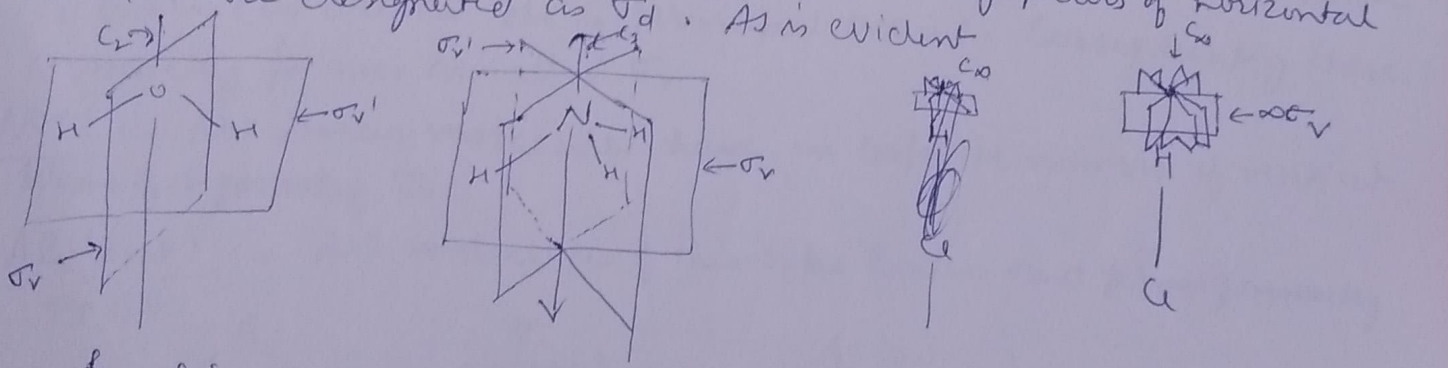
The reflection operation & the symmetry plane (σ) :- If reflection of all of the nuclei through a plane in a molecule gives a configuration physically indistinguishable from the original one, the molecule is said to have a symmetry plane. The symmetry plane is represented by σ & the reflection operator is represented by σ. Since operator σ gives a configuration equivalent to the original & since application of the same σ twice to a molecule produces its original configuration. It follows that a symmetry plane generates only one distinct operation in that $\sigma^k = \sigma$ when k is odd & $\sigma^k = E$ when k is even.

If the xz plane is a symmetry plane the reflection operation σ may be represented by

$$\sigma \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

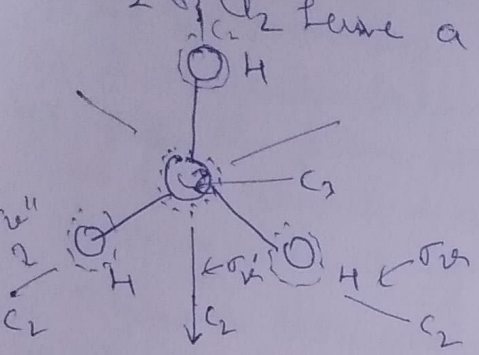
A symmetry plane (& corresponding operation of reflection) perpendicular to the direction of the principal C_n axis (i.e. the normal of symmetry plane is coincident with the C_n axis of highest order n) is called a horizontal symmetry plane & denoted as σ_h. Molecules with a horizontal symmetry plane include C_6H_6 (for which σ_h is perpendicular to C_6 axis & contains all the atoms of this planar molecule) & eclipsed conformation of ethene which has σ_h perpendicular to a C_2 principal axis.

