STEREOCHEMISTRY
Part-VII

B.Sc Hons (Chemistry)
Sem-I , Paper CC-1

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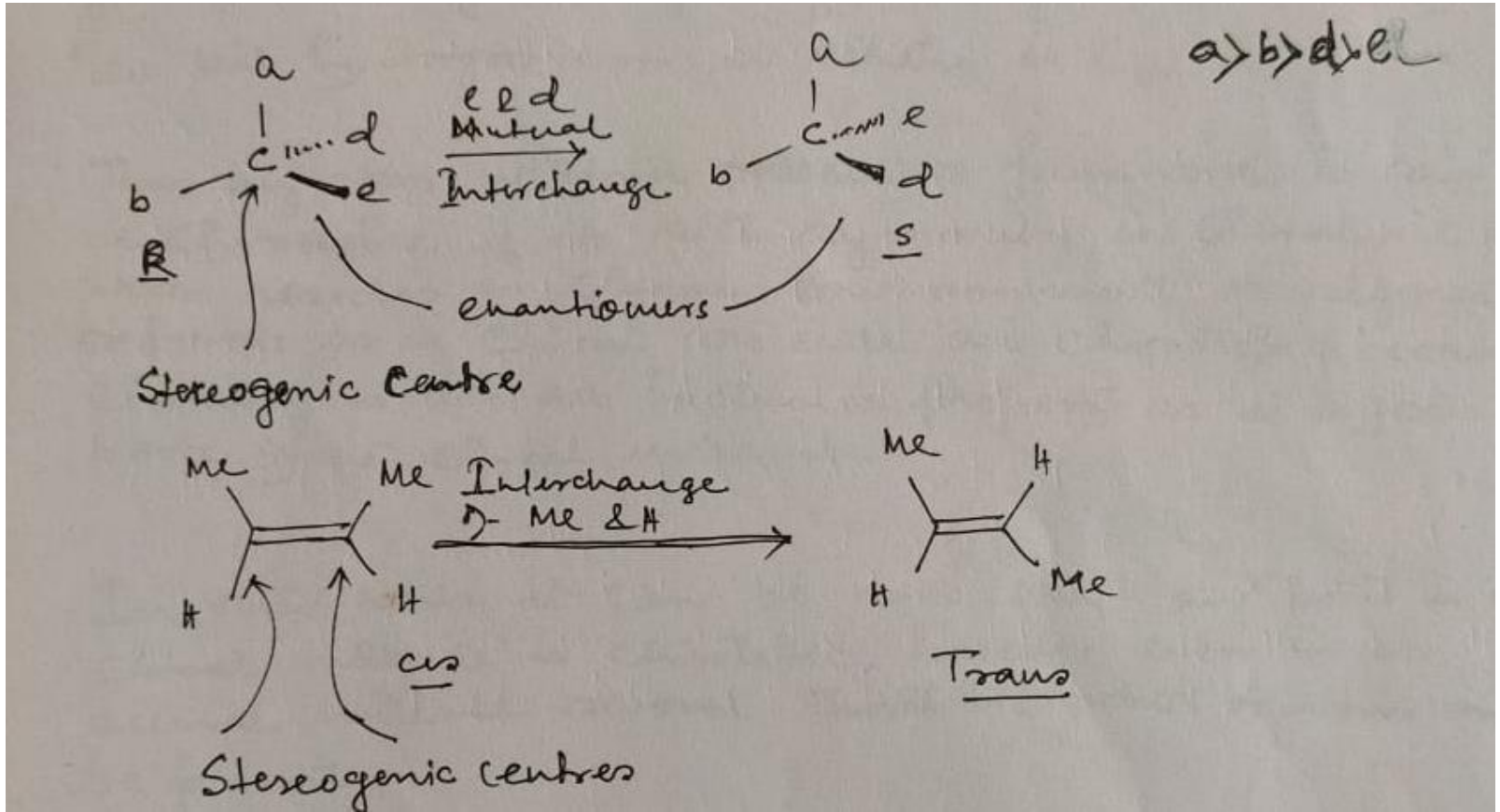
STEREOGENICITY & CHIROTOPICITY

Stereogenic centre / atom

The term may be defined as follows:

i. An atom of such nature and bearing of atom(s) and/group(s) of such nature that it can have two non equivalent configurations.

ii. An atom bearing several atom(s) and or group(s) of such nature that mutual exchange of two atom and or group will generate a new stereoisomer.



