

JANKI DEVI BAJAJ GOVERNMENT GIRLS
COLLEGE KOTA

TOPIC

STEREO CHEMISTRY OF
N, P, S COMPOUNDS

SUBMITTED BY:-

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SUBMITTED TO:-

THE DEPARTMENT
OF CHEMISTRY

STEREO CHEMISTRY

OF

N, P, S

COMPOUNDS

CONTENTS

S. NO.

TOPIC

1. STEREO CHEMISTRY
2. STEREO ISOMERISM
3. TYPES OF STEREO ISOMERISM
4. OPTICAL ISOMERISM
5. GEOMETRICAL ISOMERISM
6. STEREO CHEMISTRY OF N COMPOUNDS
7. STEREO CHEMISTRY OF P COMPOUNDS
8. STEREO CHEMISTRY OF S COMPOUNDS

INTRODUCTI STEREO CHEMISTRY

4

ON
The Branch of chemistry which Deals the study of structure at Isomerism of Organic molecules known as STEREO CHEMISTRY.

STEREO ISOMERISM

CONFIGURATION ISOMERISM

CONFORMATION ISOMERISM

→ OPTICAL ISOMERISM

→ GEOMETRICAL ISOMERISM

STEREO ISOMERISM :- Two Or more Compounds Having Same molecular formula But their spatial arrangement are Different, k/n as Stereo isomerism and this phenomenon is called STEREO ISOMERISM.

OPTICAL ISOMERISM :-

The molecules having Same molecular formula But they Shows Different Behaviour towards PLANE POLARISED LIGHT (PPL) k/n as OPTICAL ISOMERISM & The Phenomenon is c/a OPTICAL ISOMERISM.

CONDITIONS FOR OPTICAL ISOMERISM :-

- Optical Isomers should be Asymmetric in Nature. It means Symmetric Elements should be Absent in these Isomers.
- Optical Isomers should be mirror Image to each others.
- Optical Isomers should not be Super Imposed to each other.

● GEOMETRICAL ISOMERISM :- [CIS-TRANS ISOM.]

The Isomerism which arises due to Restricted (Frozen) Rotation about a Bond in a Molecule is k/n as GEOMETRICAL OR CIS-TRANS ISOMERISM.

Geometrical Isomerism is Exhibited by a Variety of Compounds, which may be Classified as follows :-

- Compounds Containing a Double Bond ;
● $C=C$, $C=N$, $N=N$
- Compounds Containing Cyclic Structure ; Homocyclic , Heterocyclic and fused Ring System .
- Compounds Having Restricted Rotation about a Single Bond due to Steric Hindrance .

STEREO CHEMISTRY OF NITROGEN, PHOSPHORUS, SULPHUR COMPOUNDS: PART - A

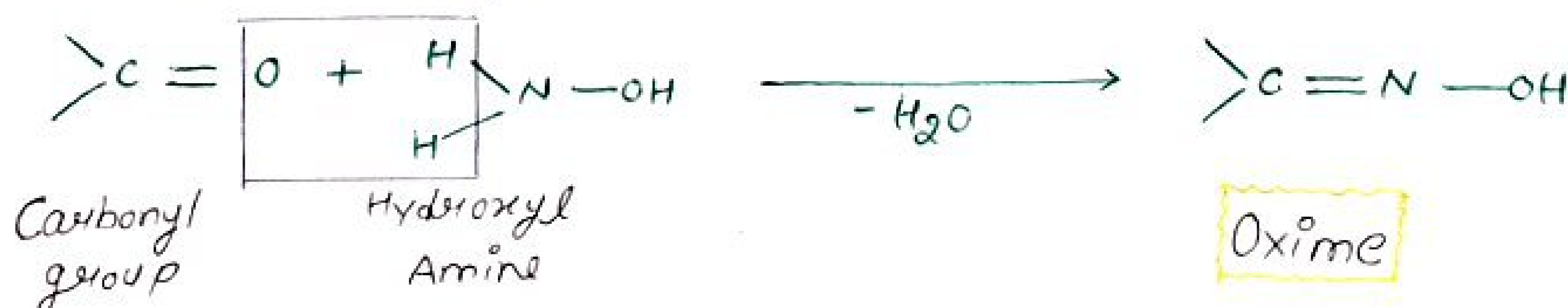
STEREO CHEMISTRY OF "N" COMPOUNDS

Like the Carbon Compounds, the Nitrogen Compounds also exhibit Both types of Stereo isomerism, i.e., the, Enantiomerism (optical isomerism) and geometrical (Cis-Trans) Isomerism.

Examples :- 1.) Oxime $[>C=N-OH]$

The Compound in which double Bond is present b/w Carbon & Nitrogen atom and N-atom has one -OH group is called Oxime.

Carbonyl group and Hydroxyl Amine is formed the Oxime Compound.



Oxime Compounds is of two Types :-

ALDOXIME & KETOXIME

A) **ALDOXIME** :- The oxime which is form from Aldehyde and Hydroxyl amine is called Aldoxime.

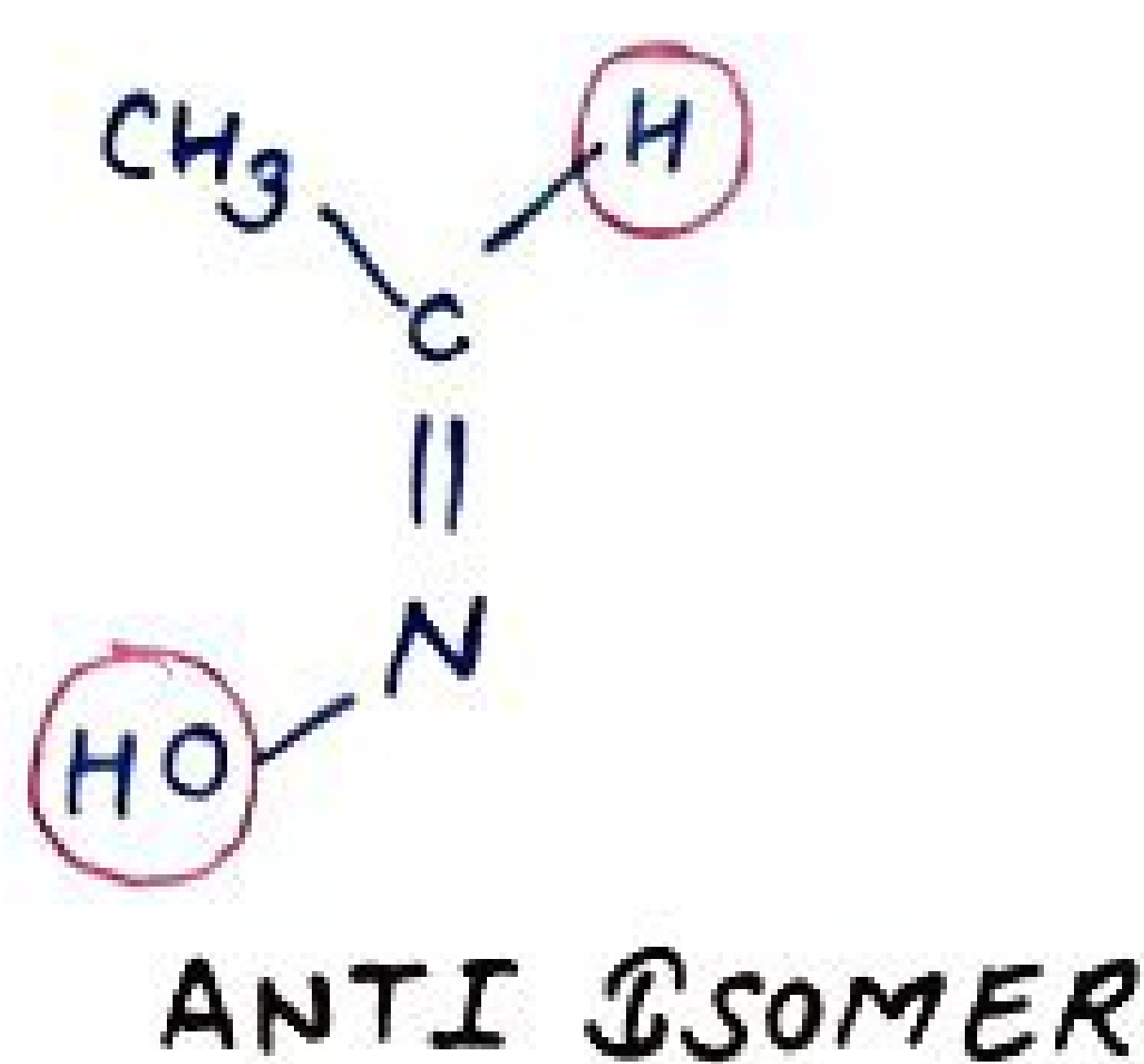
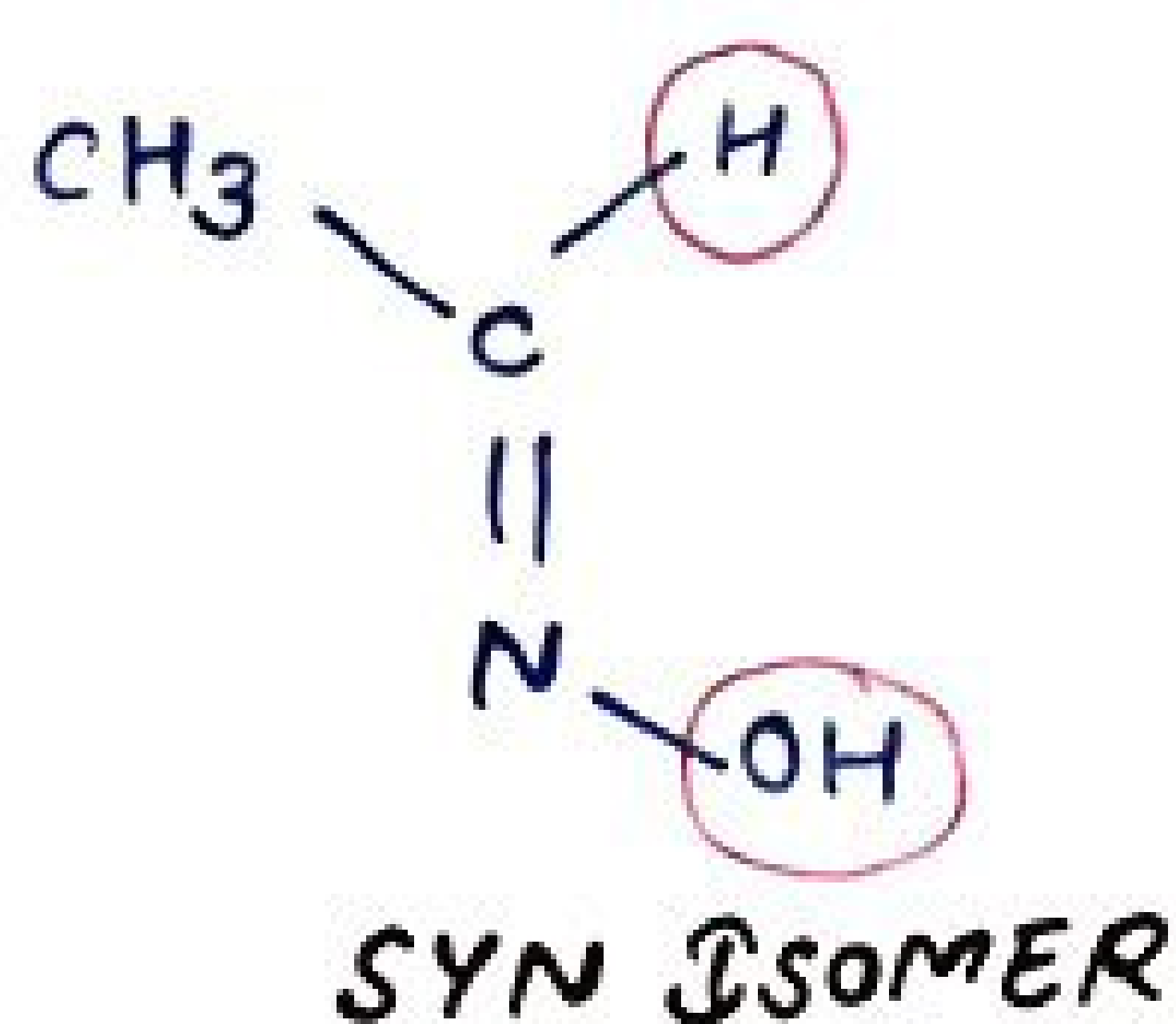
In Aldoxime atleast 1-H atom is attached with the Valency of C-atom. In aldoxime due to the presence of double bond free Rotation become Restricted so that it show Geometrical Isomerism.

But its Geometrical Isomers are of a Syn & Anti Isomers Respectively.

→ SYN ISOMERS → The Isomers in which H-atom of Carbon & -OH group of N-atom are present in same direction is of a SYN ISOMERS.

→ Anti ISOMERS → The Isomers in which H-atom of C & -OH group of N-atom are present in opposite direction is of a Anti Isomers.

