Unit I   Stereo chemistry

Stereoisomerism :—

                Compounds with the same molecular formula and of identical structure but differing only in the spatial arrangement of the constituent atoms are called stereoisomers and the phenomenon of their existence is known as ~~stereoisom~~ Stereoisomerism.

   Example :-

        Butenedioic acid ($C_4H_4O_4$)

                ($COOH \cdot CH = CH \cdot COOH$) exist in nature in two forms.

    (i) In which the two H-atoms are on the same side of the $C=C$ ~~bond~~ double bond and two $-COOH$ grs. are on the other side of $C=C$ double bond; this form is known as maleic acid.

    (ii) In which the two $-H$ atoms lie on the opposite sides of the $C=C$ double bond and two $-COOH$ grs. also lie in opposite side of the $C=C$ double bond: this form is named as fumaric acid.
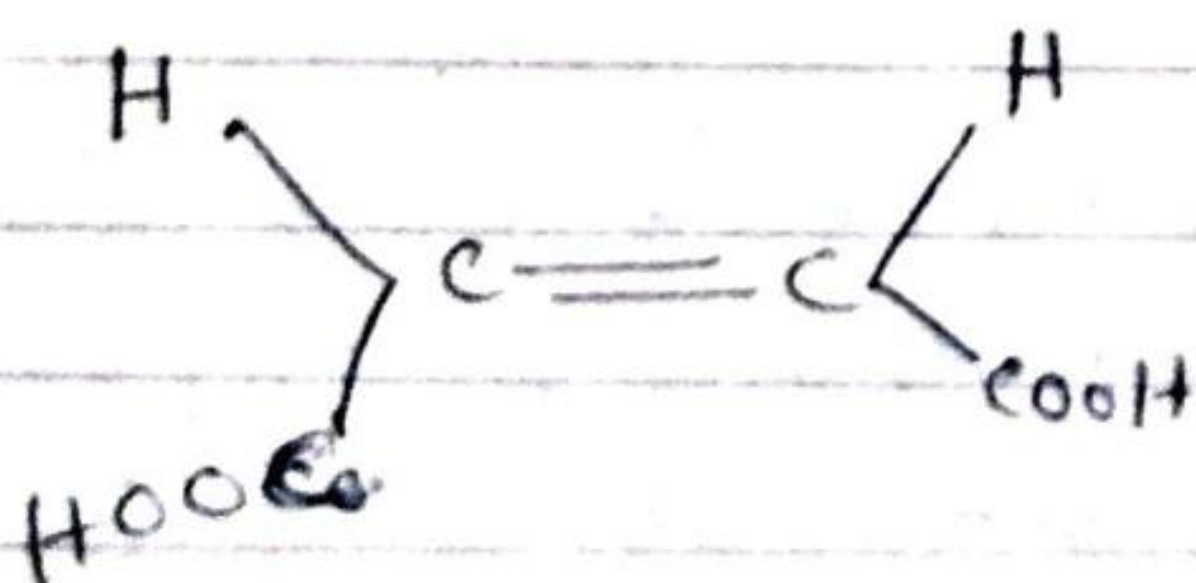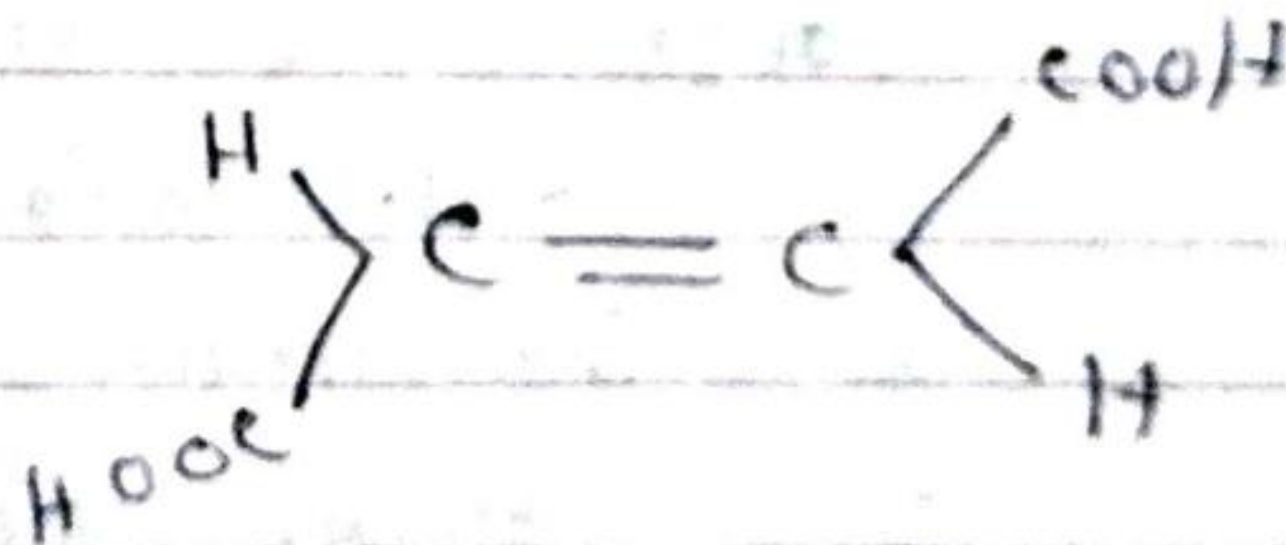
Maleic acid   Fumaric acid