Stereogenicity

So in previous slide we discussed about stereogenic centre and molecules possessing stereogenic centre with the phenomena is called stereogenicity. This phenomena involving interchanging groups giving stereoisomers, is called stereogenicity.

Chirotopic centre/ atom

Before going into the concept of chirotopicity one needs to have an idea of local or site symmetry, i.e the point group of individual atoms/groups within the particular molecule under consideration. Depending upon the nature of connectivity same atom or group may have different types of site symmetry. e.g. hydrogen atom in H_2 has $C_{\infty v}$ but hydrogen atom in Methane is C_{3v}.

Thus any atom within a molecular framework is said to be chirotopic if its site symmetry is Chiral, ie the atom resides in Chiral environment. All segments or points in a Chiral molecule are chirotopic because Chirality is an all inclusive property as it affects all parts of the Chiral molecule.

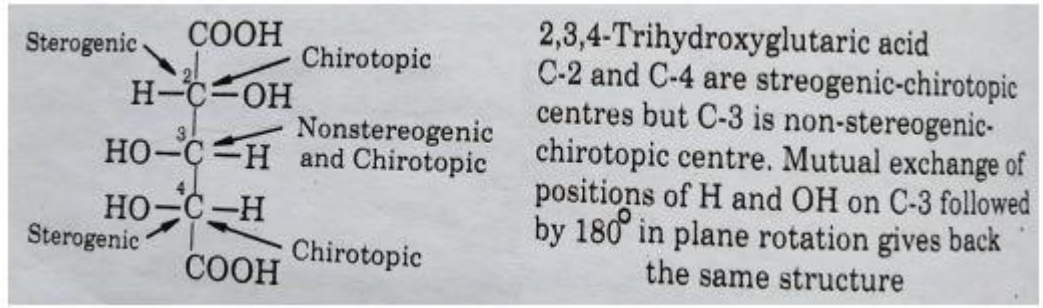
In other words it can be said that any point in a Chiral molecule is chirotopic, however even in an achiral molecule several chirotopic points or atoms may be present.

Chirotopic and achirotopic centre:

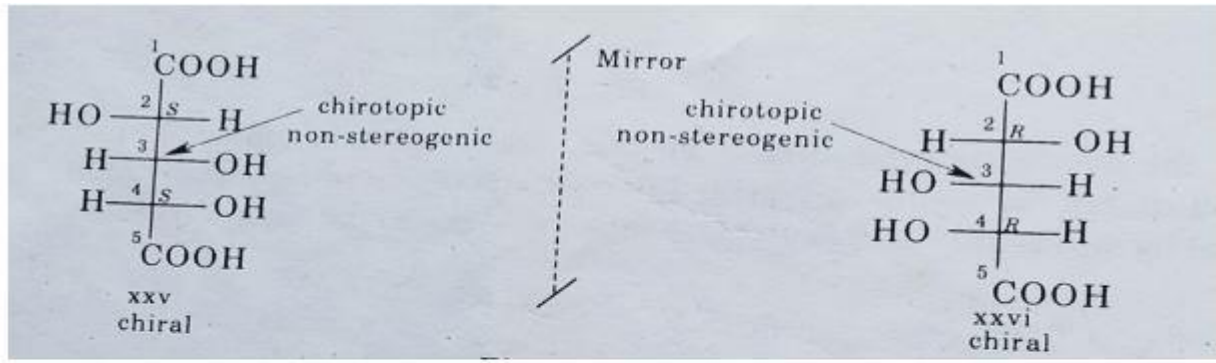
That chirality is an all-inclusive property, when considering a chiral molecule, every point in the molecule is chiral in nature. In a chiral molecule, every point in the molecule is chiral.

