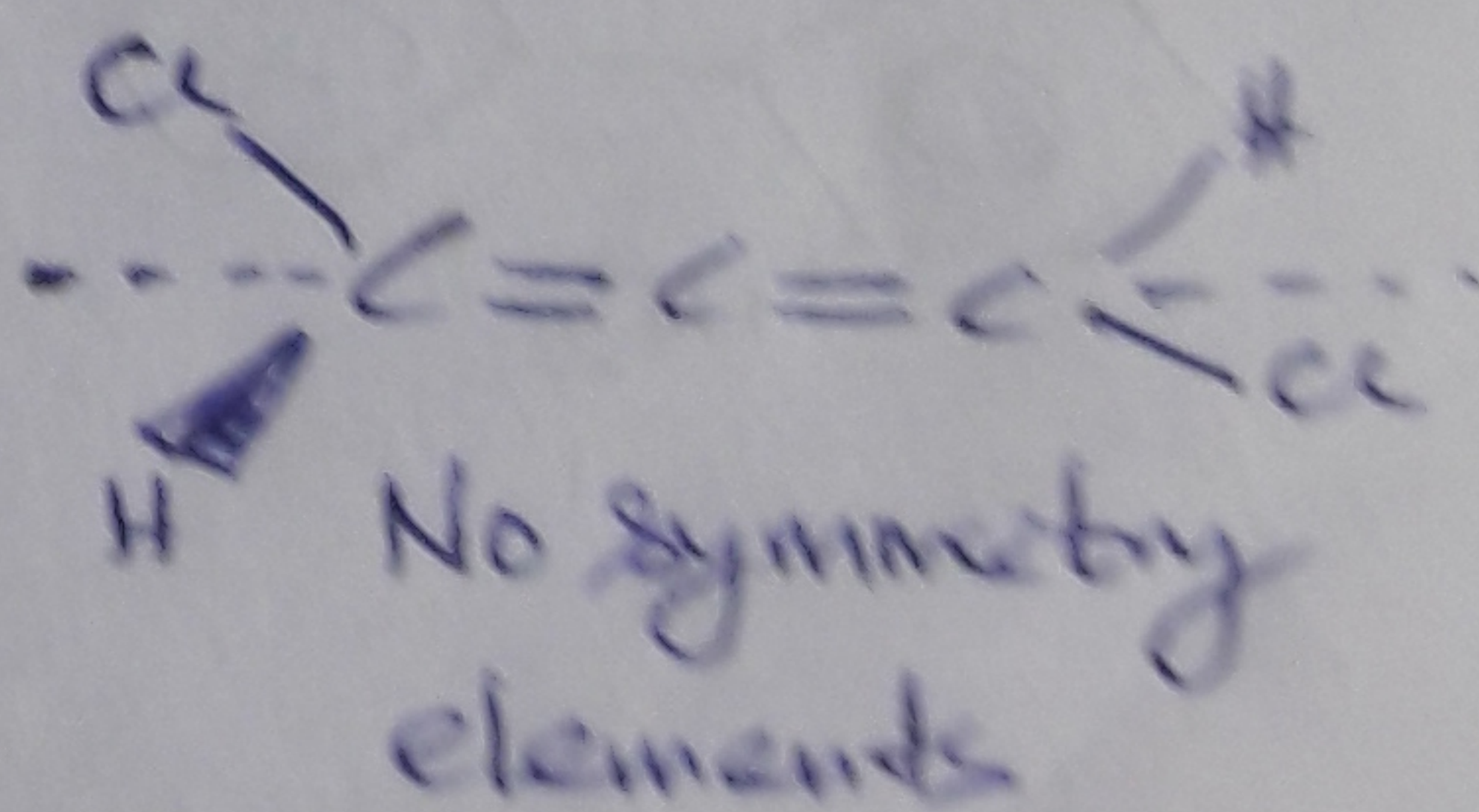
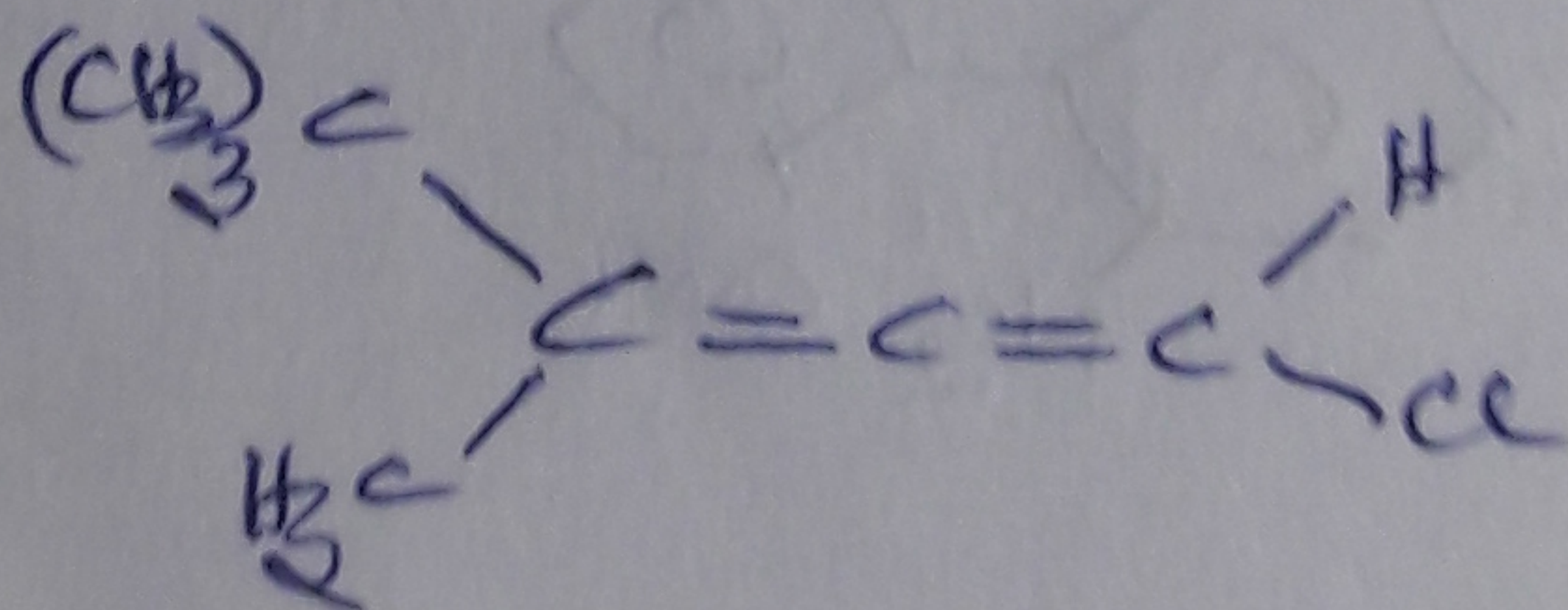
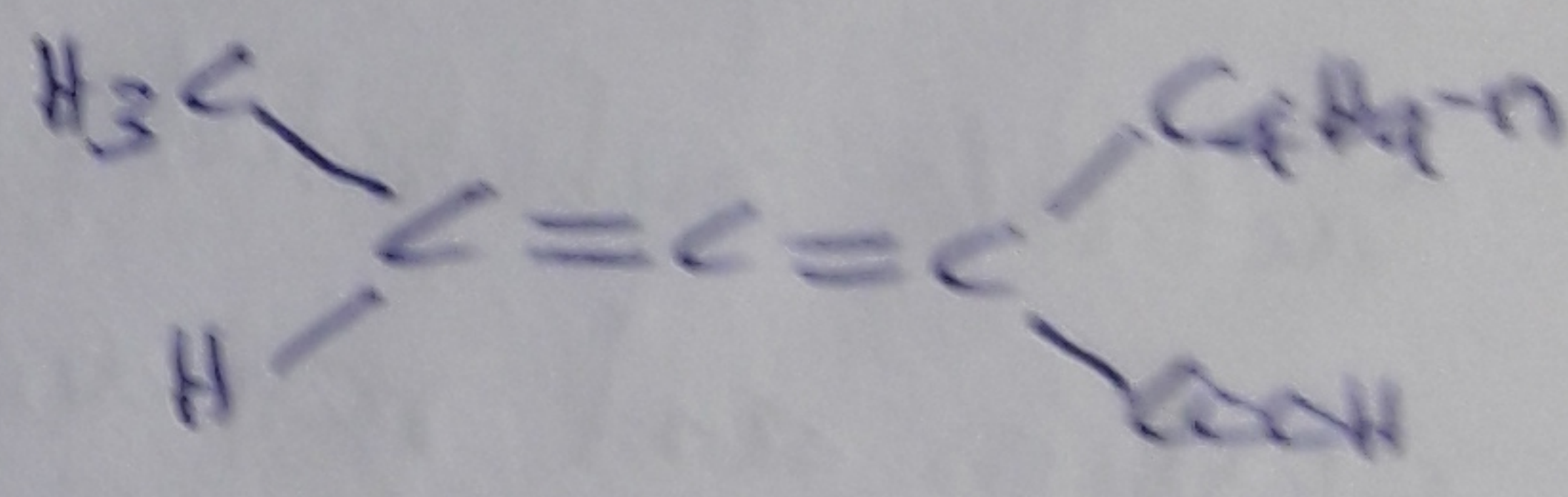
Allenes: Sufficiently substituted allenes are chiral compounds.