Geometrical Isomers of Acetaldoxime :-



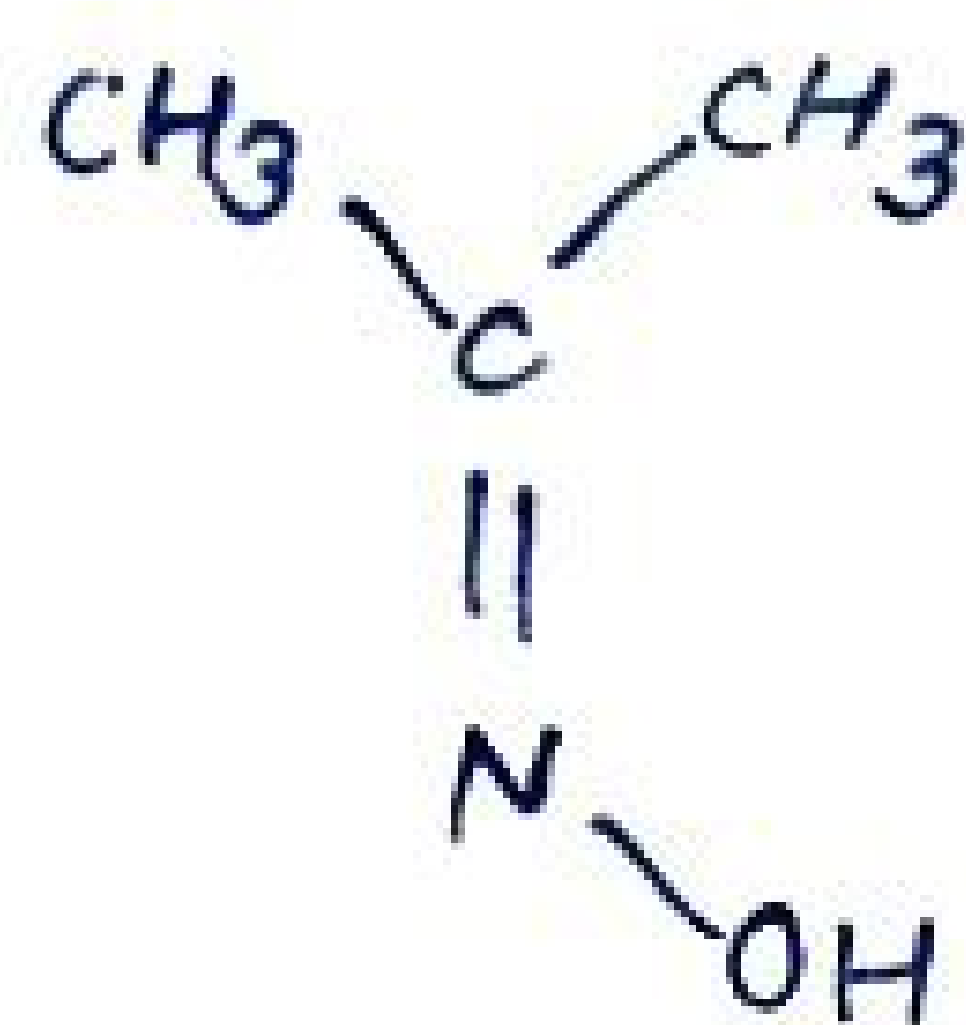
B) **KITOXIME** :- The Oxime which is form from Ketone & Hydroxyl Amine is of a kitoxime.

In Ketoxime. Both the Valencies of C-atom attached with alkyl groups.

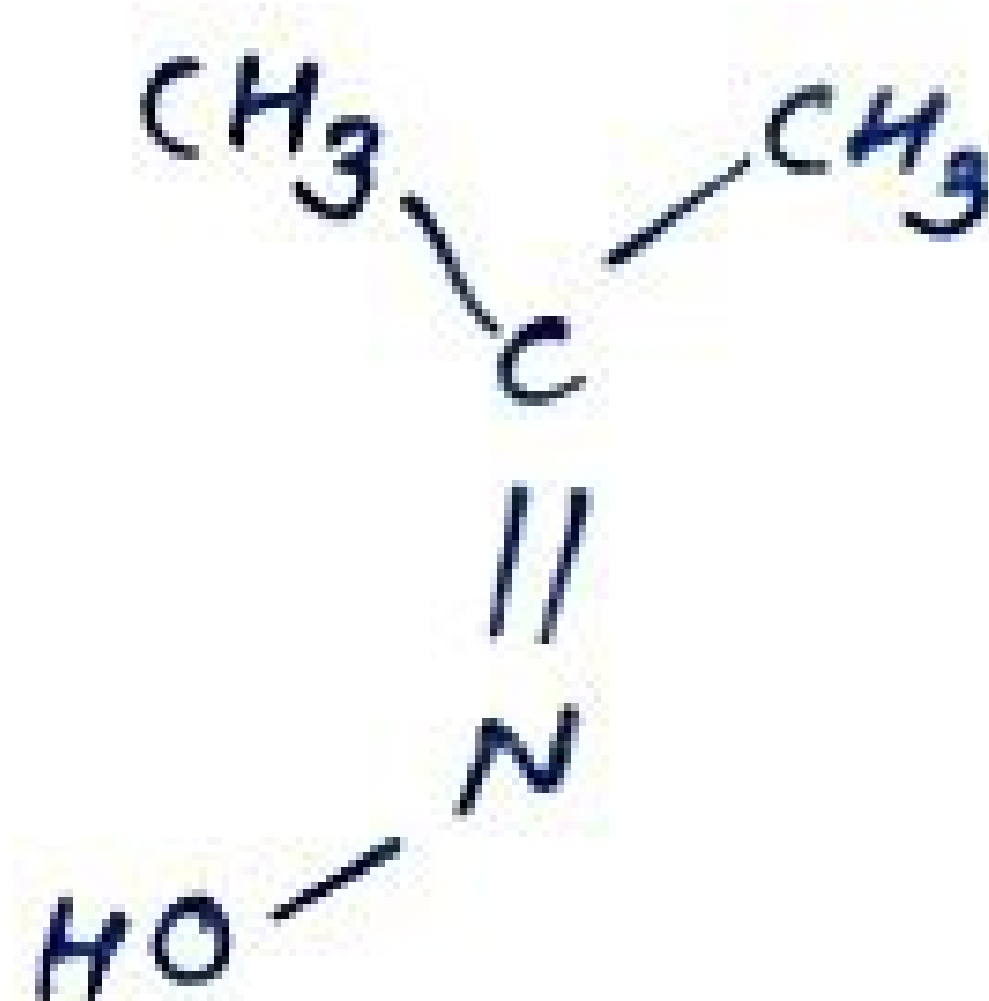
Due to the present of double Bond it Shows geometrical Isomerism.

But there is no any Rule for the nomenclature of Syn & Anti isomers. The name of Syn & Anti Isomers can given by self desigion.

Geometrical Isomerism of Acetoxime :-



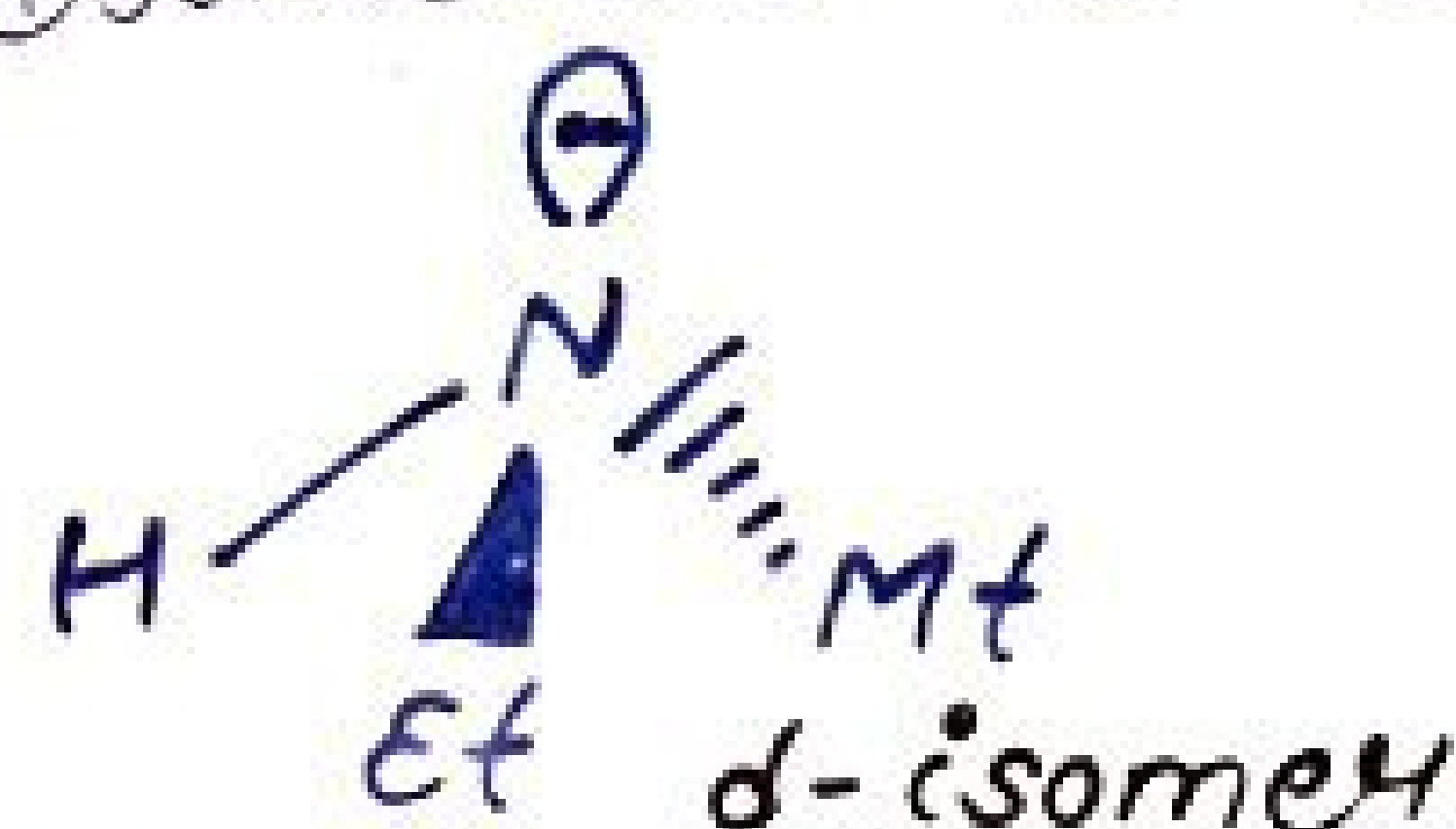
SYN ISOMER



ANTI ISOMER

Example :- 2.) Many N-atom Containing Compounds are Asymmetric in Nature so they shows optical Isomerism.

→ If in compound all the three Valencies of N-atom are attached with different atom OR groups and N-atom has One l.p. then such type of compound become Asymmetric & it Shows optical Isomerism & it forms d & l isomer.



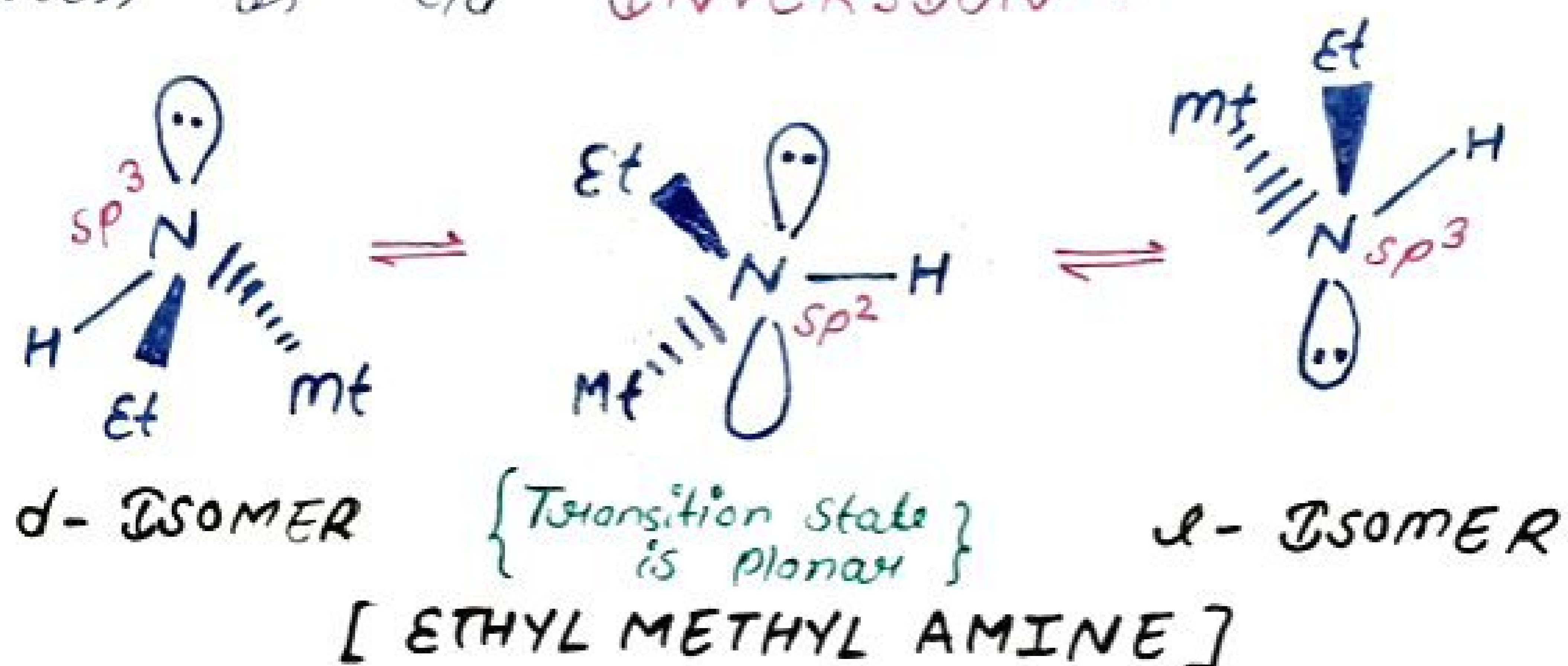
d-isomer



l-isomer

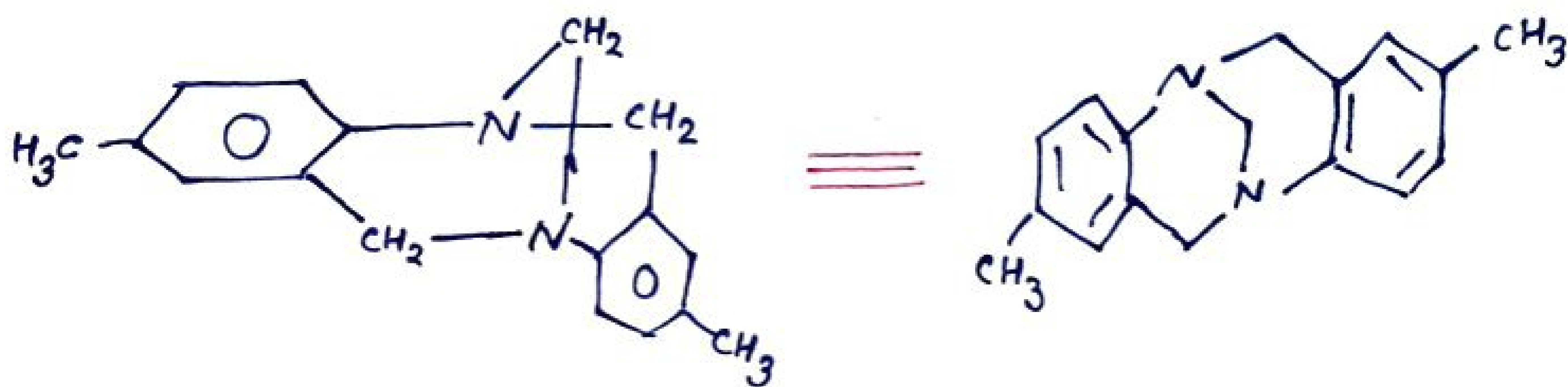
Mt → Methyl
Et → Ethyl

Such Type of Compound Shows FLIPPING and this process is called INVERSION.