            Both has diff. properties

m.p = $130°$ m.p = $281°$
highly water soluble solid   slightly water soluble solid.

Maleic acid forms anhydride when heated at 140°c, but fumaric acid forms maleic anhydride at 275°c.

The causes of different spatial arrangements in stereoisomers are :-

1. Restricted rotation of a part of the molecule about a $C-C$ single bond; this gives rise to the rotational isomerism or conformational isomerism.

2. Restricted rotation of a part of the molecule about a double bond or a ring; this gives rise the to the Geometrical isomerism.

(3) Chirality, i.e dissymmetry or asymmetry of a molecule; this gives rise the optical isomerism.

Thus Stereoisomerism are further classified as —

1. Conformational isomerism.
2. Geometrical isomerism ⎫ configurational
3. Optical isomerism. ⎬ isomerism.

Geometrical and optical isomerism are called configurational isomerism and

Conformation of molecules :→

If molecule of identical that differ from one another only by rotations about single bonds, then they are said to be conformations of the same molecule. Conformations of minimum energy are sometimes termed as conformational isomers or conformers or rotational isomers or rotamers, and the phenomenon of their existence may be called conformational or rotational isomerism.

As free rotation about a single bond is possible because of its symmetrical charge density; one of the C-atom in a C-C bond may rotate with its substituents around the single bond when the other C-atom remain static. This develops (असंख्य) innumerable spatial arrangements of the groups attached to the rotating C-atom in relation to the position of the groups on the static C-atom. Each of these spatial arrangements is known as a conformation of the molecule. The two extra cases amongst these are called eclipsed and staggered forms. Any intermediate arrangement between these two conformations is known as a 'skew' conformation.

Eclipsed conformation :—>

When the atoms and groups of the nearer C lie exactly opposite with respect to the atoms and groups of the farther C atom, the conformation is known as eclipsed conformation.

Staggered conformation :—>

When the atoms and groups attached to the nearer C atom appear to be as far aparts as possible from the atoms and groups attached to the farther C atom, the configuration is known as staggered conformation.

Projection of conformations

The conformations are generally projected on the plane of the paper in three ways -

(1) Newman projection formula
(11) Flying - Wedge projection formula
(11) Sawhorse projection formula

(1) Newman Projection formula,

(a) C-atom nearer to the observer represented as circle.

(b) Its 3. σ bonds shown by drawing solid lines from point out side the circumference to the center of the circle

© The further C-atom and the C-C bond are not shown as they lie behind the nearer C-atom.

(d) the 3 σ bonds of the further C-atom shown by solid lines which drawn from the circumference of the circle outside of.

Thus the two extreme conformations of ethan molecule as (eclipsed and staggered) and one skew form may be represented by the Newman projection formulae.