Resolved allenes:

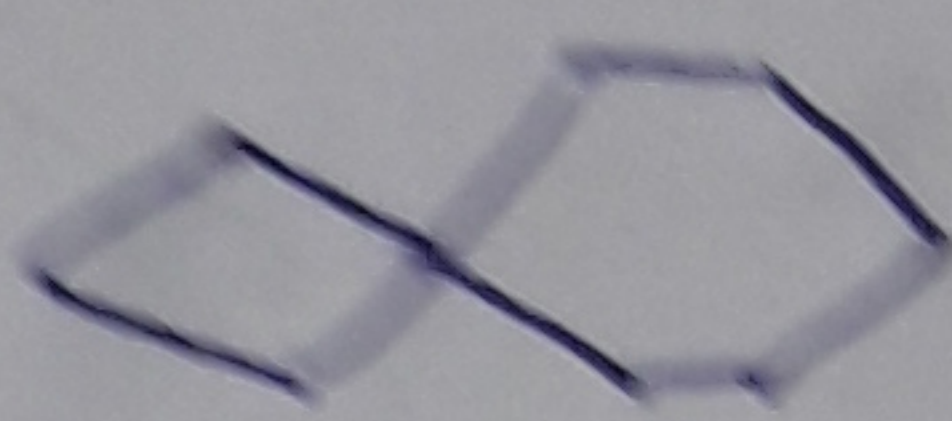
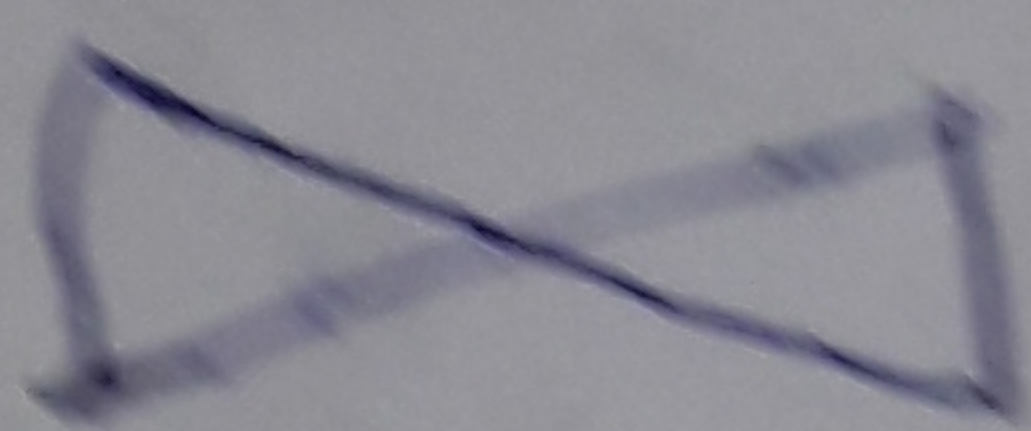


$\alpha\text{-C}_{10}\text{H}_7$



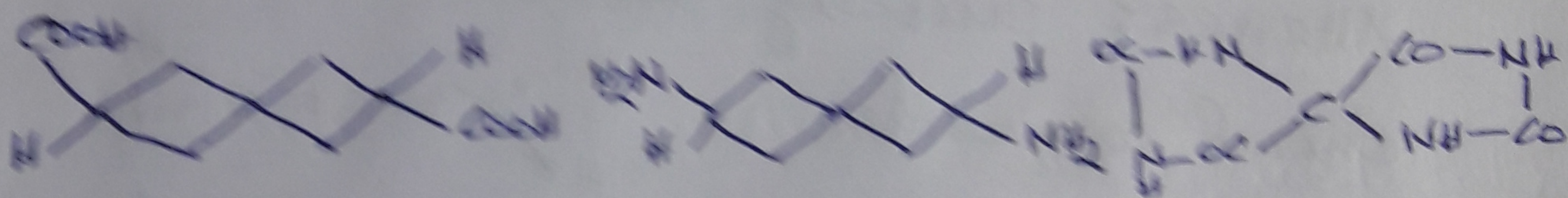
$\text{No. of double bonds - odd} \Rightarrow \text{geometrical isomerism}$
 $\text{No. of double bonds - even} \Rightarrow \text{optical isomerism.}$

Spiranes: Compounds containing one carbon atom common to two rings. The two rings are joined by the common tetrahedral carbon atom and are right angles to each other.