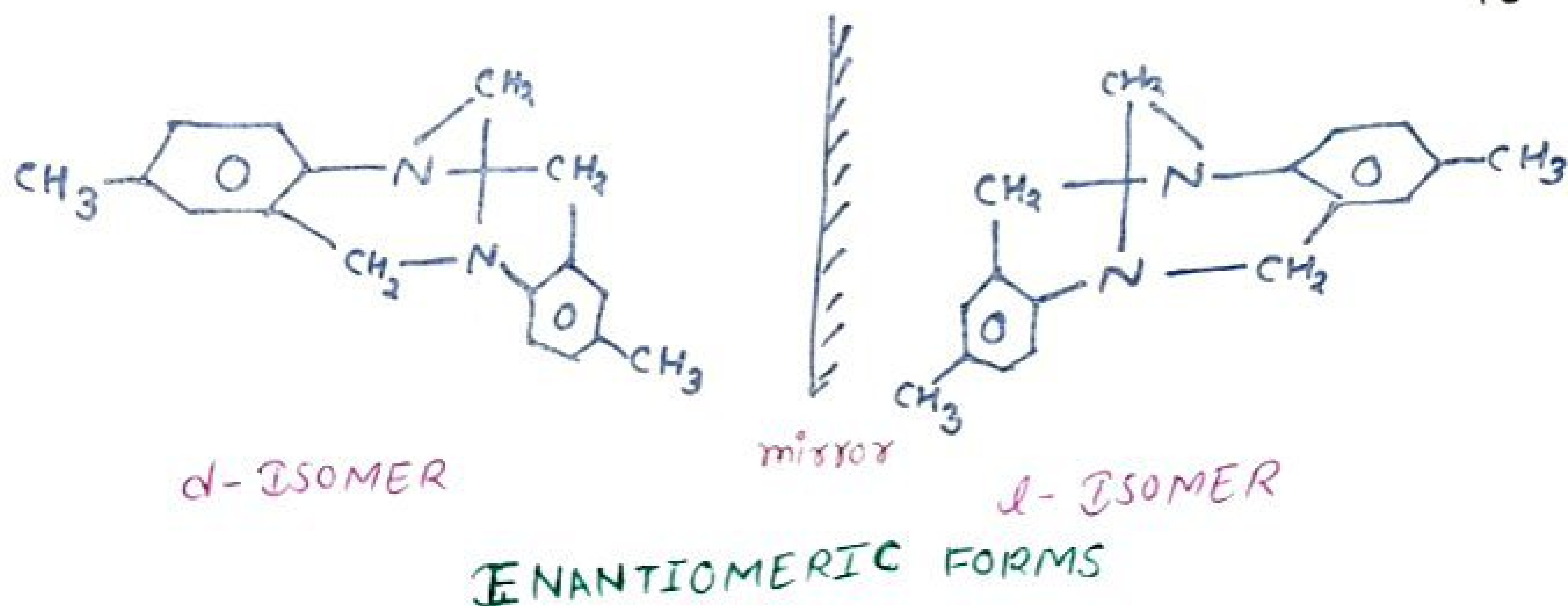


→ When the N-atom is present at a Ring Junction in Bridged Ring Systems, the Pyramidal inversion is not possible without Bond Breaking. Thus, with proper substitution the tricoordinate nitrogen becomes a stable Centre of chirality as in "TROGER BASE"

- which has been resolved (Prelog & Wieland 1944)
- By CHROMATOGRAPHY ON powdered (+) LACTOSE.



TROGER'S BASE

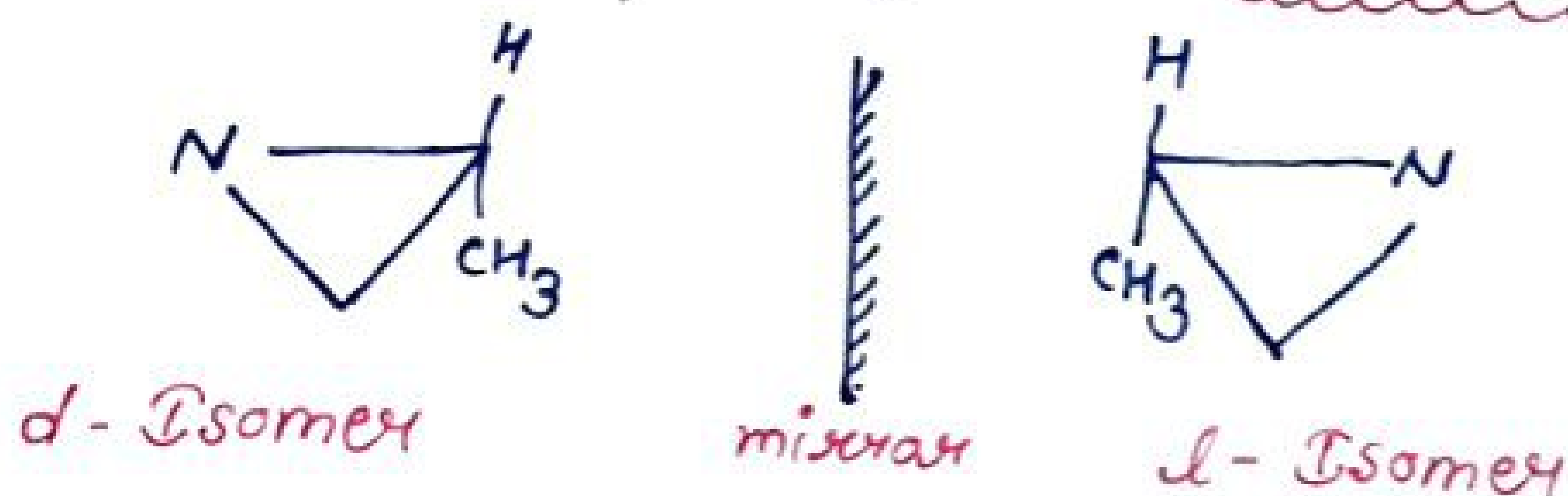


● Example :- 3.) **AZIRIDINE :-**

Three membered Containing ring Compound in which N-atom is present as Hetero atom is called Aziridine.

→ Molecule become Asymmetric due to presence of Hetero N-atom and Shows optical Isomerism.

It has two Optical Isomers d & l Respectively and they are Isolated easily at -50°C temperature.



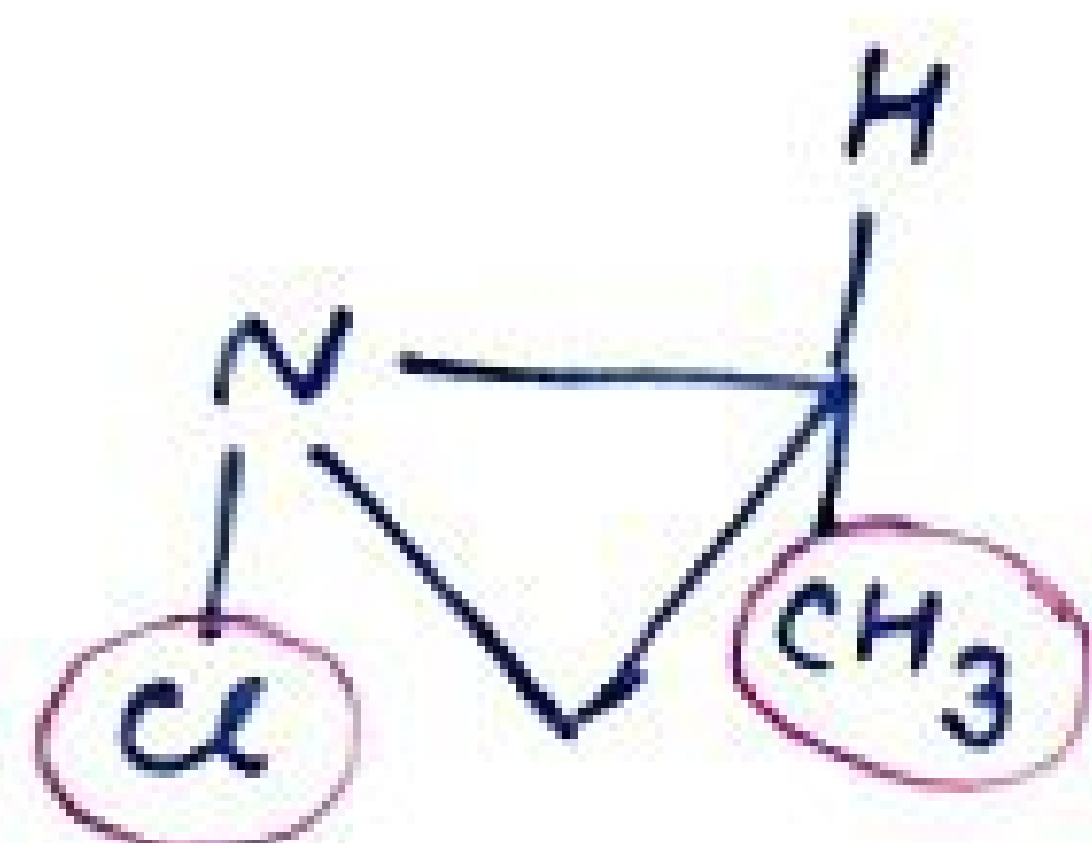
Aziridine Compound shows optical Isomerism as well as Geometrical Isomerism.

And Its Isomerism depends upon following two factors :-

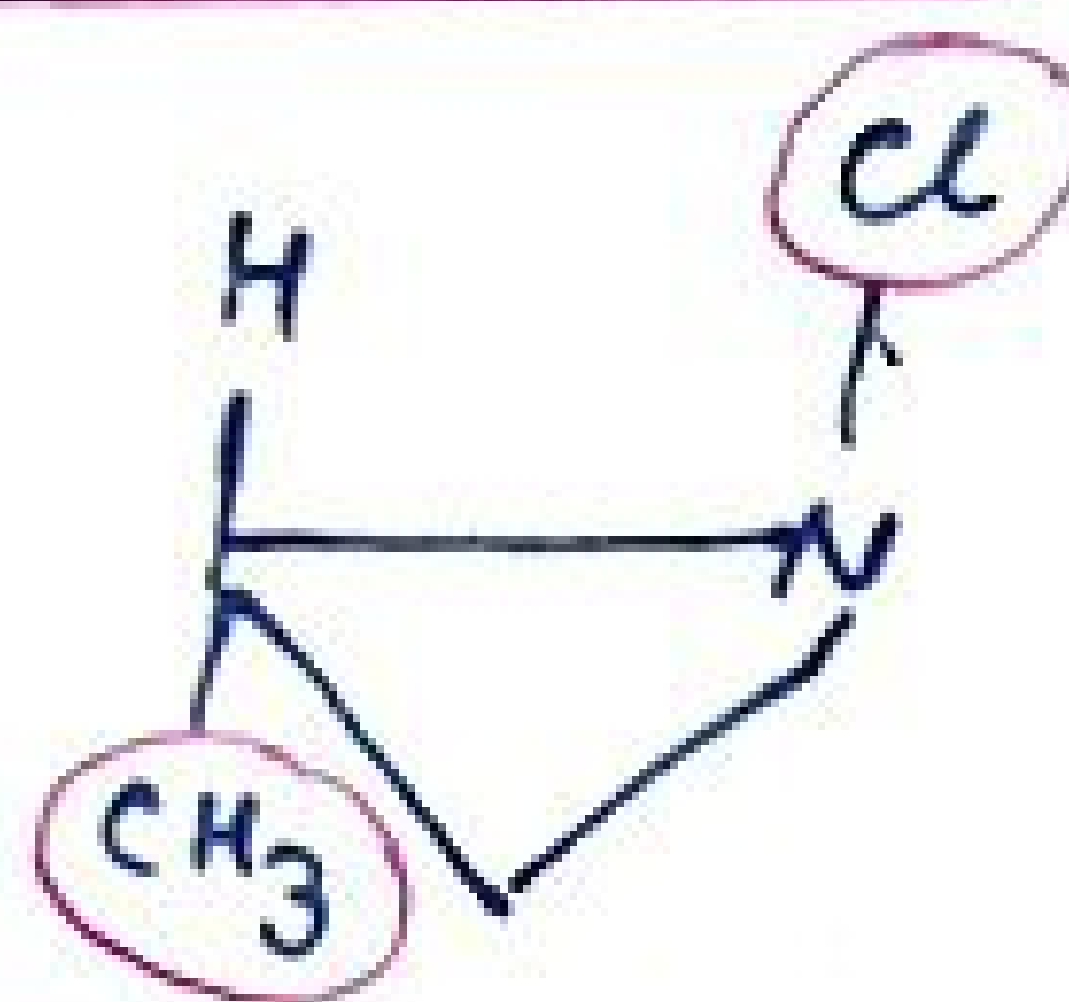
- 1.) Nature of N-atom
- 2.) Nature of Substituted group present at N-atom

If the Bulky group is present at N-atom then the compound Aziridine becomes Rigid and free Rotation becomes Restricted. So that this molecule shows Geometrical Isomerism and it form Cis & Trans geometrical Isomers.

The Isomer in which Substituted group of Nitrogen and neighbouring C-atom are placed at same direction
 ● is called Cis Isomer & Vice-versa.