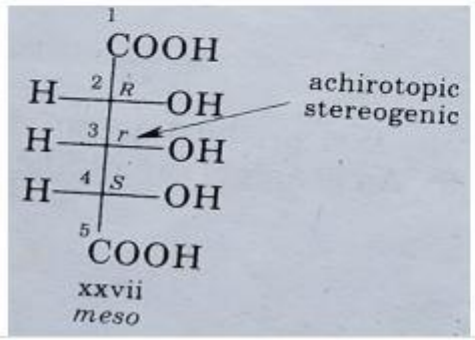
Molecular models built from atoms properly represent symmetry elements of molecules but provide incomplete information of local or site symmetry ,i.e., symmetry point group of every atom or set of atoms within the molecule

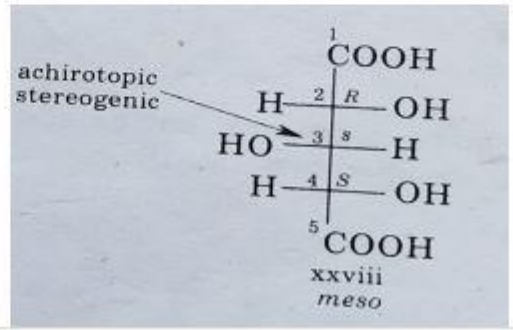
The site symmetry of atoms in molecules falls into two classes, chiral and achiral. It should be remembered that main classification of chirality and achirality is a function of geometric shape. An atom within a molecular framework is said to be chirotopic if its site symmetry is chiral, i.e., the atom resides in a chiral environment. The molecule(s) bearing chirotopic centre need not be as a whole chiral. An atom within a molecular framework is said to be achirotopic if its site symmetry is achiral, i.e., a point or atom located on a plane of symmetry or a centre of symmetry or at the point where an alternating axis of symmetry interacts in reflection plane is achirotopic. So in a chiral molecule, every point is chiral or that belongs to achiral environment and that point is called a chirotopic point.



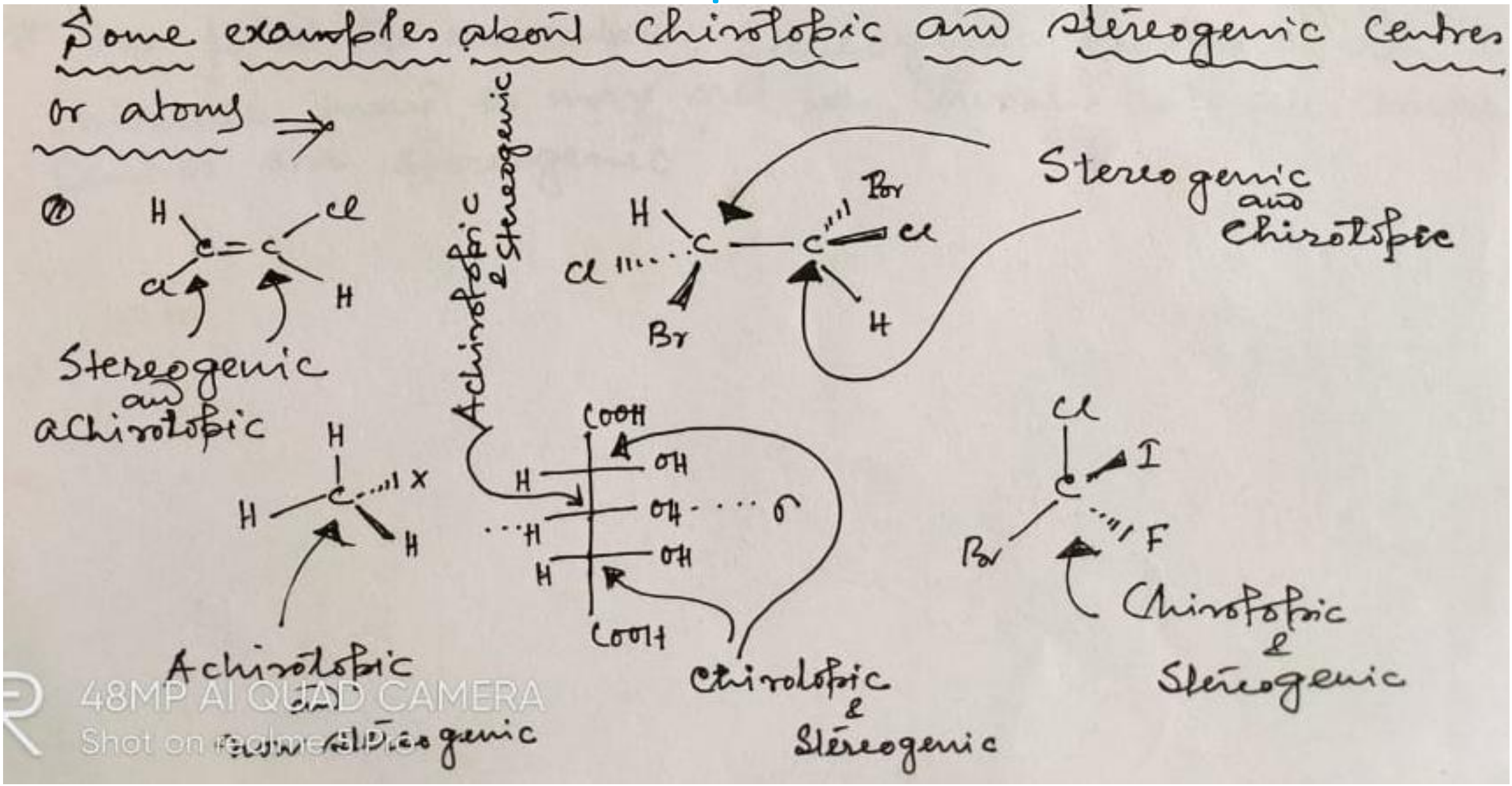
2,3,4-Trihydroxyglutaric acid
C-2 and C-4 are streogenic-chirotopic centres but C-3 is non-stereogenic-chirotopic centre. Mutual exchange of positions of H and OH on C-3 followed by 180° in plane rotation gives back the same structure