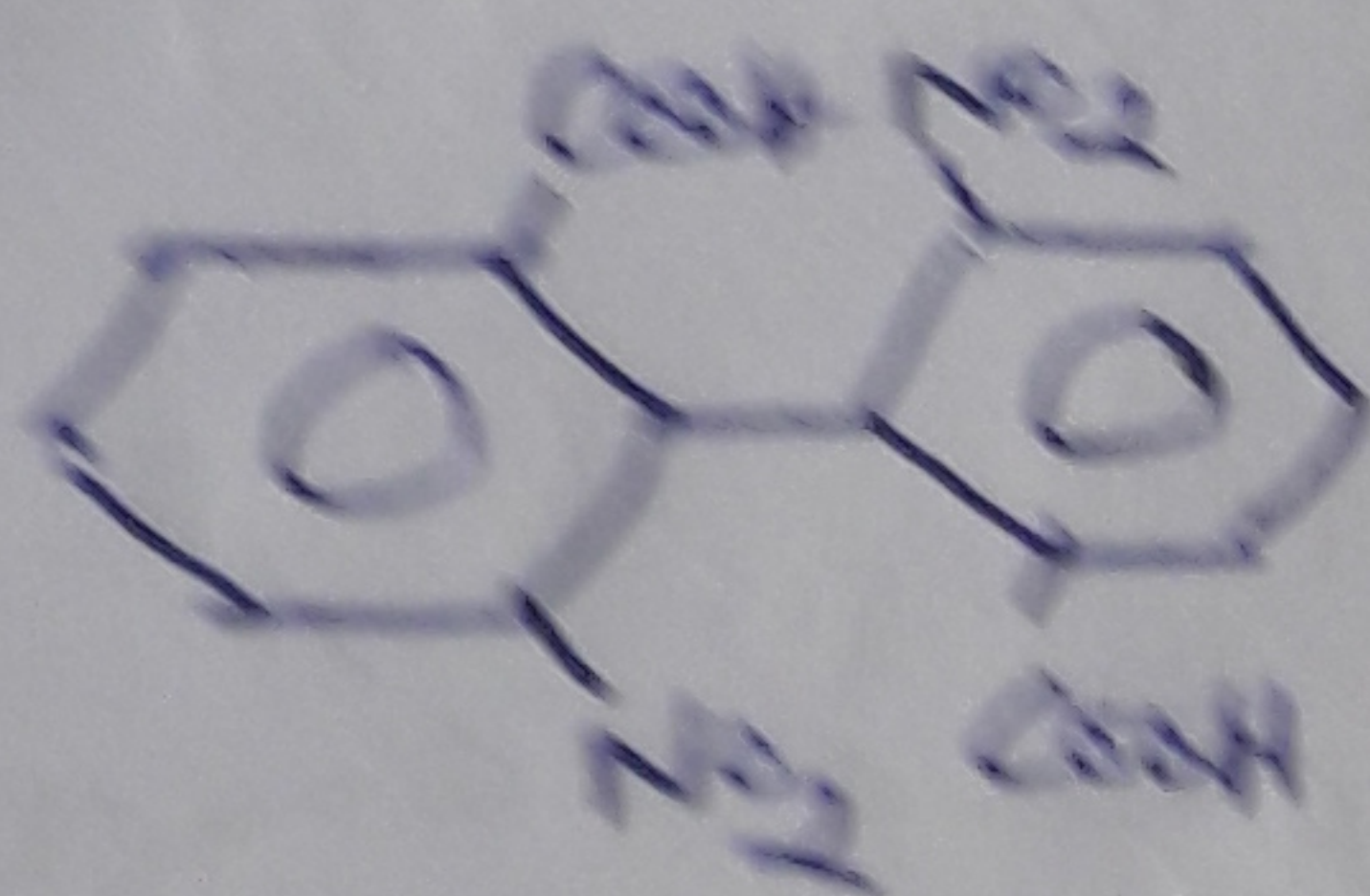
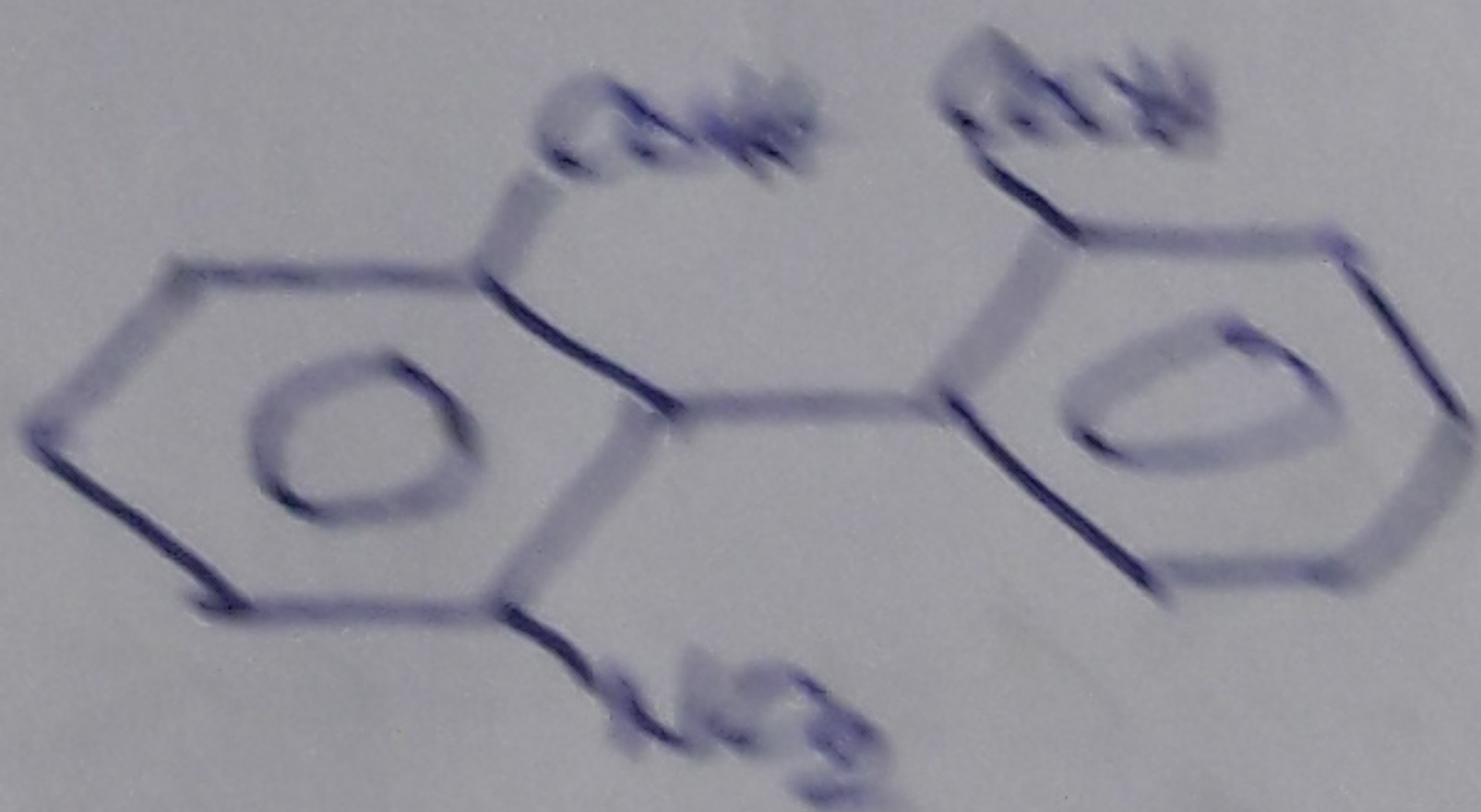


Suitable substitution produces molecules with no elements of symmetry and so optically active.