Cis ~ 1-chloro-2-methyl Aziridine



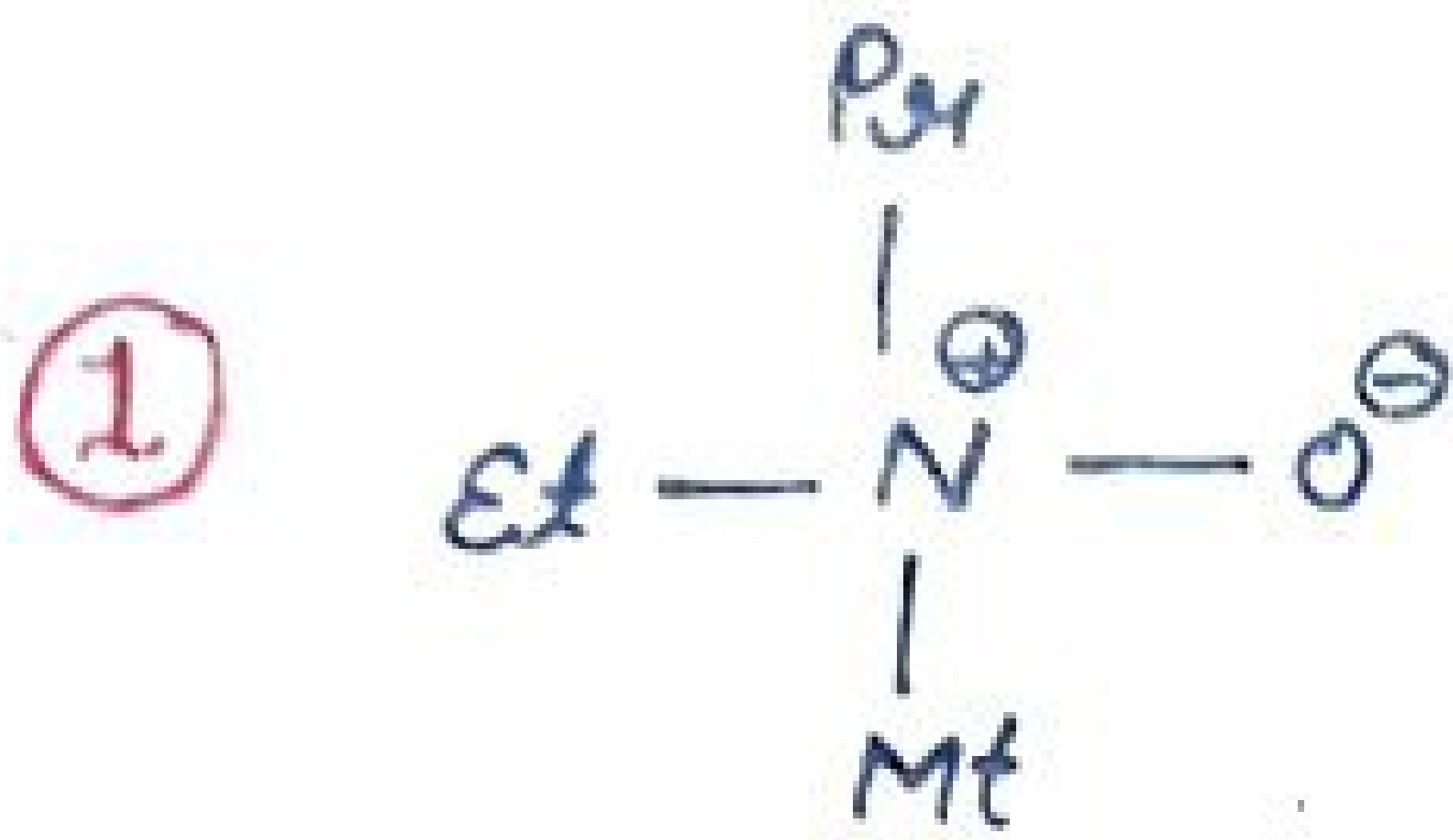
Trans ~ 1-chloro-2-methyl Aziridine

● Example - (iv) 3° AMINE OXIDE :-

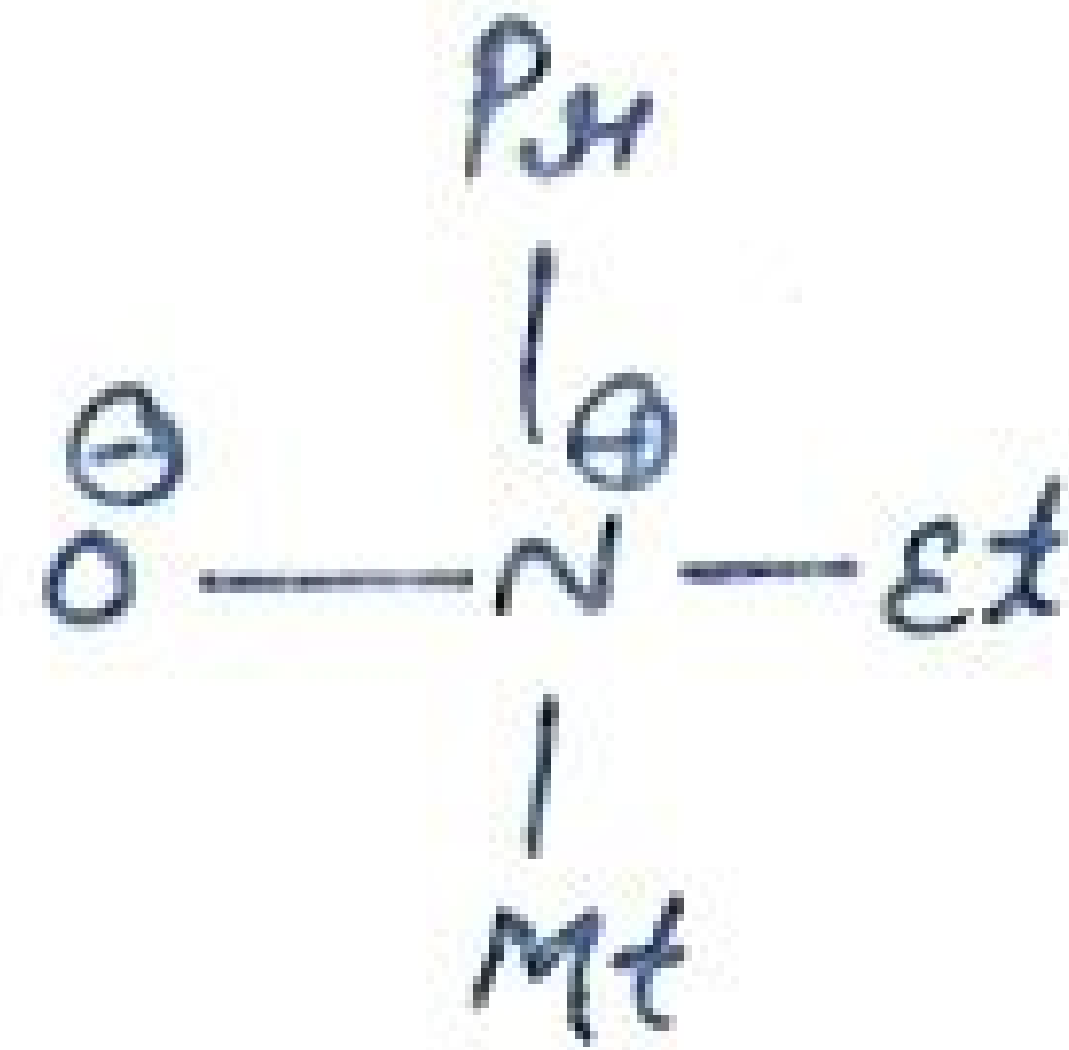
In 3° -Amine Oxide, all the 4-Valencies of N-atom are attached with Different groups. So this N Behaves as chiral nitrogen and due to its presence molecule becomes Asymmetric and shows optical Isomerism.