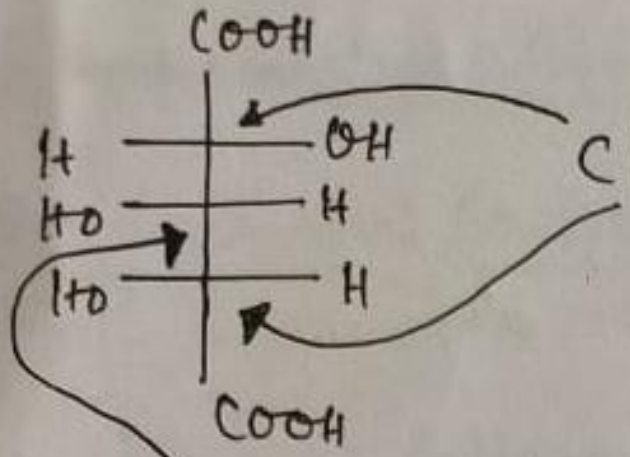






Examples

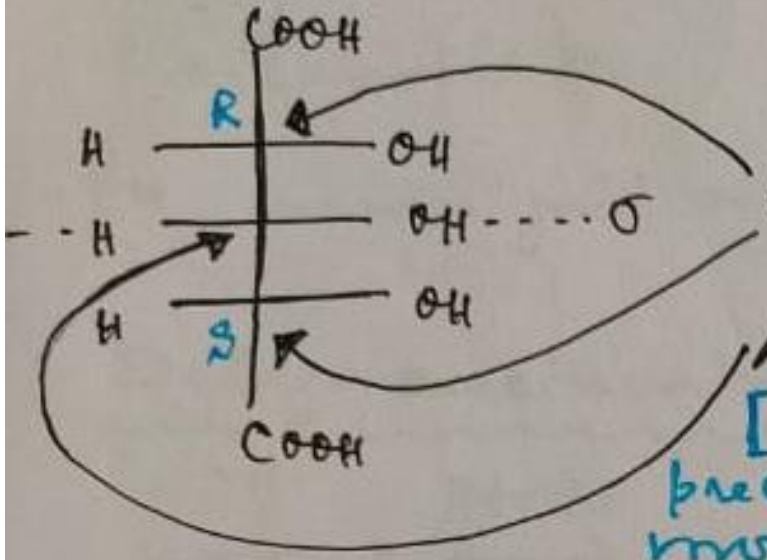

Some examples about Chirotopic and Stereogenic Centres or atoms ⇒
Stereogenic and achirotopic
Achirotopic & Stereogenic
Stereogenic and Chirotopic
Achirotopic & Stereogenic
Chirotopic & Stereogenic
Chirotopic & Stereogenic



Chirotopic and Stereogenic

Chirotopic and non stereogenic

(S. Sengupta - 151)