Resolved spiranes:



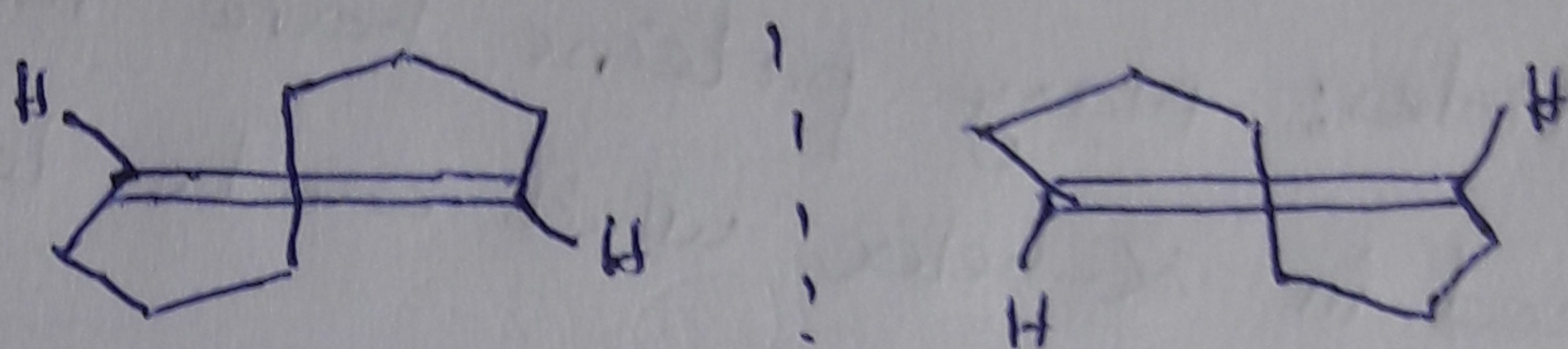
Biphenyls: $(C_6H_5)_2$ The chirality of biphenyl is due to restricted rotation about the double bond. Suitable substitution at the ortho positions prevent rotation and remove symmetry.



(7)

Trans-cyclooctene

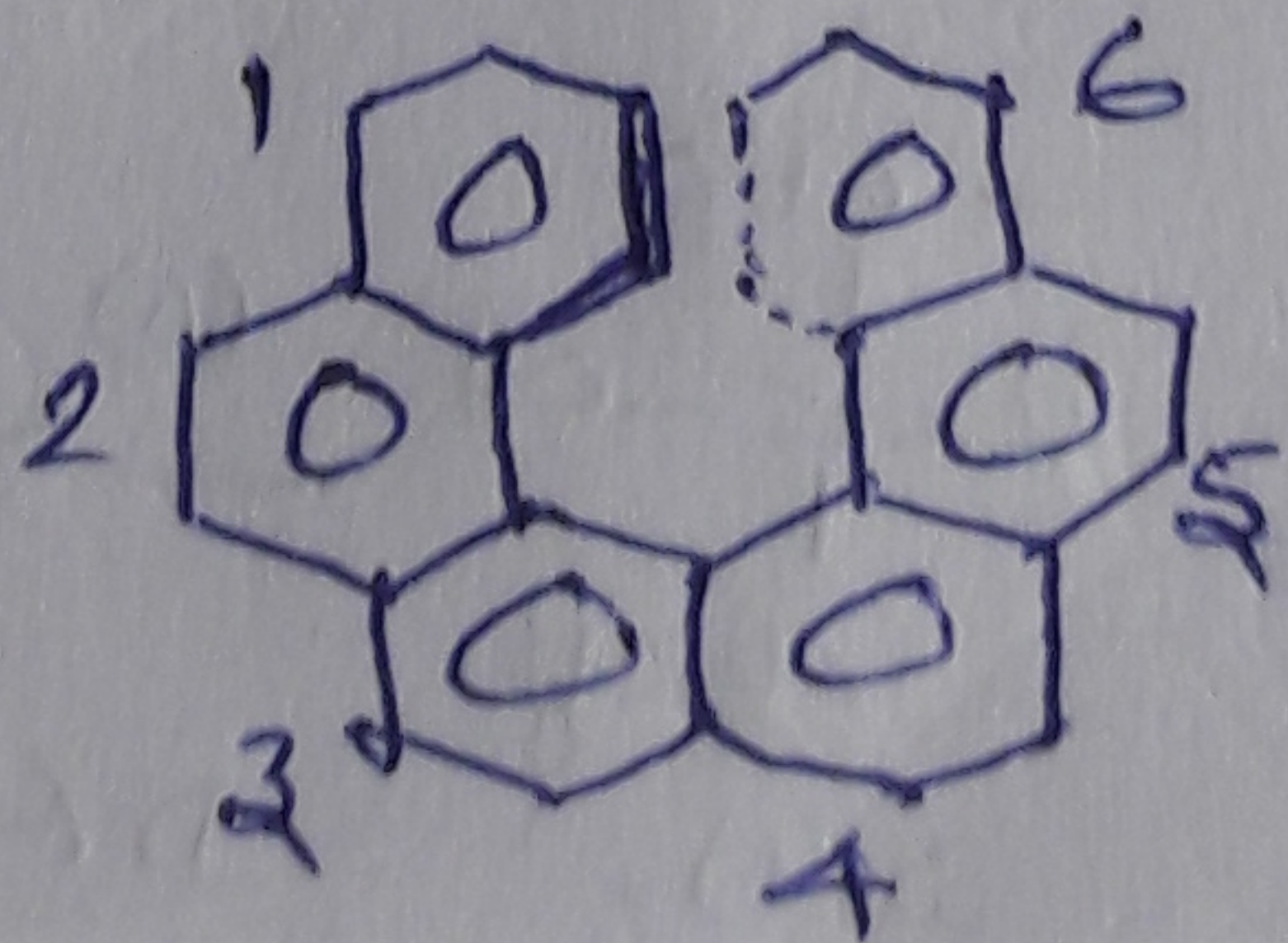
This compound has helical shape and carbon atom lies above the plane of double bond on one side and below it on the other. Hence there is substantial π bond torsion. This gives rise to the idea of P and M helicities but only one exists. Hence only one pair of enantiomers exist and not four stereoisomers.