for Example →

Mt → -CH₃
 Et → -CH₂-CH₃
 Pr → -CH₂-CH₂-CH₃



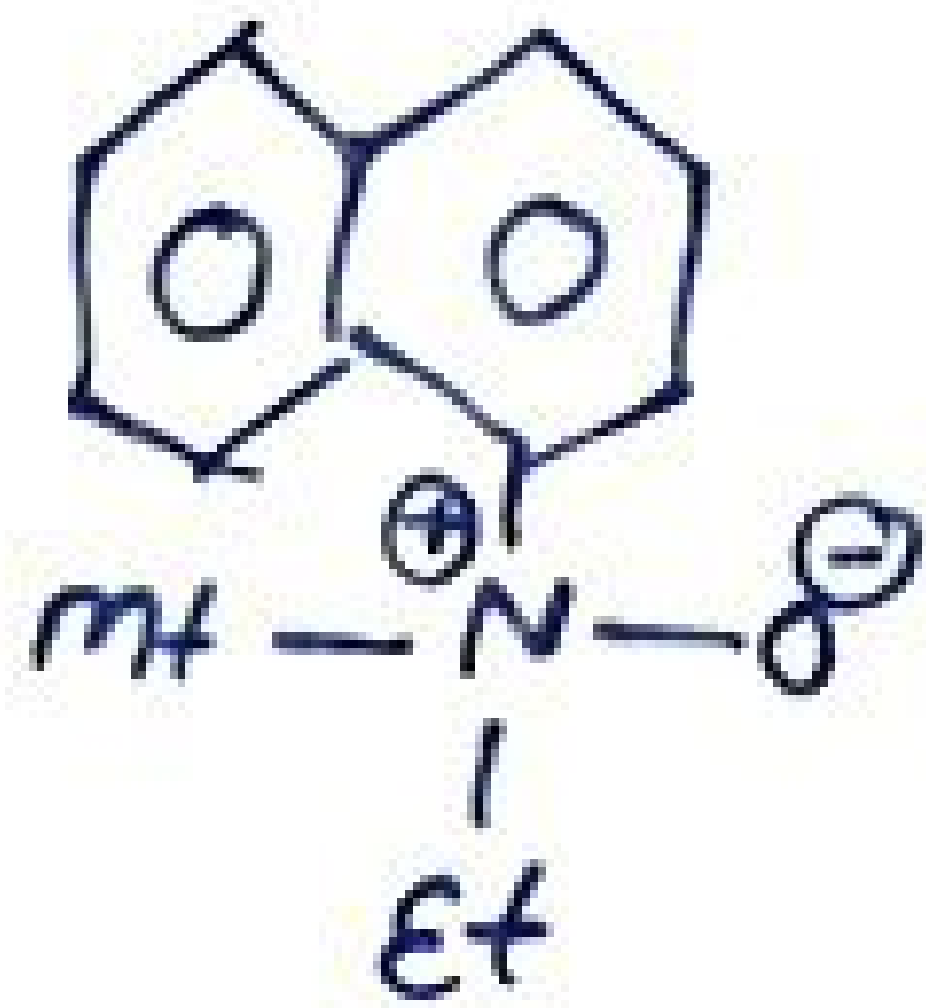
d- ISOMER



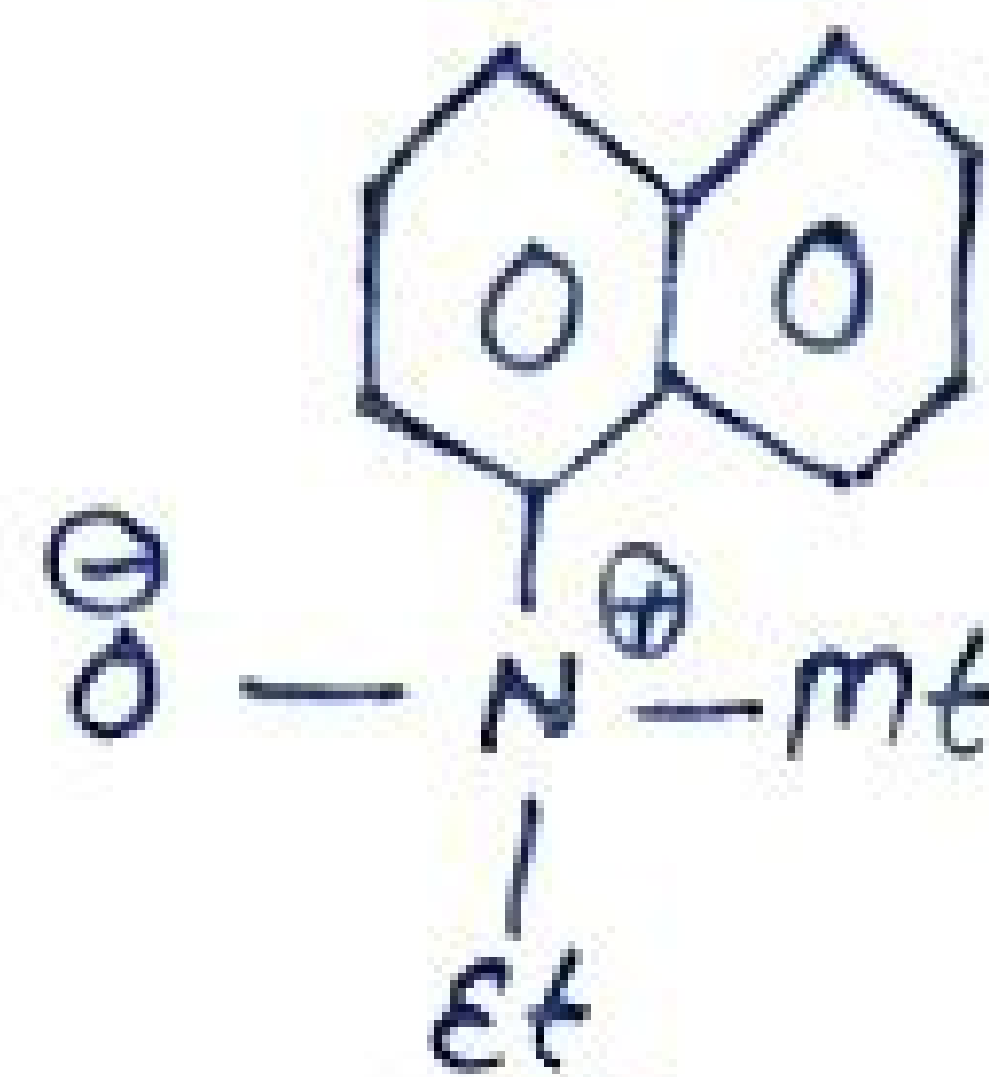
l- ISOMER

ETHYL METHYL PROPYL AMINE OXIDE

②



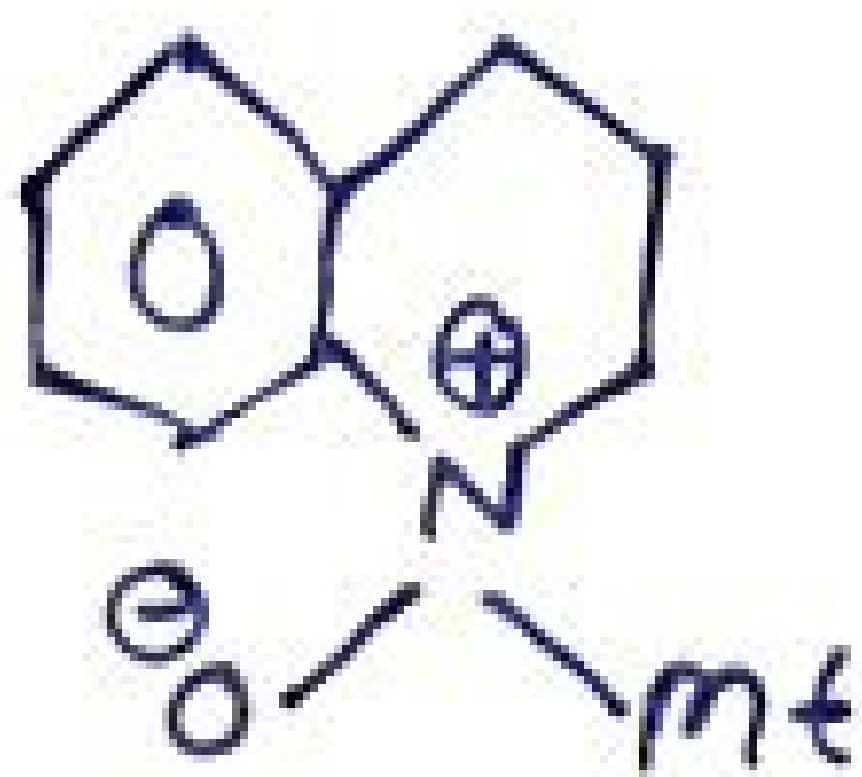
d- ISOMER



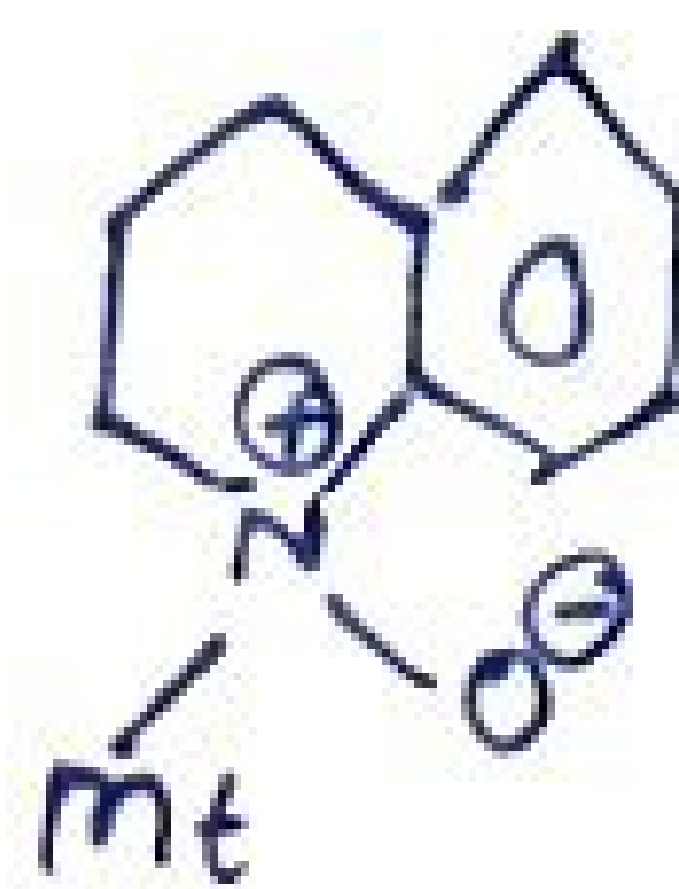
l- ISOMER

ETHYL METHYL NERPHALENE AMINE OXIDE

③



d- ISOMER

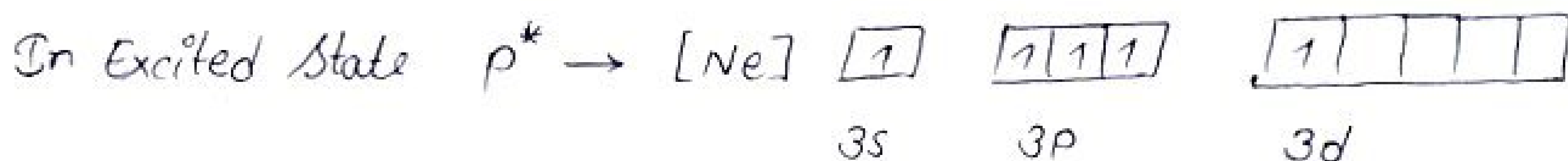


l- ISOMER

KEROLENE OXIDE

STEREO CHEMISTRY OF P COMPOUNDS

Phosphorus and Arsenic can exhibit valencies of 3, 4, 5 ... hence they give rise to more possible configurations than nitrogen.



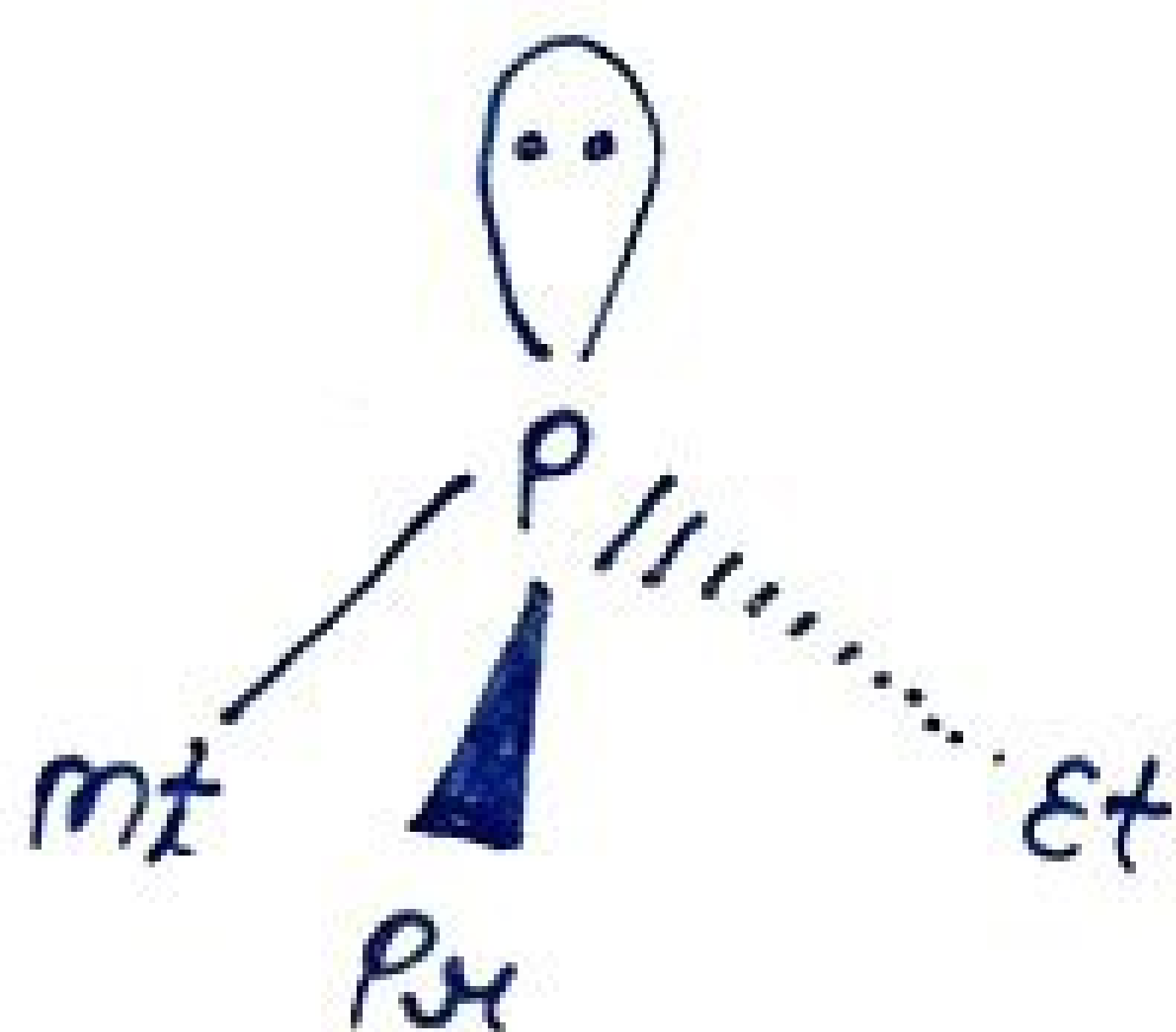
Valency of 'P' = 3, 4, 5

● Thus it forms 3, 4, 5 valent compounds.

Phosphorus atom has vacant d-orbitals. So it shows 3, 4, 5 valencies.

A) TRIVALENT PHOSPHORUS Compound :- (3-valency) :-

Ex:- Ethyl Methyl Propyl Phosphine \rightarrow



In this compound phosphorus atom is sp^3 hybridized & it has one l.p. of e^- . So that it has pyramidal

● Structure. In this compound different groups are attached with the valencies of P-atom. So its behaviour is like a chiral atom. Compound gets asymmetric due to the presence of chiral P-atom and shows optical

Isomerism.

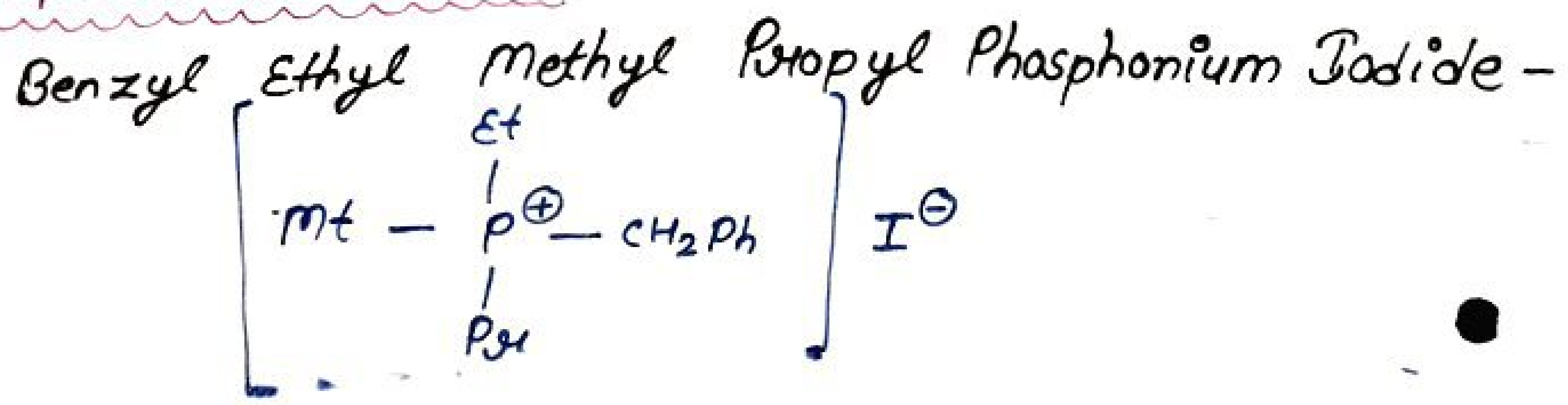
B.) QUADRIVALENT (QUATERNARY) PHOSPHORUS COMPOUND :- (4-Valency) :-

Ex:- Phosphonium Salt -

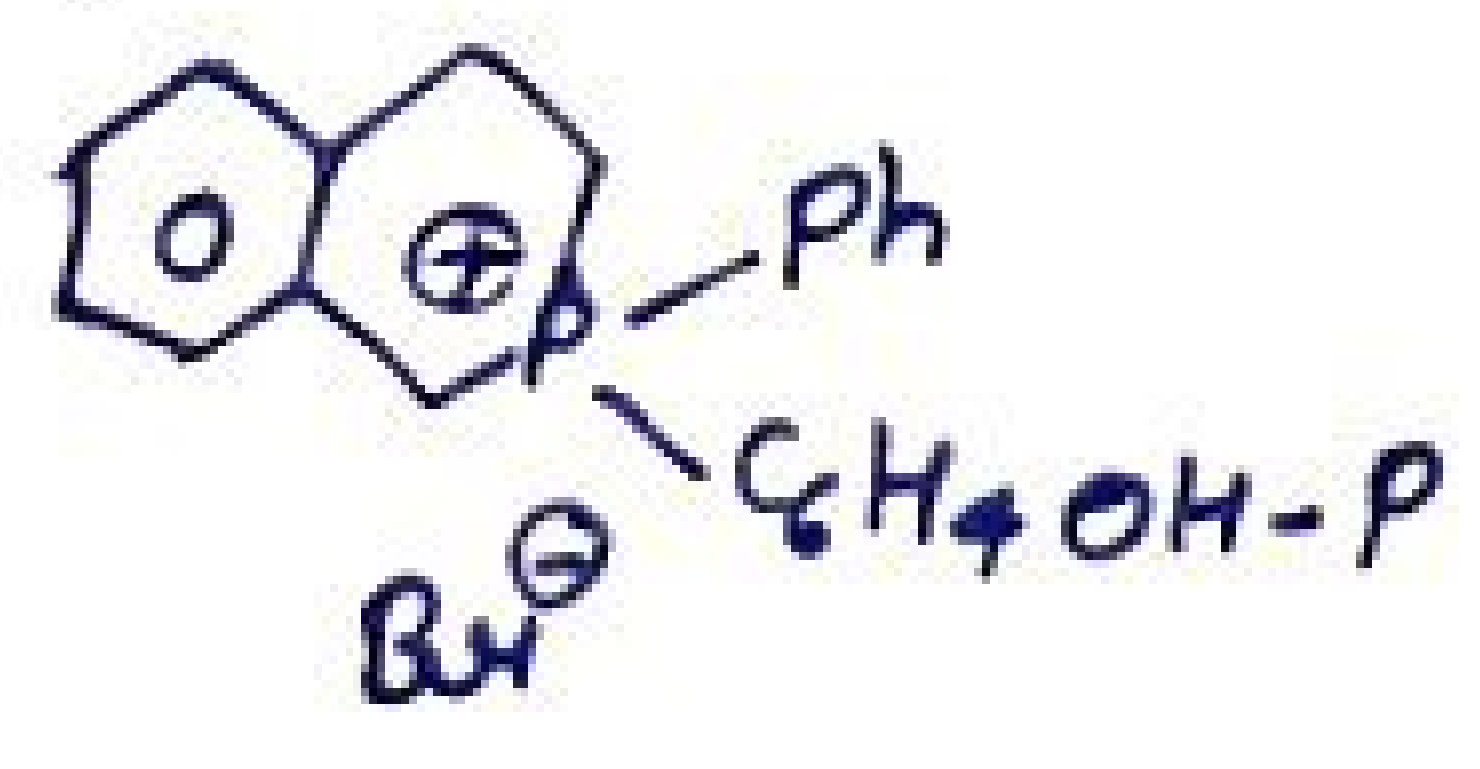
Generally, Phosphonium Salt Containing alkyl groups.