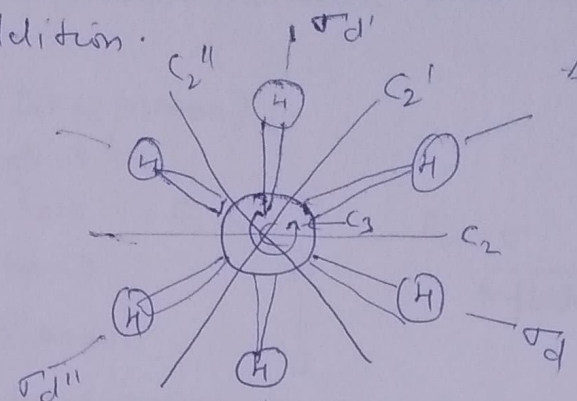
Symmetry planes that contain the principal C_n axis are called vertical symmetry planes & generally are symbolized as σ_v. Dihedral symmetry planes that bisect the angles formed by pairs of horizontal C_2 axes are designated as σ_d. As is evident

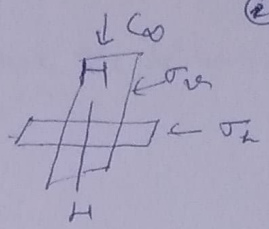


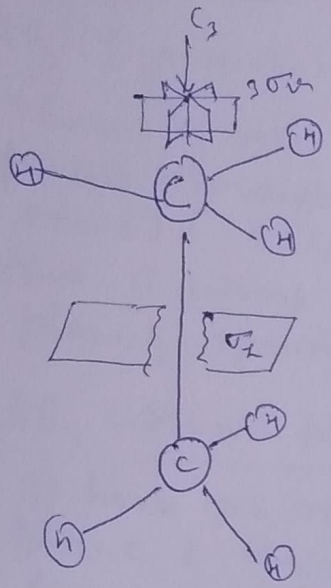
from figure, a H_2O molecule has two vertical symmetry planes σ_v & σ_v' which are perpendicular to each other. One of these symmetry planes (σ_v) comprises the plane of molecule, & the other (σ_v') is perpendicular to it. The two fold axis (C_2) lies in the intersection of two symmetry planes. Ammonia has three σ_v containing the C_3 axis & benzene has six σ_v containing the C_6 principal axis. The linear molecule HCl has an infinite number of vertical symmetry planes of type σ_v, all of which include the C_∞

rotational axis. Homonuclear diatomic molecules such as H_2 & Cl_2 have a σ_h in addition.

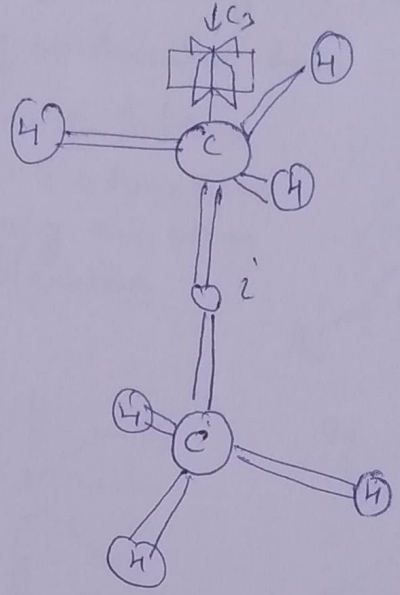








Eclipsed



Staggered.

The staggered conformation of ethane to possess three vertical σ_d which contain the principal C_3 axis & which bisect the three horizontal C_2 axes. In the eclipsed conformation of ethane, however, each of the three vertical symmetry planes contains one of the three horizontal C_2 axes (as well as the C_3 principal axis). Consequently these symmetry planes are called σ_v.