Molecules with helical structures:

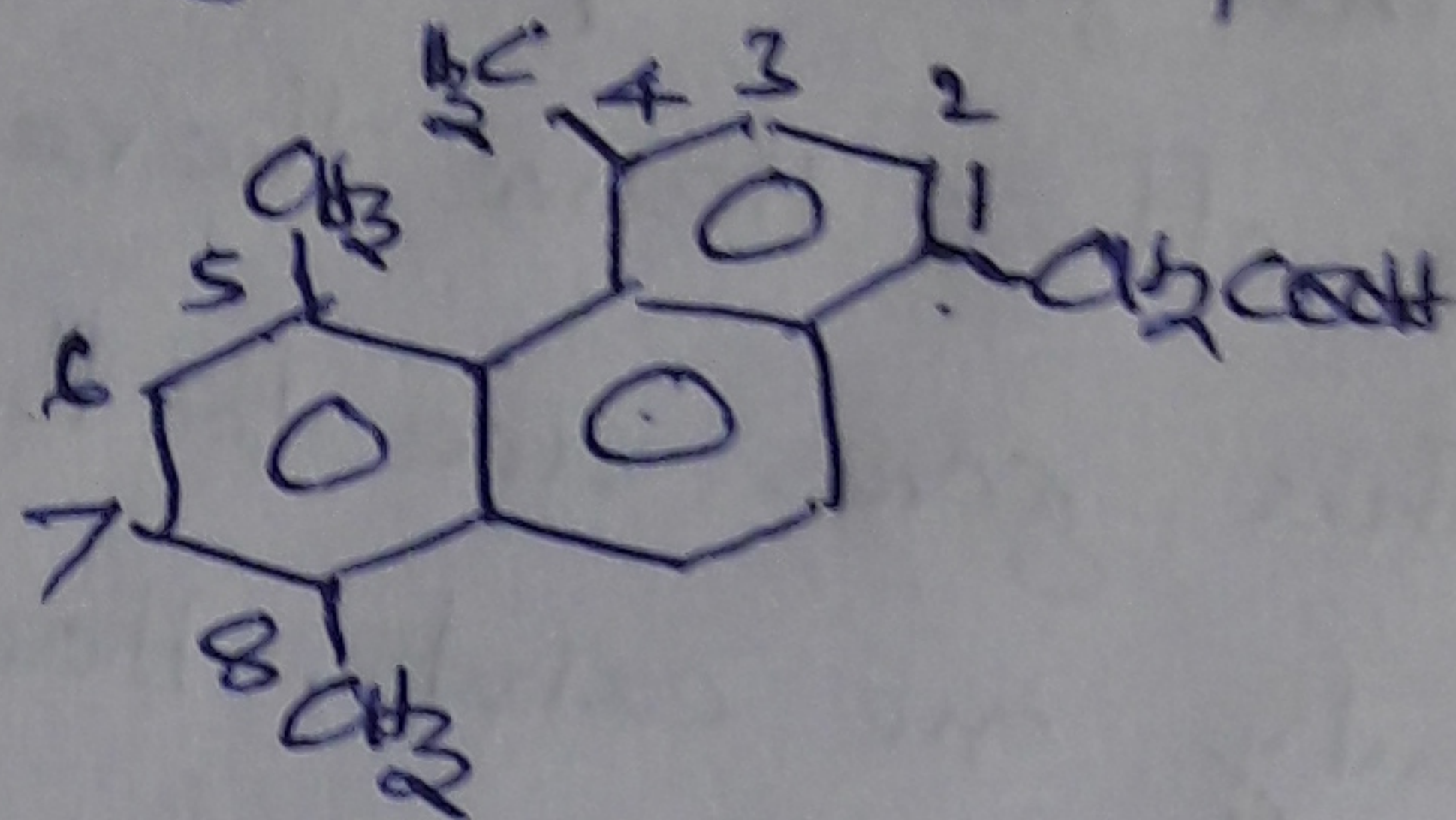
Helices are chiral objects, right handed is designated P (plus) and left handed is M (minus).

Hexahelicene: can be left handed or right handed in orientation. The middle rings (3 & 4) lie in a plane and terminal rings lie above and below the plane. Resolved into stable enantiomers.



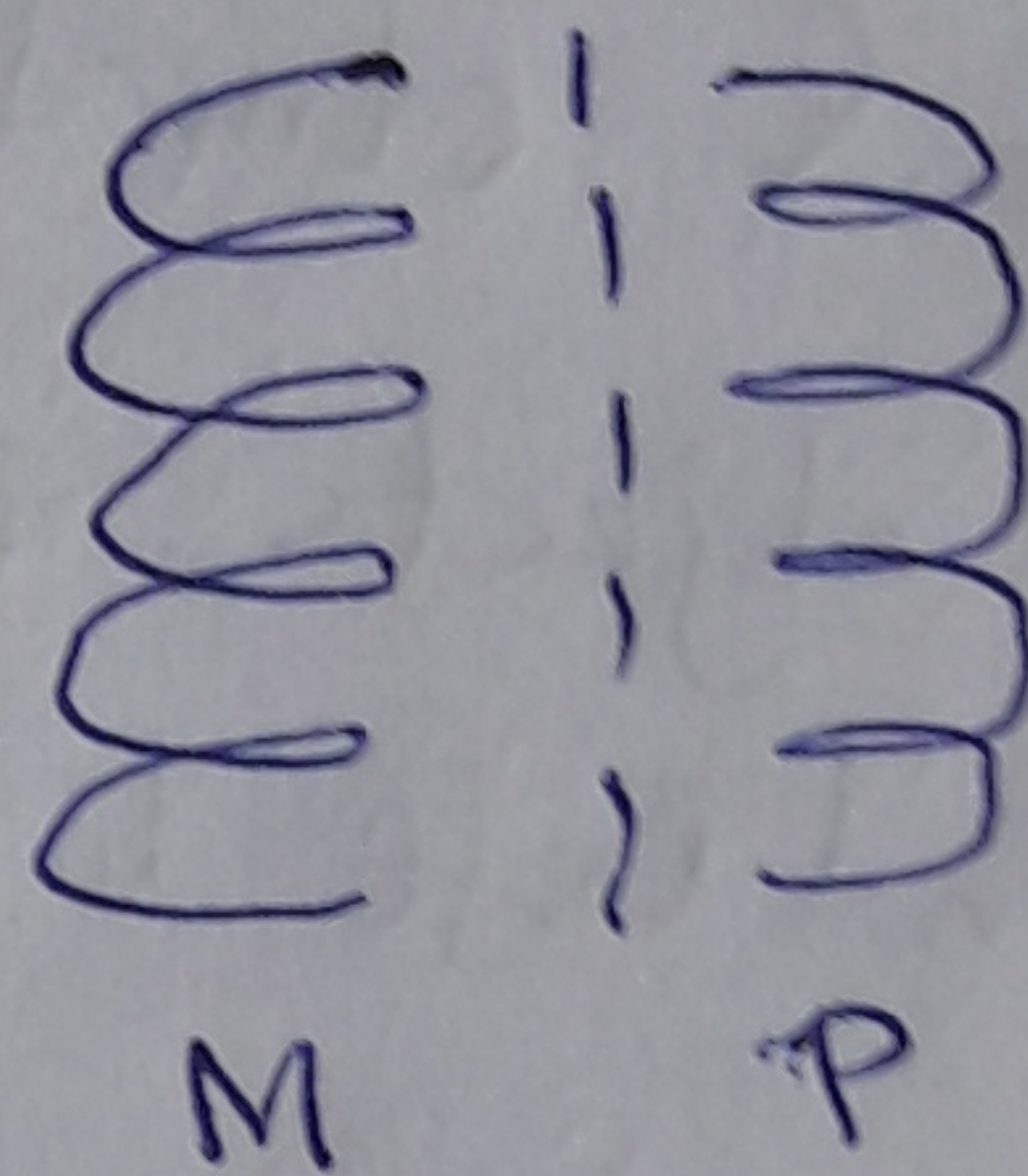
(8)