However In this following quaternary phosphonium salt Different groups are attached with the Valency of P-atom. Due to presence of chirality in molecule it become asymmetric and shows

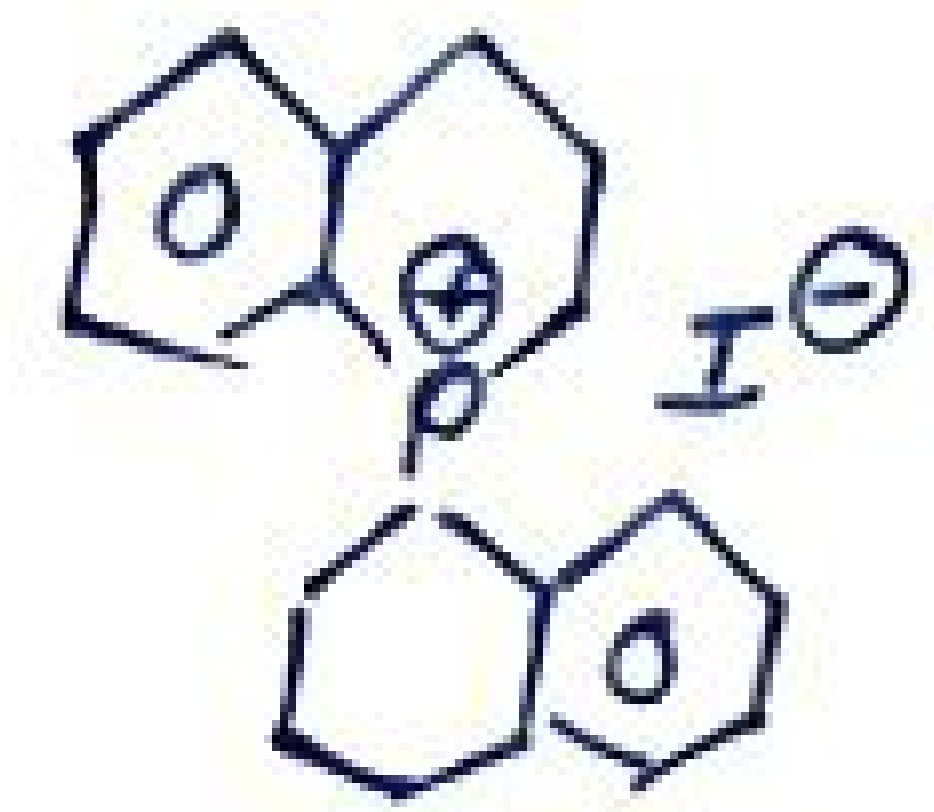
optical Isomerism



➔ As Expected Phosphonium Salt Containing Phosphorus in the Ring are more optically active and can easily be Resolved -



2-Ph-Hydroxy Phenyl 2-Phenyl-1,2,3,4 Tetrahydro-iso Phosphorinolinium Bromide



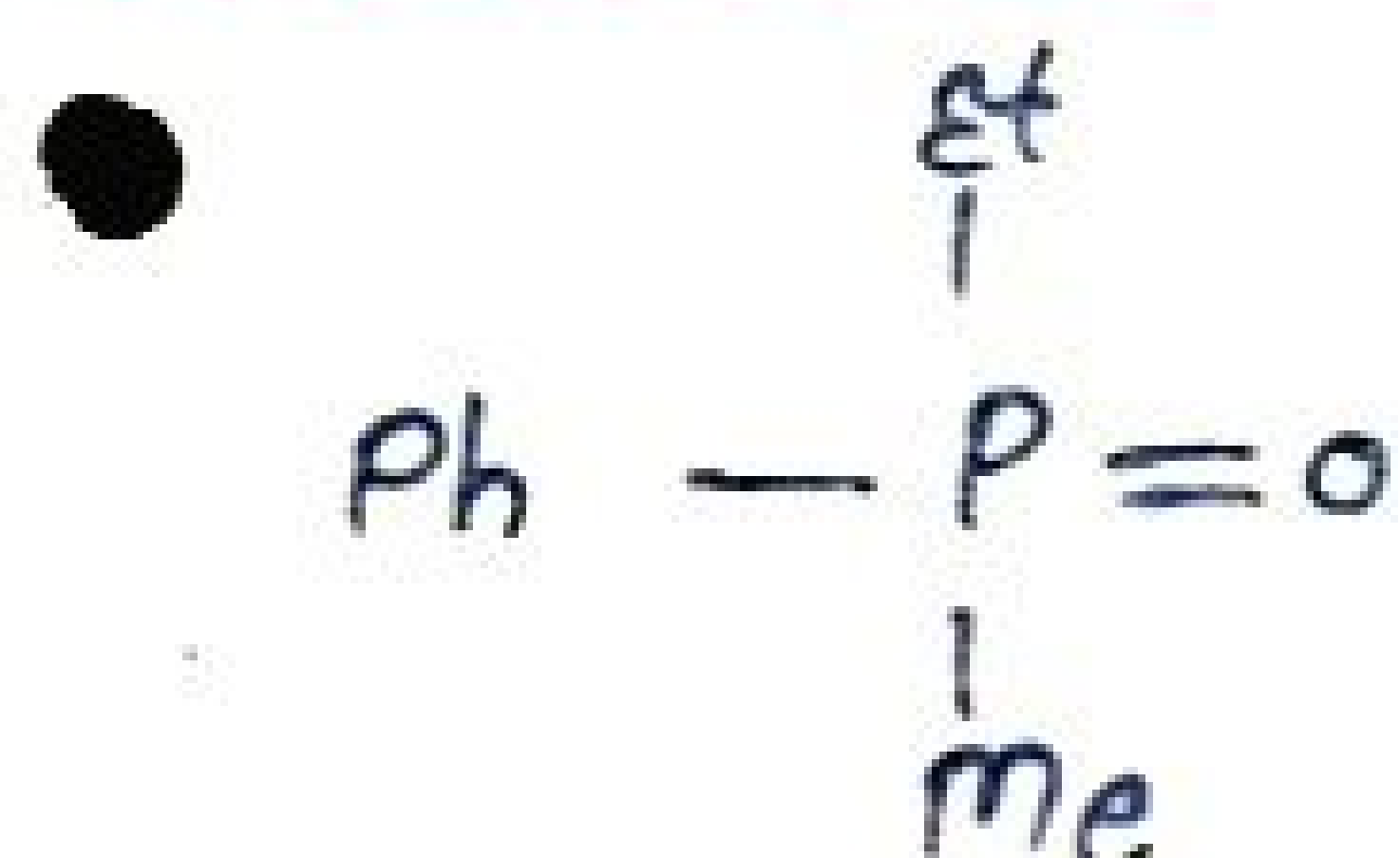
P-Spirobis-1,2,3,4-Tetrahydro phosphorinolinium Iodide

C) QUINQUEVALENT PHOSPHORUS COMPOUNDS :-

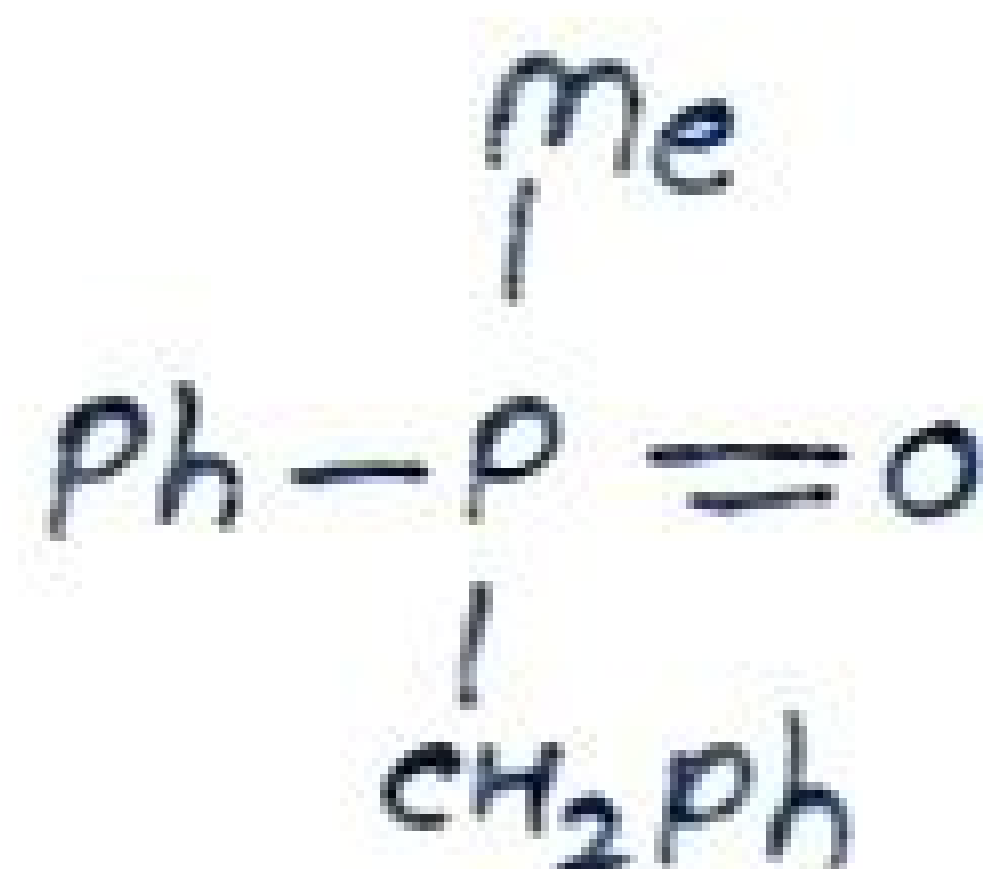
In Many Compounds Due to the presence of double bond the molecule has non-linear structure.