NOTE :- All linear molecules have an infinite number of vertical plane of symmetry σ_v

AB (Ans) :- All molecules of this type

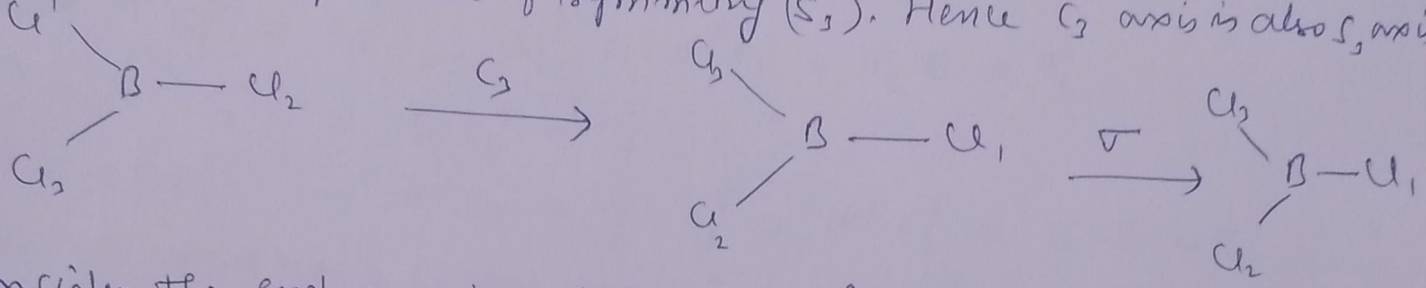
The operation of Improper Rotation & the Improper Axis (S_n):

The operation of Improper rotation consists of a rotation by $2\pi/n$ radians about an axis followed by reflection in a plane perpendicular to the axis. Thus Improper rotation operator S_n is the product of two operators:

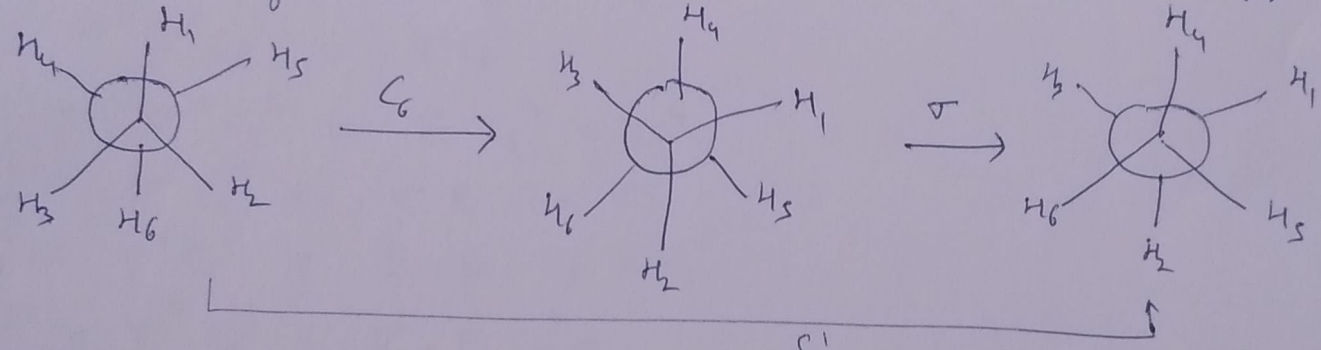
$$S_n = \sigma C_n.$$

This means that the operators C_n & σ are applied successively. As we will see, a molecule need not possess the symmetry element σ of C_n to have the symmetry element S_n.

In BCl_3 the C_3 axis is perpendicular to the molecular plane. Rotation 120° (C_3) followed by reflection about the molecular plane gives an indistinguishable configuration. Hence the molecule is said to possess an Improper axis of symmetry (S_3). Hence C_3 axis is also S_3 axis.



Consider the end-on-view (Newmann Projection) of staggered configuration of ethane.



Rotation about the C–C bond through an angle of 60° followed by reflection about the perpendicular plane at the center of symmetry gives an indistinguishable configuration. Hence C–C bond axis is the S_6 axis

NOTE: No C_6 axis exists in the molecule, only S_6 axis is present.

Classification of Schonflies Point Groups:- When the symmetry operations of molecules, or of other three-dimensional objects are examined it is found that certain combination of operations occurs together. Since all the symmetry elements of a molecule intersect at some point, the symmetry groups are referred to as point groups. ~~Each point group is designated~~ Thus point groups may be defined as collection of symmetry elements present in a molecule that obeys mathematical rule for formation of a group.