Eclipsed   staggered   Skew
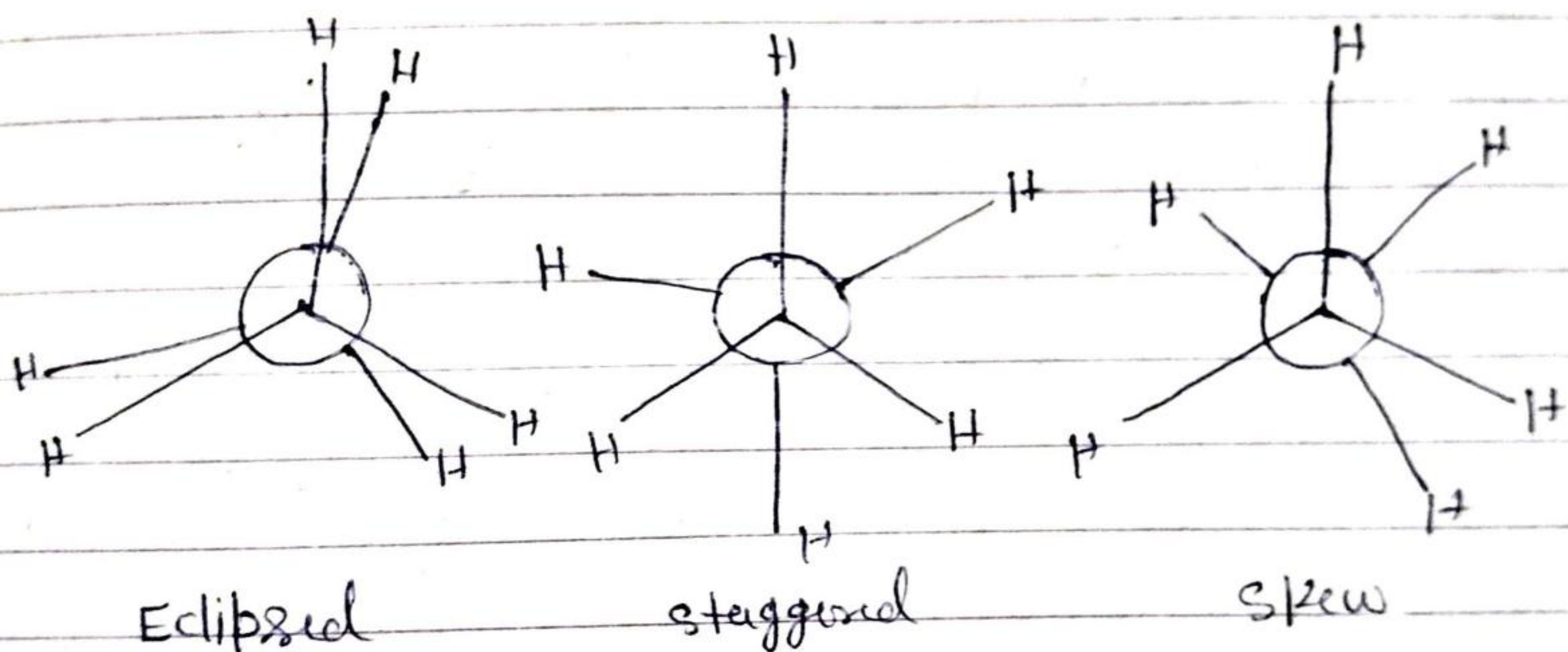
Newman projection formula of C_2H_6

Dihedral angle or angle of torsion :→

In Newaman projection formula the angle between an H on the nearer C-atom and an H on the further C atom in the plane of the paper is called dihedral angle or angle of torsion. (as this originates from the rotation i.e torsion about a single bond).