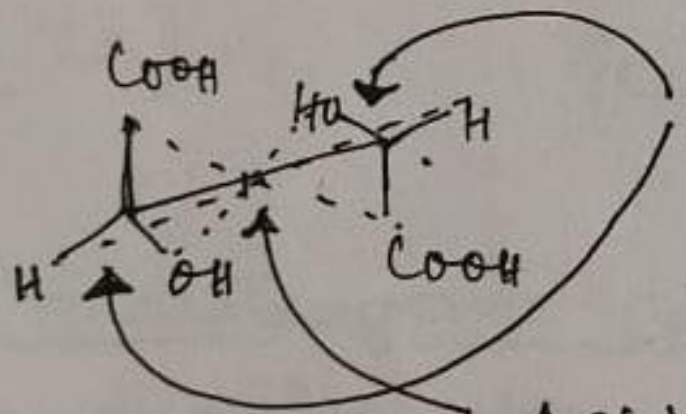
Chirotopic as well as stereogenic

Achirotopic Centre but stereogenic

[The middle carbon atom is achiral or more precisely prochiral due to presence of two homomorphic substituents at both sides]

All the three atoms lying on O (H, C and OH) are achirotopic in nature.

All the three atoms lying on C (H, COOH and OH) are achirotopic in nature.



Chirotopic and stereogenic

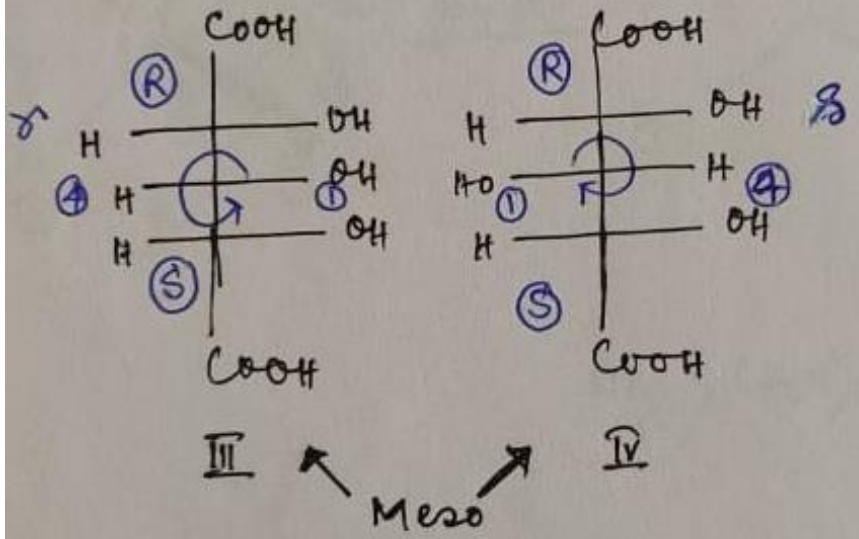
Achirotopic point (as it is the centre of symmetry)

* One point to remember: Stereogenic centres of a molecule may or may not be Chiral, but all Chiral Centres are Stereogenic