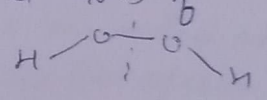
Each point group is designated by a Schoenflies symbol. The Schoenflies symbol designates sufficient symmetry elements to obtain the other symmetry elements & all distinct operations of the point group. There is, in principle, an infinite number of point groups. The external symmetries of crystals fall into only 32 point groups.

Point group C_1:- This group contains molecules with no symmetry. e.g. $CHBrClF$. These molecules do have the identity element (E.)

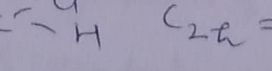
Point group C_s:- This group of molecule that only have a reflection plane σ e.g. CH_2ClF (E, σ)

Point group C_i:- Molecules like 1,2-dibromo-1,2-dichloroethane, which have only a center of inversion i belong to this group (E, i)

Point groups C_n:- Molecules possessing only an n-fold axis of rotation belong to C_n point group e.g. H_2O_2 (E, C_2)



Point groups C_{nv}:- A molecule with an n-fold axis of rotation & n vertical mirror planes, (which necessarily collinear with the n-fold axis) belong in one of these point groups e.g. CH_2Cl_2 (C_{2v} = $(E, C_2, \sigma_v, \sigma_v')$

Point groups C_{nh}:- A molecule with an n-fold axis & a plane of symmetry perpendicular to this axis belong to one of these point groups. Such a plane is referred to as a horizontal mirror plane. The C_{2h} point group necessarily involves a center of symmetry as well. e.g.  $C_{2h} = (E, C_2, i, \sigma_h)$

Point groups D_n:- A molecule with a C_n axis & a C_2 axis perpendicular to this ~~axis~~ axis is in this point group

Point groups D_{nd}:- A molecule with C_n axis, a perpendicular C_2 axis & a dihedral mirror plane is in this point group. The dihedral mirror plane is in the point group. collinear with the principal axis & bisects the two perpendicular

axes. e.g. C_2H_2 ($D_{\infty h}$), $H_2C=C=CH_2$ ($D_{2d} = E, 2S_4, C_2, 2C_2', 2\sigma_d$)

Point groups D_{nh}:- The molecules of this point group have a horizontal mirror plane, that is perpendicular to the principal axes.

e.g. C_2H_2 ($D_{\infty h} = E, 2C_\infty, \infty \sigma_v, i, 2S_\infty, \infty C_2$)

C_2H_4 ($D_{2h} = (E, C_2(z), C_2(y), C_2(x), i, \sigma_{xy}, \sigma_{yz}, \sigma_{xz})$

Point groups S_n:- To be one of these point groups the molecule has to have an n-fold improper rotation axis

Special Point groups:- Linear molecules are either $C_{\infty v}$ or $D_{\infty h}$. A heteronuclear molecule, like CO, is $C_{\infty v}$ because the molecular axis is an ∞-fold axis, & they have an infinite number of vertical mirror planes. Homonuclear diatomic molecules or polyatomics such as acetylene are $D_{\infty h}$, because the molecular axis is ∞-fold, & there is an infinite number of perpendicular C_2 axes since the molecule is symmetrical. Tetrahedral molecules are T_d. The T_h point group has all of the symmetry of a cube. Octahedral molecules, such as SF_6, are O_h. Molecules with the symmetry of icosahedron or dodecahedron are I_h. $[B_{12}H_{12}]^{2-}$ atoms with spherical symmetry are K_h.

Crystallographic symmetry:- We will come to know that in solid state there are seven crystal systems, fourteen Bravais lattices (or space lattices), 32 crystallographic point groups & 230 space groups. A crystallographer must determine to which crystal system, Bravais lattice, point group & space group a given unknown crystal belong. The additional symmetry which ~~not~~ ultimately produces space groups in crystals is a consequence of unique feature not found in molecules.