Di means two and hydral means base i e Dihedral angle means the angle between two bases of the two tetra-hedral of two single bonded carbons.
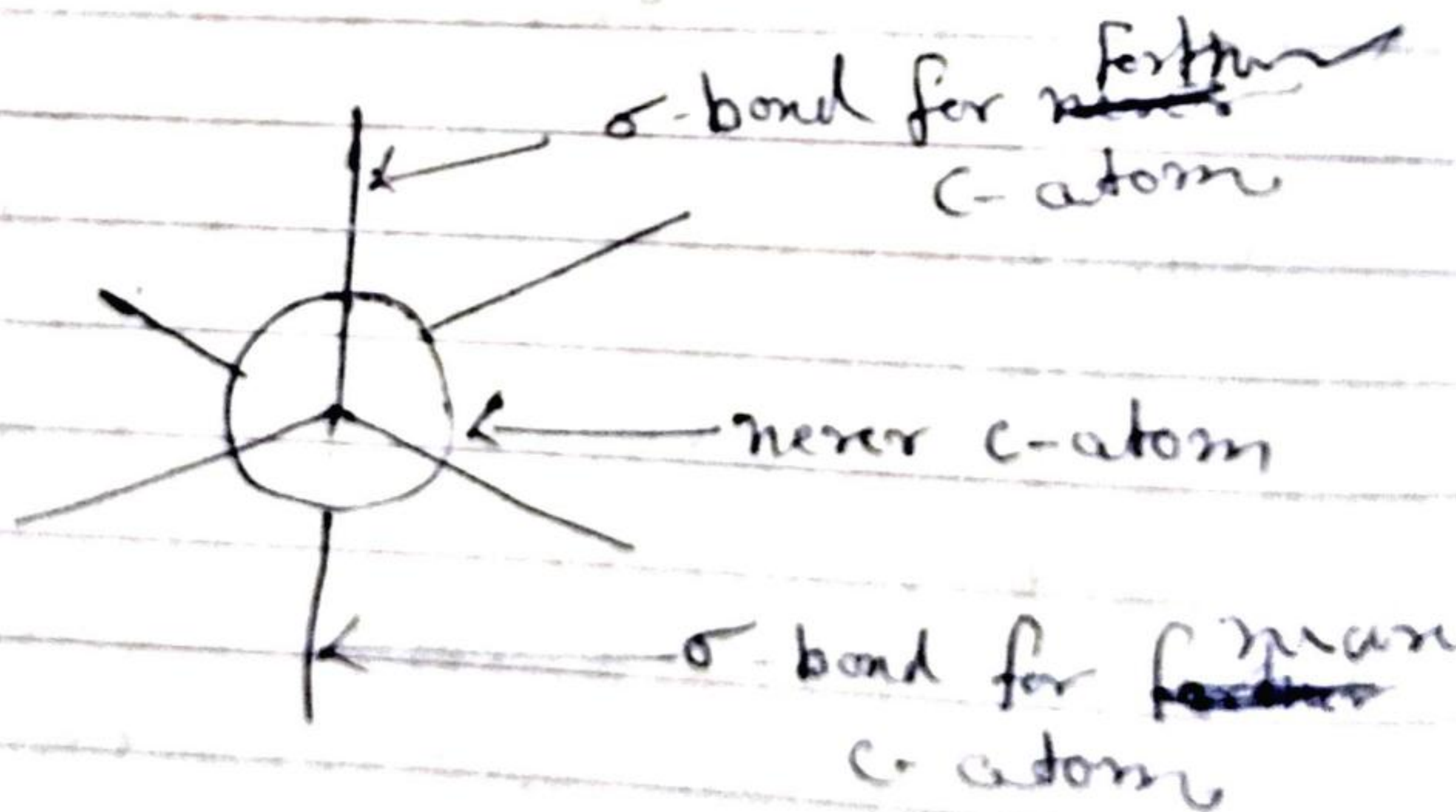
Dihydral angle is denoted by ϕ. As rotation about an single bond may vary from $0°$ to $360°$, this angle also vary $0°$ to $360°$. If

$\phi = 0°$ or $120°$ or $240°$ eclipsed conformation

$\phi = 60°$ or $180°$ or $300°$ staggered conformation.

$\phi =$ any angle except these Skew conformation

σ-bond for farther C-atom

nearer c-atom

σ bond for near C-atom

For ethane there Staggered conformation are the same and its eclipsed conformation are also identical.