Aromatic compounds: Suitable substitution forces the molecule to buckle from the most favourable planar arrangement, Example:

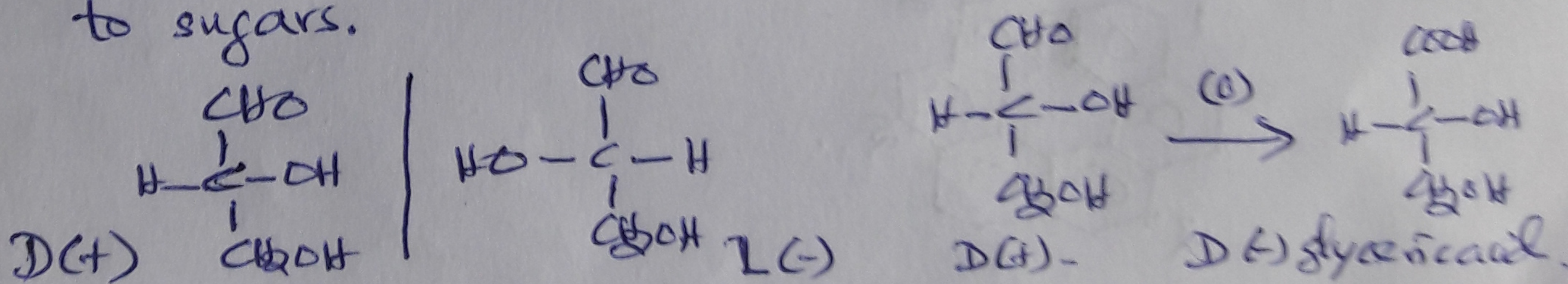


4,5,8-trimethyl-1-phenanthryl acetic acid.

Polypeptides: Many proteins have their chains stabilized in α -helix which can be left or right handed.



Absolute Configuration: To distinguish between enantiomers, Rosanoff proposed that one compound be chosen as a standard and a configuration be arbitrarily assigned to it. The compound chosen was glyceraldehyde because of its relationship to sugars.

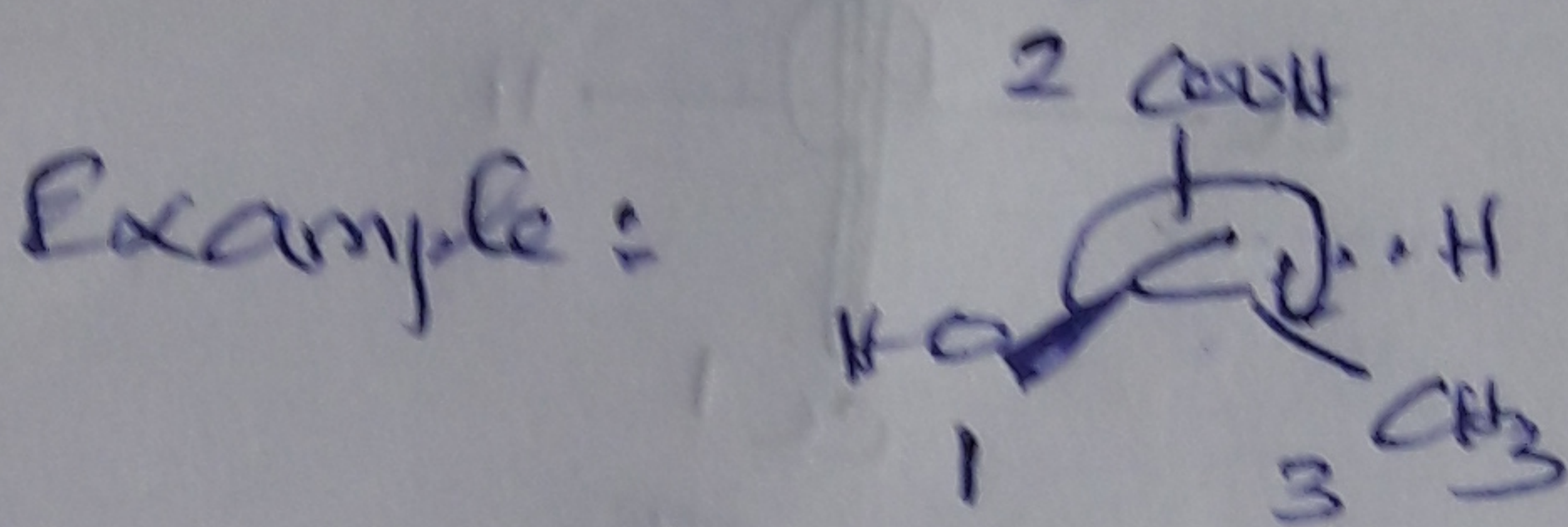


①

When a compound has been placed in the D or L series, its absolute configuration is said to be known.

R-S Nomenclature: Relative Configuration
Cahn-Ingold-Prelog rules:

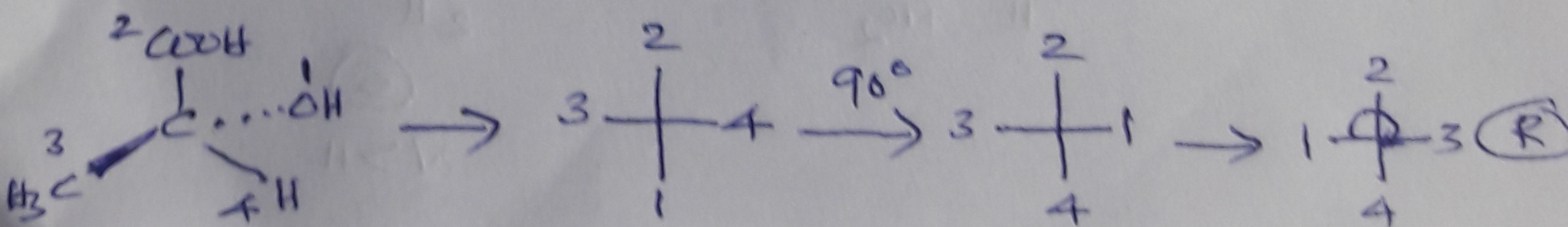
- ① Groups are ordered by sequence rules.
- ② Molecule is so mounted with lowest priority group behind.
- ③ Remaining arrangement given R or S.