So that it becomes asymmetric & shows optical

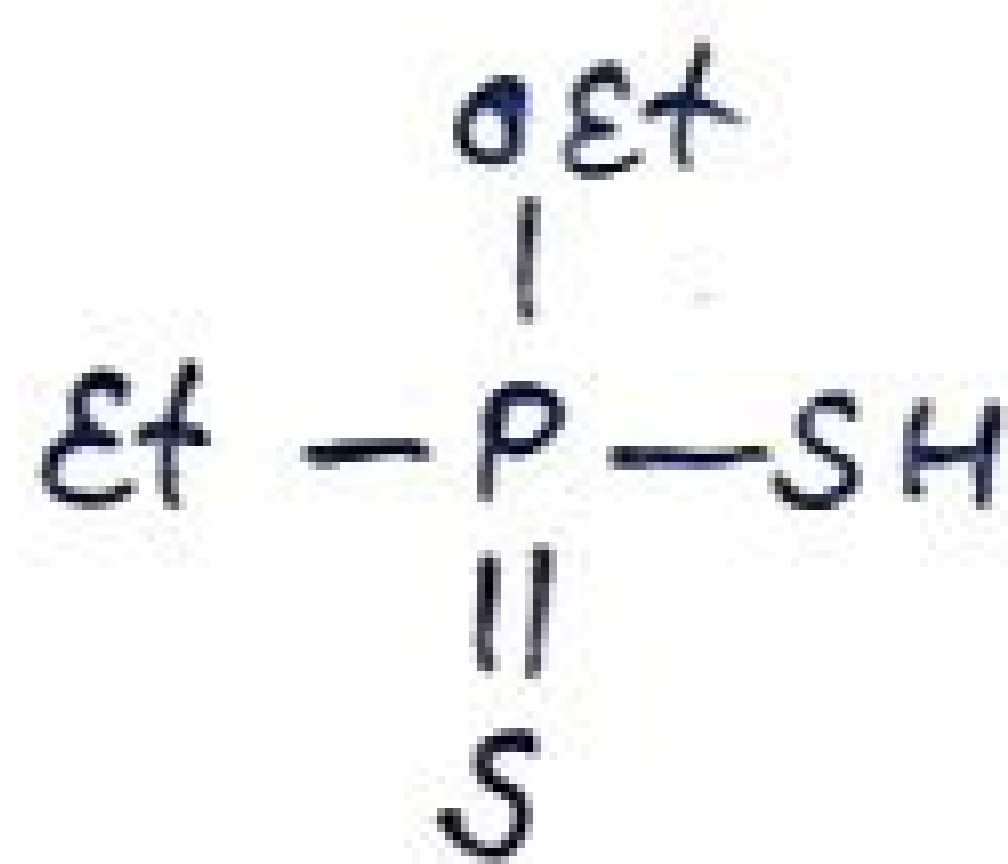
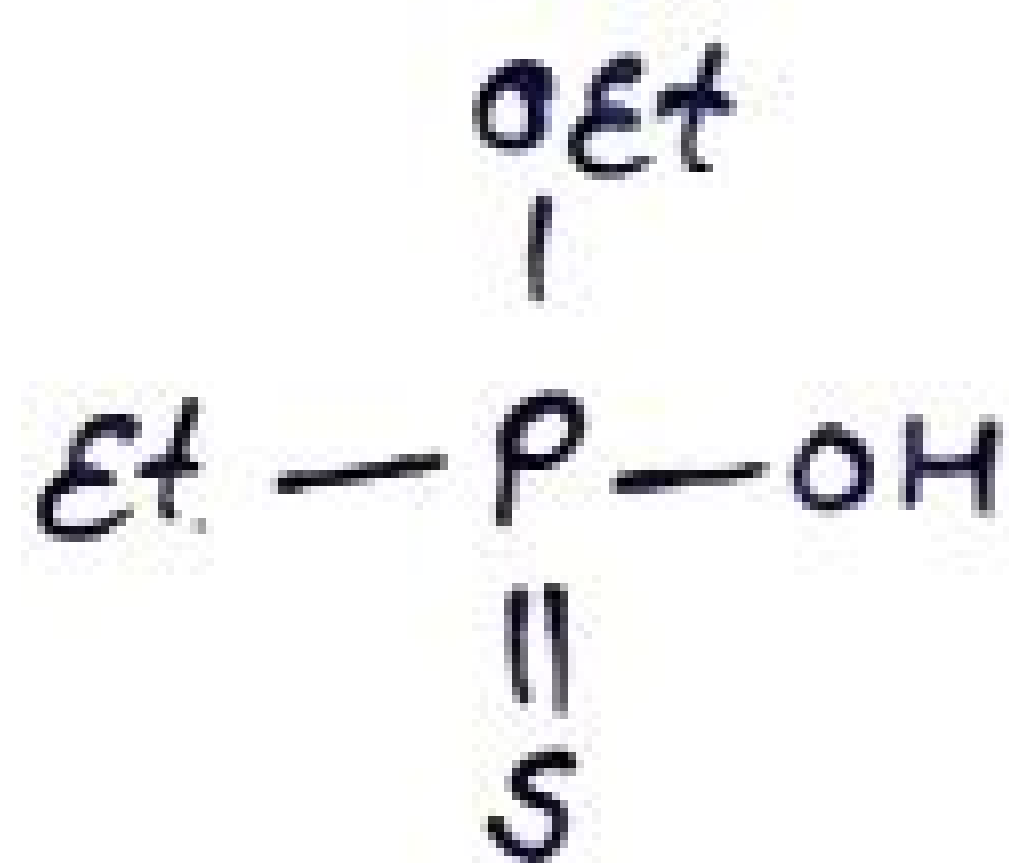
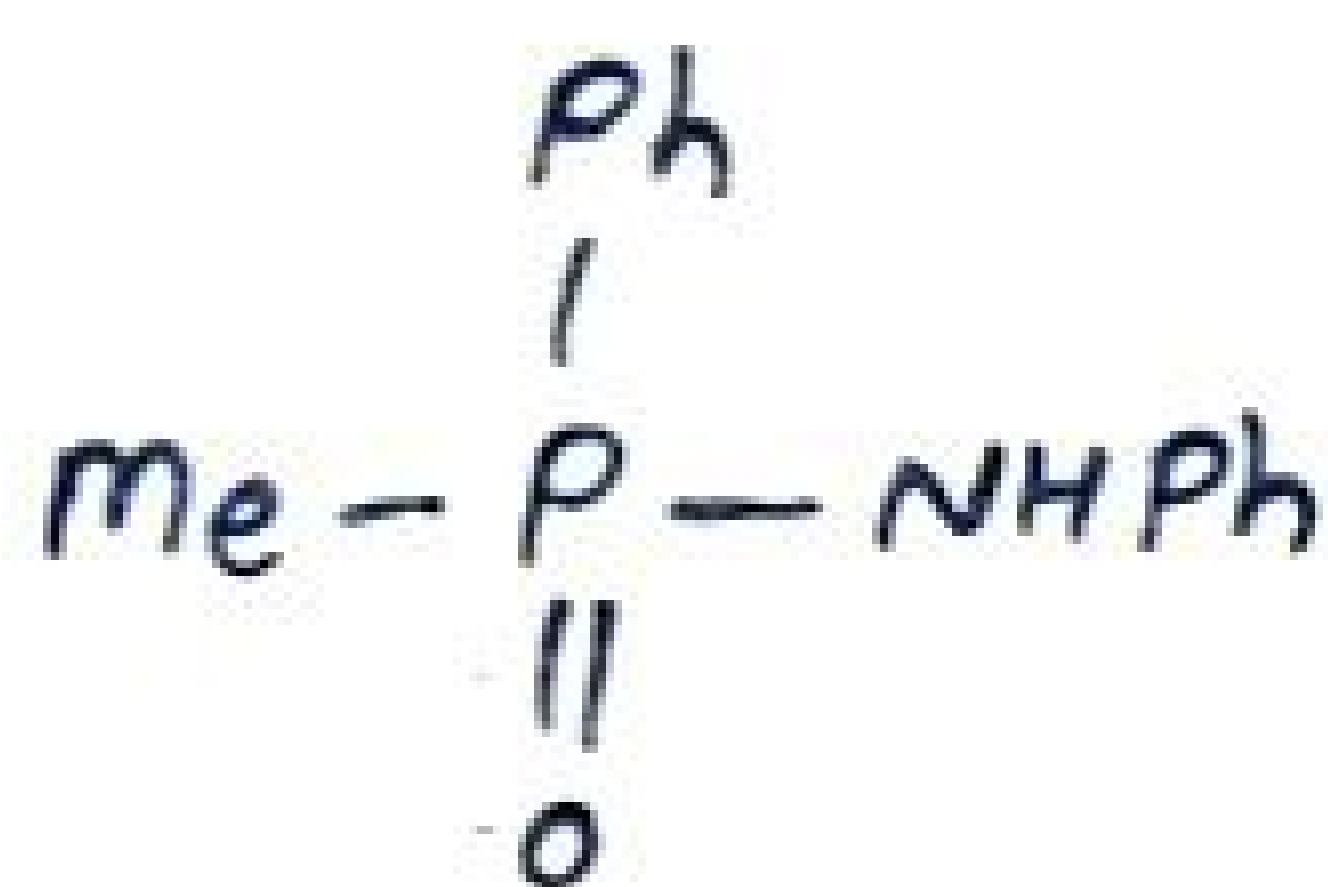
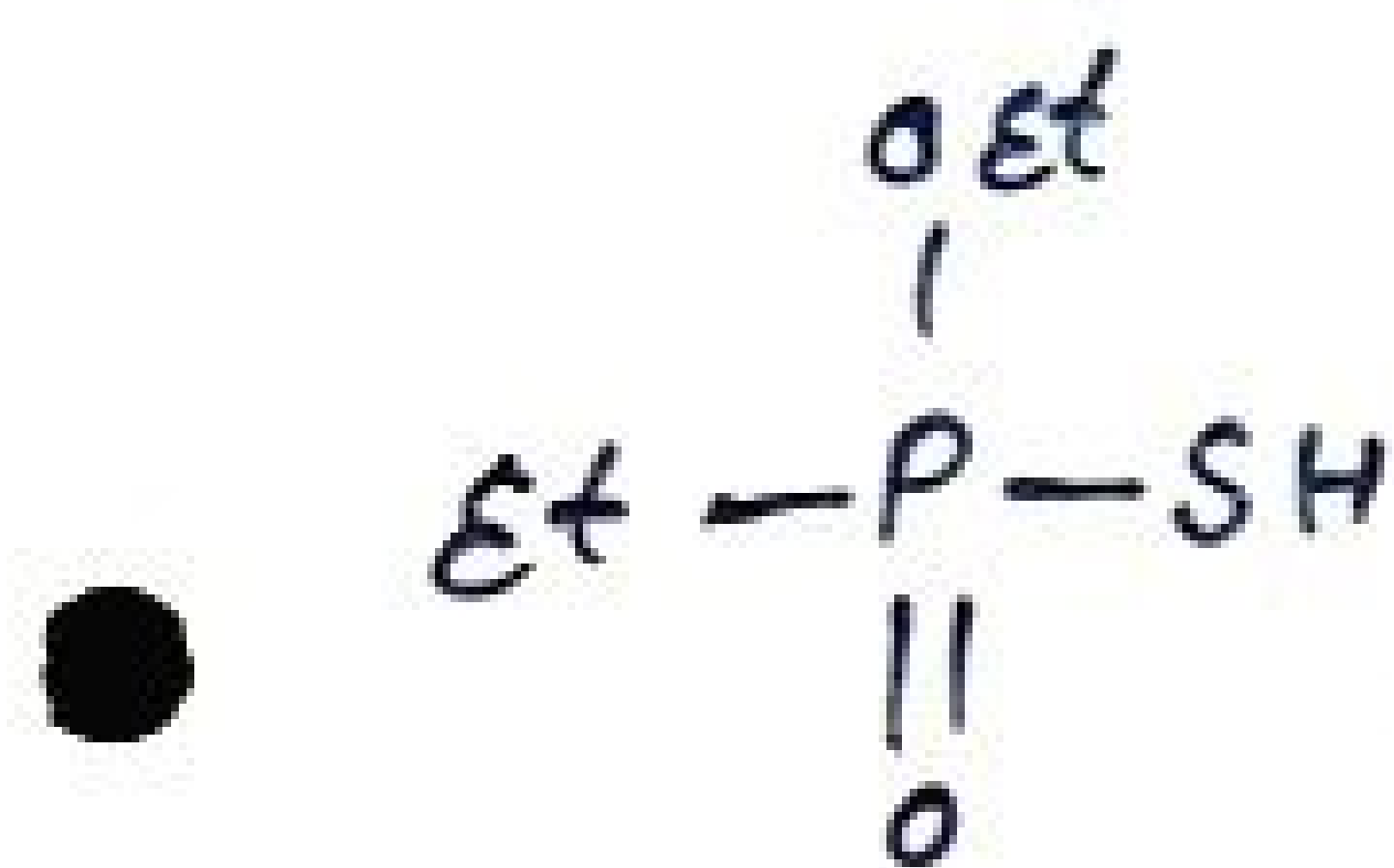
Isomerism.



Ethyl Methyl Phenyl
Phosphone



Benzyl Methyl Phenyl
Phosphone



STEREO CHEMISTRY OF S COMPOUND

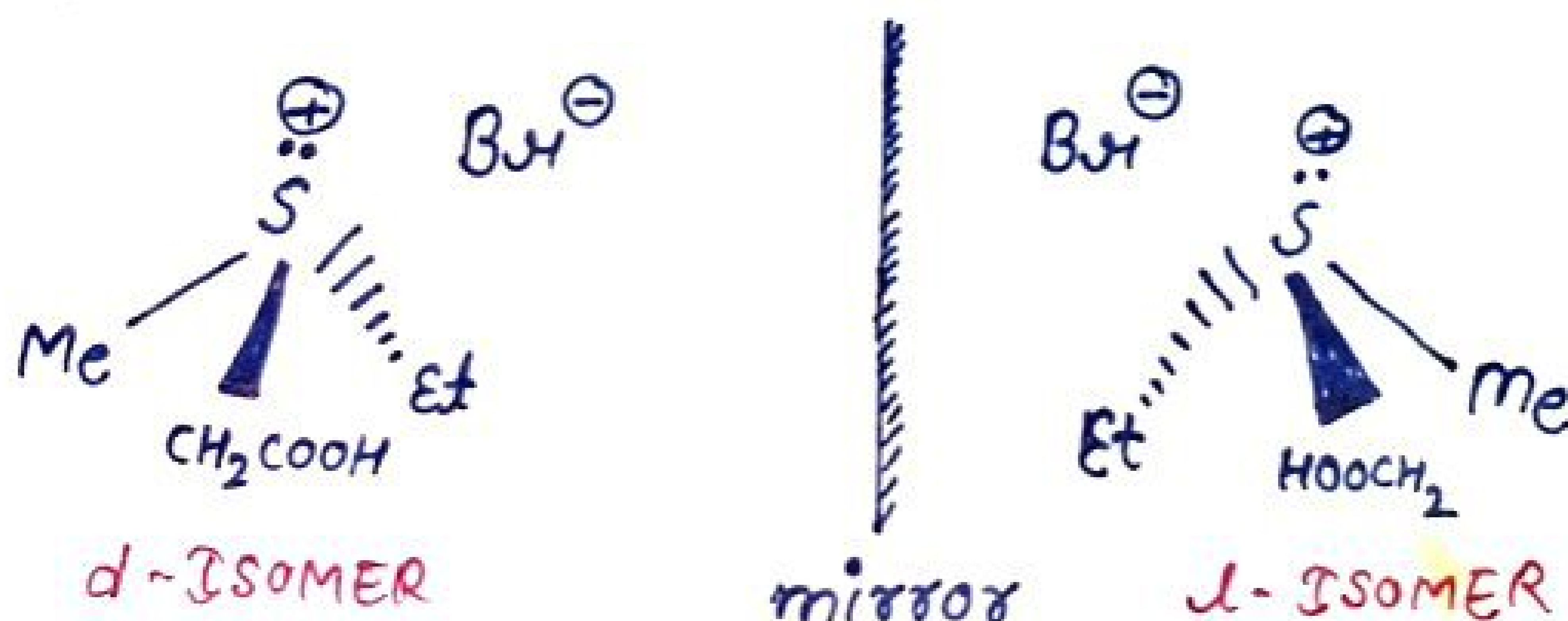
Various Types of Sulphur Compounds have been found to exhibit optical Activity i.e., they show Enantiomerism (optical Isomerism).

There are 3 types of sulphur Compounds which show optical Isomerism. :-

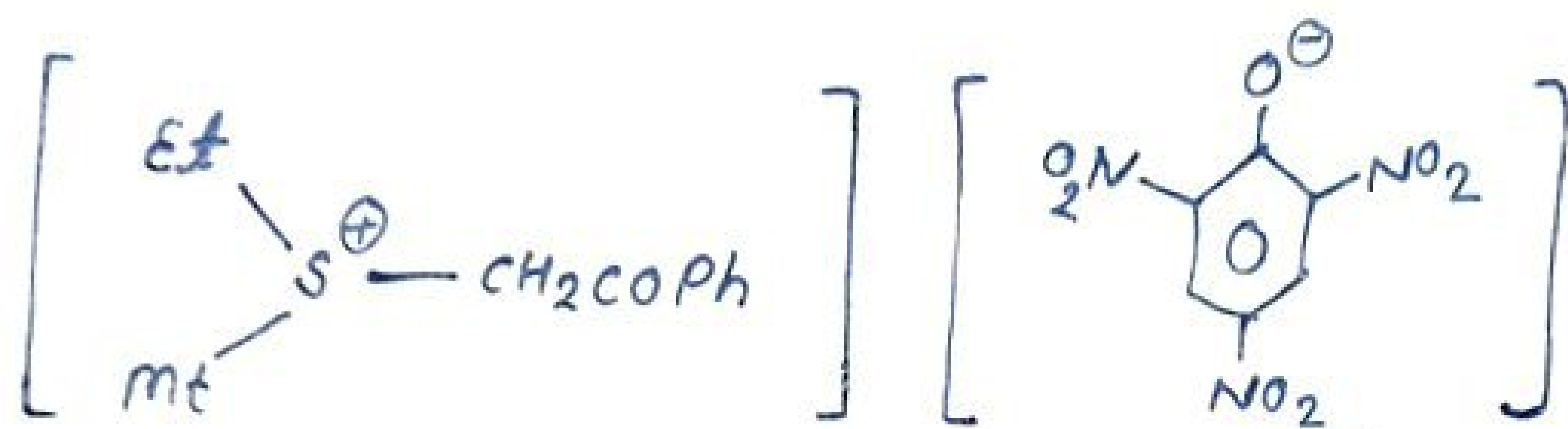
1.] SULPHONIUM SALT :- Several chiral

Sulphonium Salts of the type $R^1R^2R^3S^{\oplus}X^{\ominus}$ have been resolved into their enantiomers. For Ex:-

It has been proved that Carboxymethyl Ethyl Methyl Sulphonium Bromide exist in the following Enantiomeric forms :- [NON-PLANAR STRUCTURE]