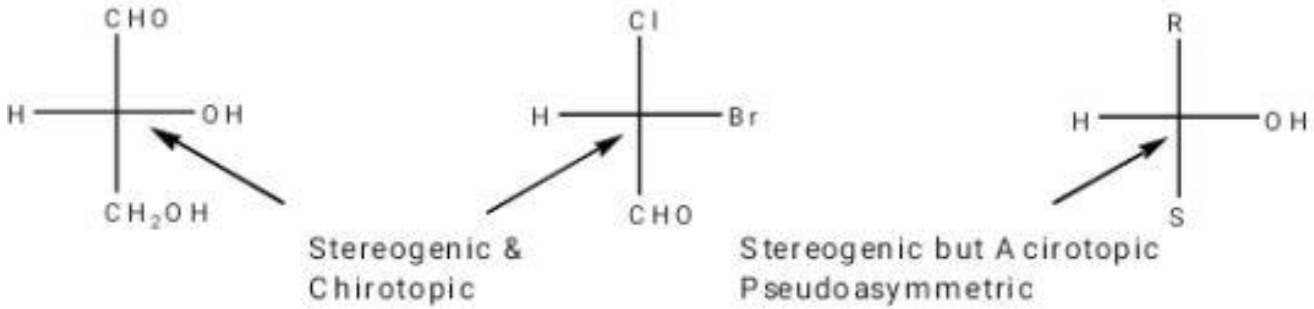
Pseudoasymmetric centre

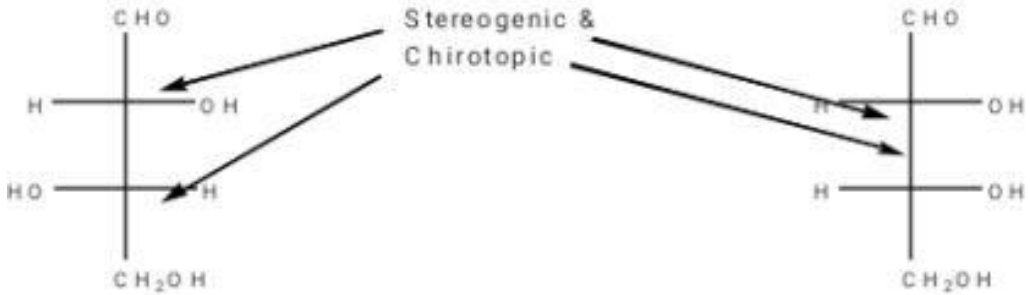
In the optically inactive (meso) isomers of 2,3,4 Trihydroxy glutaric acid (forms III & IV) C_3 is stereogenic but-a chirotopic. Such Centres are called PSEUDOASYMMETRIC Centres and are designated as $Ca^{\oplus}abc$ where a and $a^{\oplus}$ are two enantiomorphous ligands.

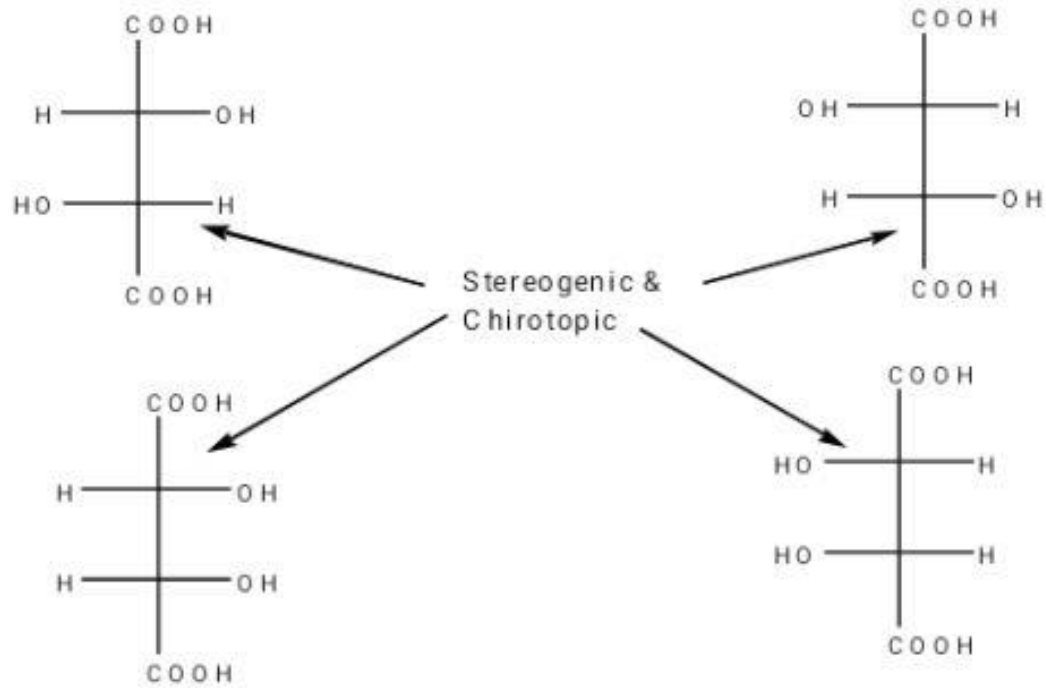
Unlike R and S notations, the pseudoasymmetric centres are named as "r" and "s" (small letter). In case of pseudoasymmetric centres 'R' group gets preference over "s".



The Specification that — "A Chiral Centre should contain four different ligands" does not hold good for a pseudoasymmetric centre.


CHO
H
OH
CH2OH
Cl
H
Br
CHO
R
H
OH
S
Stereogenic &
Chirotopic
Stereogenic but Acirotopic
Pseudoasymmetric


CHO
H
OH
HO
H
CH2OH
Stereogenic &
Chirotopic
CHO
H
OH
H
OH
CH2OH


COOH
H
OH
HO
H
COOH
Stereogenic &
Chirotopic
COOH
OH
H
H
OH
COOH
COOH
H
OH
H
OH
COOH
COOH
HO
H
HO
H
COOH