Sequence rules: ① Atom with higher atomic number gets higher priority.

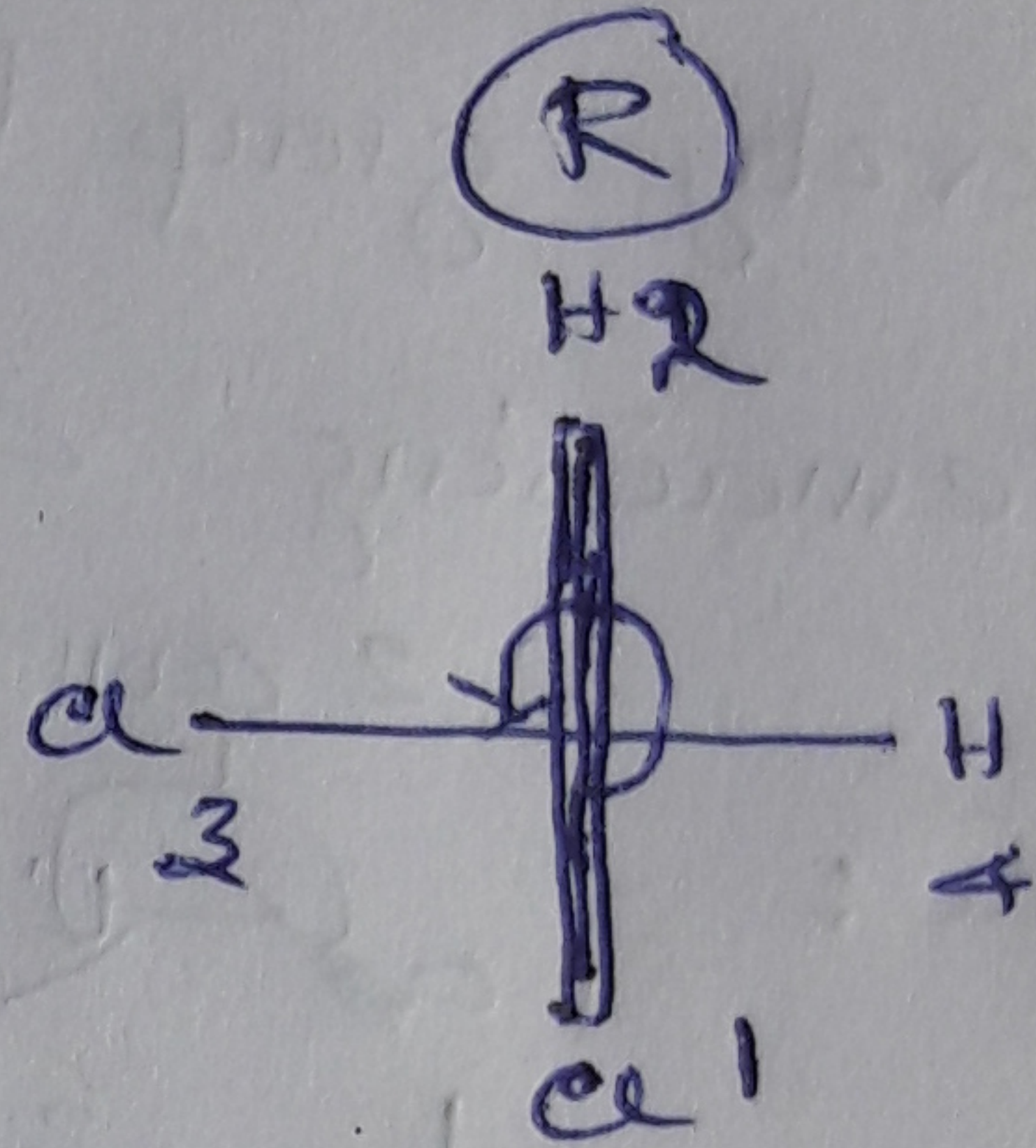
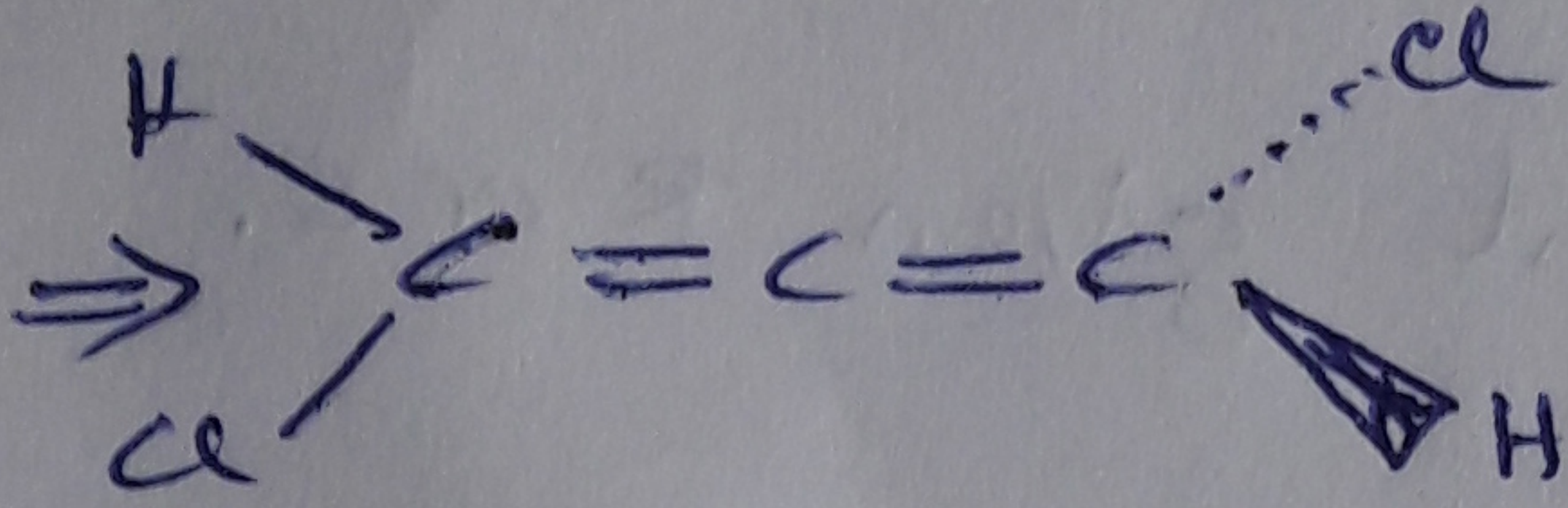
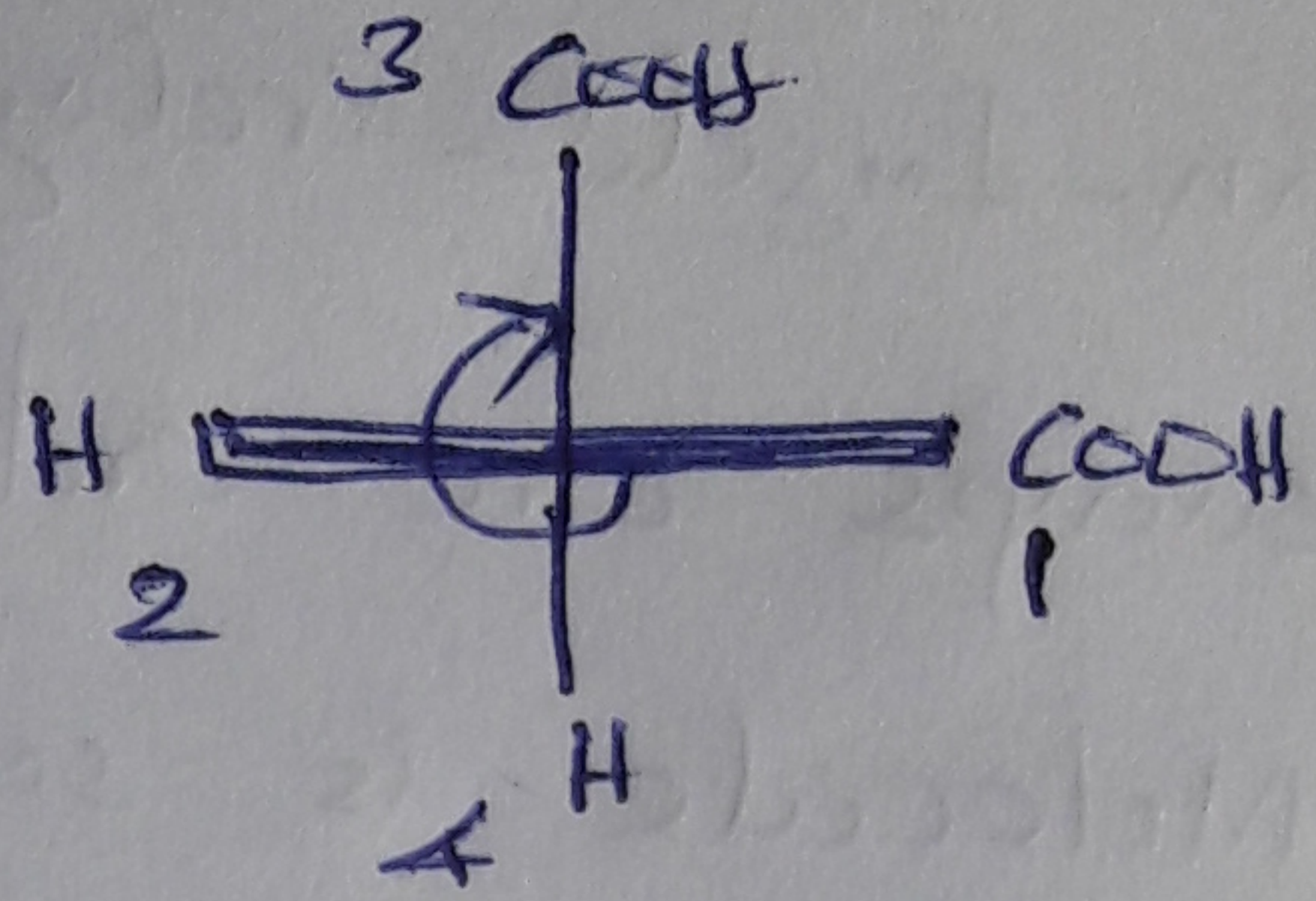
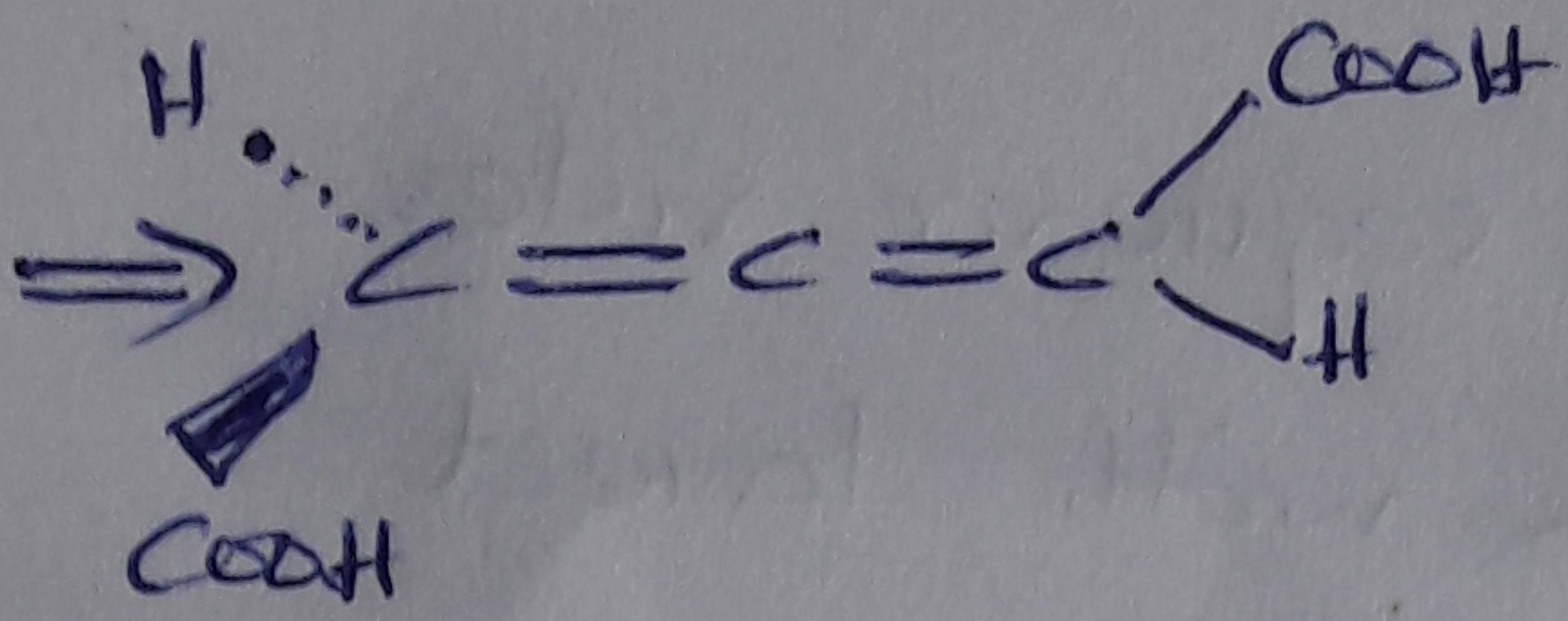
② If two atoms are same, neighbour atoms are considered.

③ Double/triple bonds are considered as 2/3 single bonds.



(10)

RS nomenclature of allenes: To name allene the three dimensional formula is transformed into Fischer projection and the near groups are given priority over far groups. For example,



RS nomenclature of biphenyls: The three dimensional formula is transformed into Fischer projection and near groups are given priority over far groups.