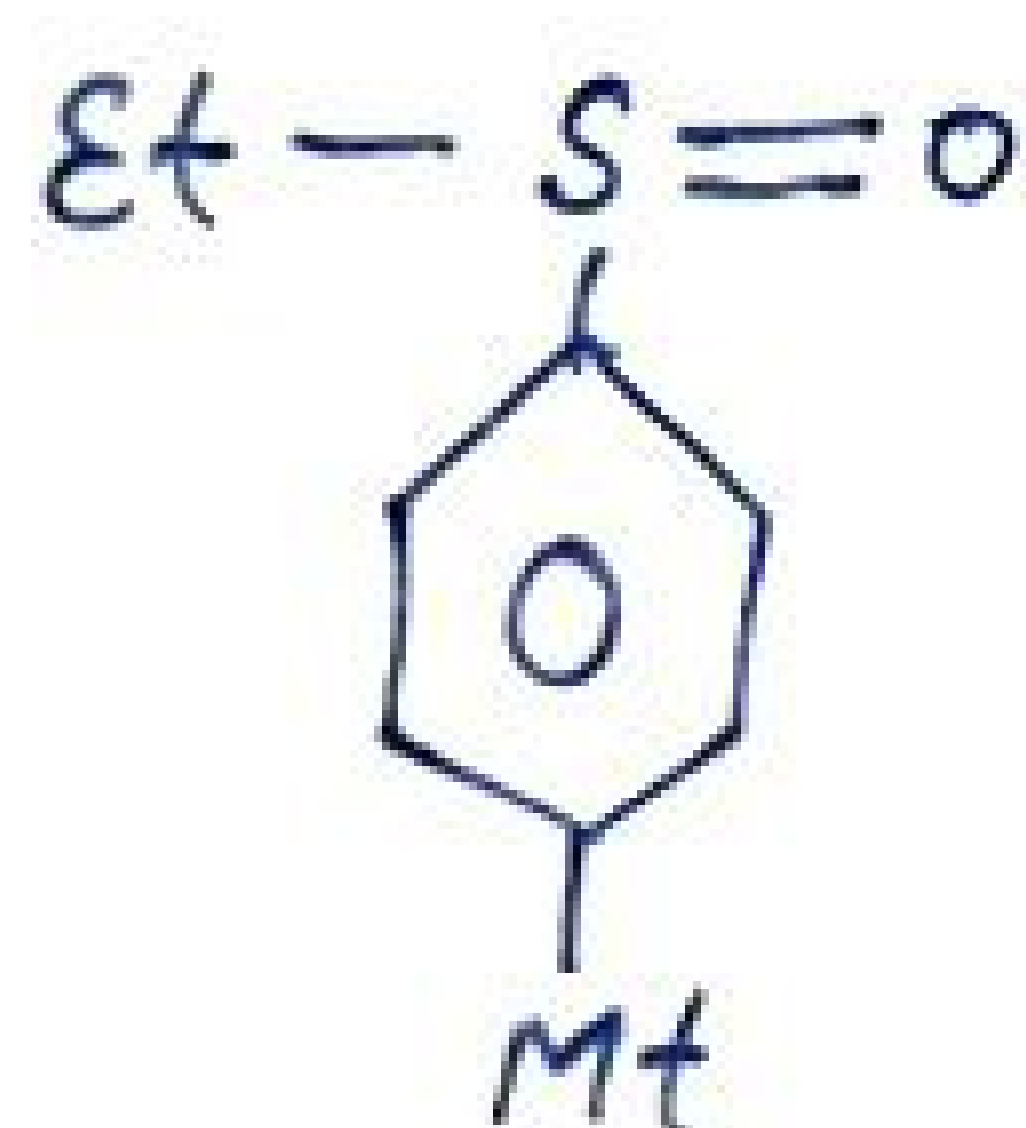


Ethyl Methyl Phenacyl Sulphonium Picrate :-¹⁸

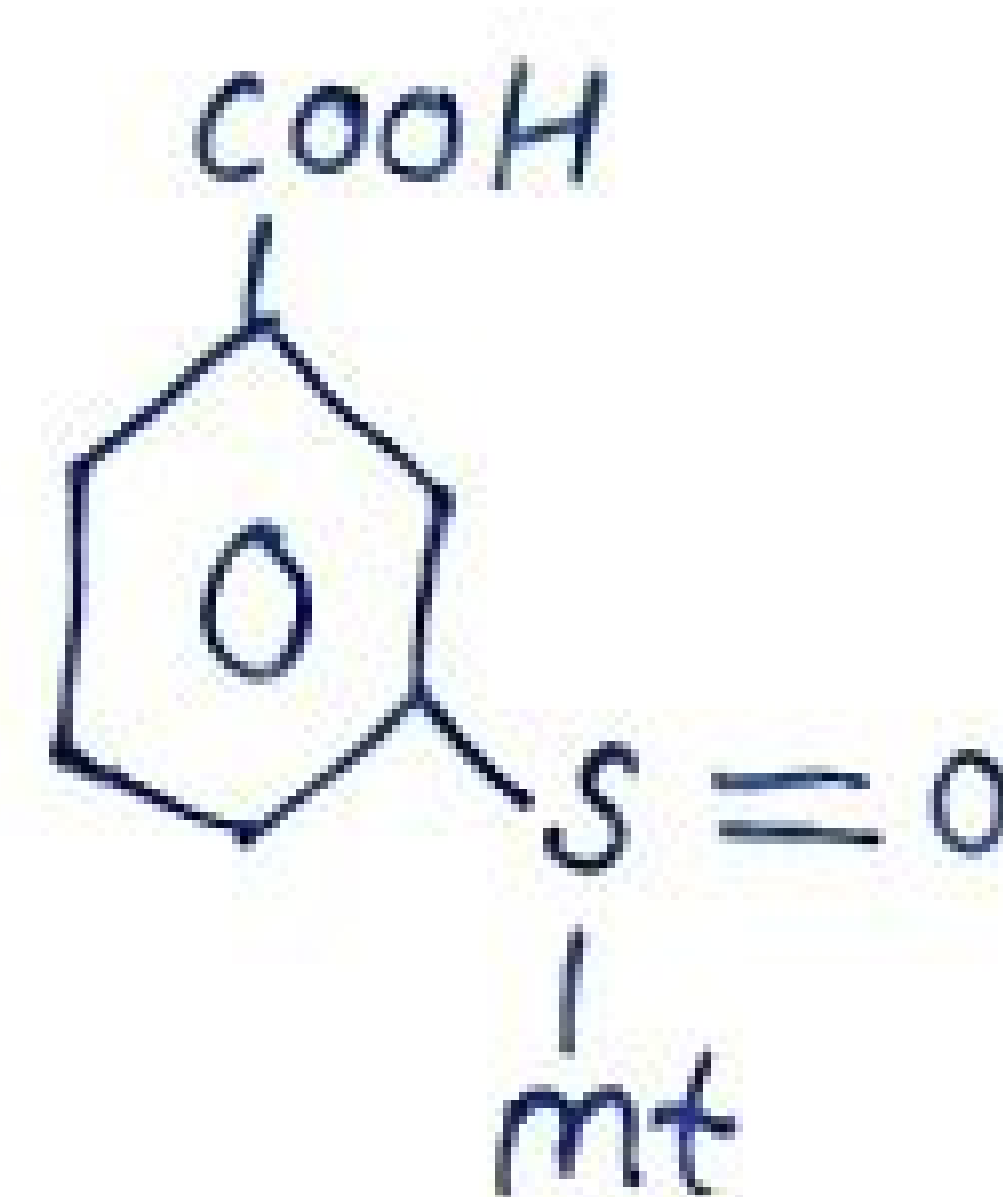


2.] SULPHONATE / SULPHOXIDE :- In such type of

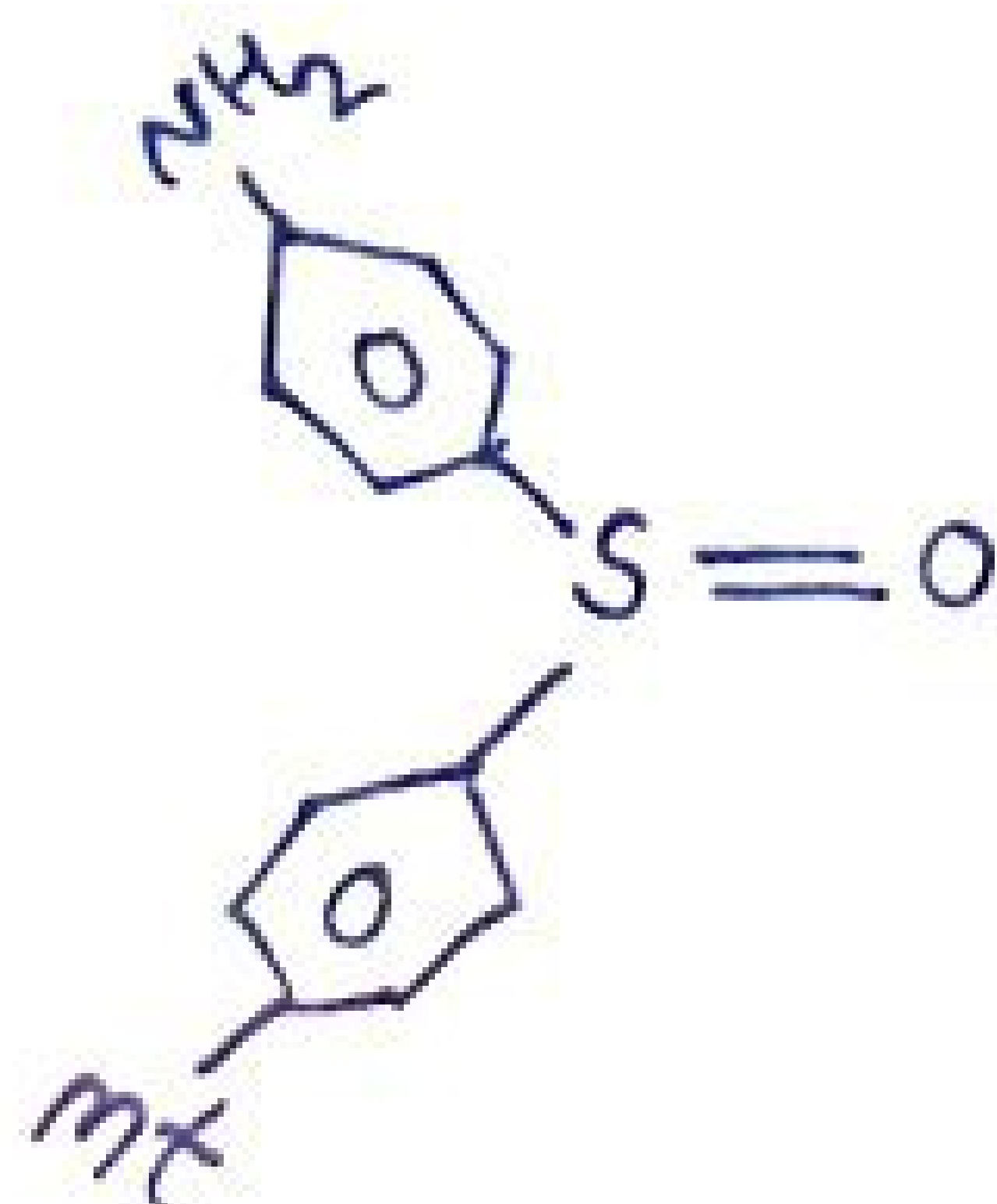
Compounds due to presence of double bond & Benzene Ring compound gets Non-planar. So it gets Asymmetric & shows optical Isomerism.



Ethyl p-Methyl Phenyl Sulphonate



m-Carboxyl Phenyl Methyl Sulphonate

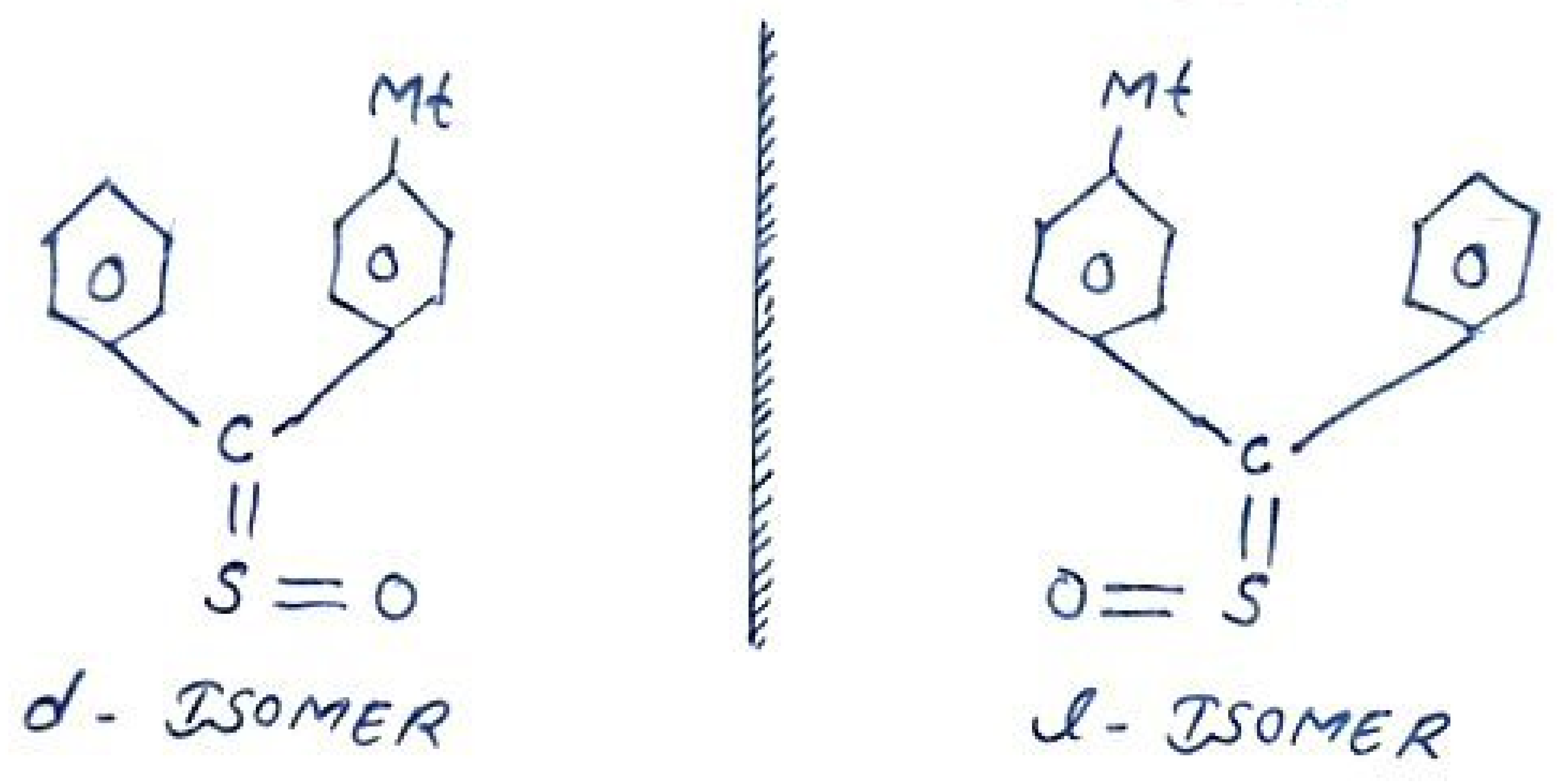


p-amino p-Methyl Bi Phenyl Sulphonate

3.] SULPHINE :- $C=S=O$ group containing

Compounds are called Sulphine.

These Compounds are Rigid and Non-planar. So they becomes Asymmetric and shows Optical Isomerism.



p-Methyl BiPhenyl Sulphine

REFERENCES

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